Advanced Materials and Processes II

Part 1

Edited by Hongbing Ji, Yixin Chen and Shengzhou Chen

TRANS TECH PUBLICATIONS

Advanced Materials and Processes II

> Edited by Hongbing Ji Yixin Chen Shengzhou Chen

Advanced Materials and Processes II

Selected, peer reviewed papers from the 2nd International Conference on Chemical Engineering and Advanced Materials (CEAM 2012), July 13-15, 2012, Guangzhou, China

Edited by

Hongbing Ji, Yixin Chen and Shengzhou Chen



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Trans Tech Publications Ltd Kreuzstrasse 10 CH-8635 Durnten-Zurich Switzerland http://www.ttp.net

Volumes 557-559 of Advanced Materials Research ISSN 1022-6680

Full text available online at http://www.scientific.net

Distributed worldwide by

Trans Tech Publications Ltd Kreuzstrasse 10 CH-8635 Durnten-Zurich Switzerland

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Trans Tech Publications Inc. PO Box 699, May Street Enfield, NH 03748 USA

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Preface

The 2nd International Conference on Chemical Engineering and Advanced Materials (CEAM 2012) was successfully taken place in Guangzhou, China, on July 13–15, 2012. CEAM 2012 is organized by Guangzhou University, Guangdong University of Technology, Wuyi University, Guangdong University of Petrochemical Technology, Fine Chemical Research Institute of Sun Yat-Sen University, Chemical Industry and Engineering Society of Guangdong, and Zhongkai University of Agriculture and Engineering.

The objective of the 2012 International Conference on Chemical Engineering and Advanced Materials (CEAM 2012) is to provide a forum for the discussion of new developments, recent progress, and innovations in the chemical engineering and advanced materials. It addresses all aspects of these fields. The emphasis is on current and future challenges in research and development in both academia and industry. It emphasizes long-term, fundamental research aimed at discovering novel phenomena, processes, and tools.

All those contributions have been peer reviewed through processes administered by the scientific committee. Reviews were conducted by the expert referees of international and domestic of China before accepted for publication. This book covers the subject areas of supermolecular chemistry and crystal engineering, polymer chemistry, physical chemistry of solid surface and catalysis, electrochemistry, inorganic and materials, chiral catalysis and organic synthesis, food chemistry, food flavor chemistry and food sensory science, theoretical and computational chemistry, chemical biology and medicinal chemistry, analytical chemistry and environmental chemistry.

We are grateful to all authors for submissions to this conference and for sharing the information and experience they've acquired. We are very delighted to welcome you to next conference. Enjoy the high quality technical program and the beauty of the local region.

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CHAPTER 1:

Non-Ferrous Metal Material

Different additives to inhibit magnesia (MgO) hydration

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Keywords: magnesia, hydration, citric acid

Abstract: Magnesia (MgO) is a fundamental component of many minerals found in nature and is used widely in our life, especially in refractory industry. However, the antihydration of MgO is a key concern in refractory suspension processing, MgO additions only in form of coarse particles(\geq 50 µm) or its contents of up to 10 wt.% are as a result of their high possibility to take place hydration reaction in water and the reaction can lead to volumetric expansion obviously. In the present work, citric acid (CA) can complex with Mg²⁺ in the MgO suspension under the condition of 4h and 25°C, and the deposit of magnesium ion-CA complexes become protective coating to inhibit magnesia react with water to form Mg(OH)₂.The test results of RSV of different additives shows CA is the best antihydration compound to inhibit MgO hydration comparing with EDTA-2Na, sodium pyrophosphate(SP), trimeric sodium phosphate(TSP), which RSV is only 5.3ml when its dosage is 0.3%wt.

Intruduction

Magnesium oxide (MgO) or magnesia is an important raw materials in the refractory industry, for MgO based refractory castables present a wide technological interest because they associate versatility, high refractoriness and resistance to basic slag. MgO, as the simplest oxide in terms of geometric and electronic structure, is among the oxides that have been most extensively studied with respect to hydration both experimentally and theoretically, it has a typical example of an ionic and insulating oxide, and this oxide has a simple NaCl structure and is characterized by morphological defective features such as steps, corners or reverse corners, which are known to be dominant irregularities at the surface of oxide polycrystals as well as thin oxide films[1].

Nevertheless, Magnesia hydration is a key concern in refractory castable processing, it is due to the volumetric expansion that follows magnesia hydration is related to the density mismatch between the magnesium oxide (ρ = 3.5g/cm³) and its hydroxide, magnesium hydroxide(ρ = 2.4g/cm³), the reason above can result in cracks or even explosion during the first heating-up. There are a great number of studies describing the MgO hydration behavior in castables systematically[2,3]. Most of the chemistry at the surface of MgO is due to the presence of highly reactive defect sites, these sites can be morphological defects such as edges, kinks, steps, and terraces, where the surface ions are low-coordinated, or they can correspond to cation or anion vacancies. In MgO these vacancies are classified as F centers, when an oxygen atom is missing, or V centers, when a Mg atom has been removed. F and V centers are naturally present in the bulk of MgO (like the Schottky defects, pairs of cation and anion vacancies), but their concentration can be considerably increased, for instance by X-rays or neutron irradiation of the solid.

Some results reported have shown that by reducing the MgO hydration rate, major improvements in castable mechanical strength can be attained. In this study, we report on different additives, CA SP, TSP, EDTA-2Na, were added to light burned magnesia suspension to check their effectiveness as antihydration additive. SEM of the unhydrated MgO particle, particles size distribution before and after MgO particle hydration, relative sedimentation volume(RSV) of different addives were used to provide information related to antihydration effect.

Experimental Section

2.1 Materials and methods

Suspensions of light burned magnesia (D50 = 6.67µm and 99.0wt% MgO,China) with 10 wt% of solid content were used for the experiments in water or ethanol. Compounds with various contents were evaluated as different additives candidates: CA, SP, TSP, EDTA-2Na. Whenever used, the amount of different additives were 0.1 wt%,0.3 wt%,0.5 wt%,0.7 wt%, 0.9 wt%, respectively. The 10 wt% suspensions were useful to evaluate the hydration results of MgO by means of SEM of the unhydrated MgO particle, particles size distribution before and after MgO particle hydration, and relative sedimentation Volume(RSV). The data of RSV were recorded as a function of amount with the help of a thermal bath, the suspensions were kept at 25°C for 4 h during the experiments.

2.2 Characterization

Laser particle size analyzer (Microtrac S3500, Microtrac Inc., USA) is able to measure particle size distribution analysis before and after MgO particle hydration, and the morphologies of unhydrated MgO particle is characterized by the SEM(JSM-6360LV, JEOL Ltd., Japan). In RSV test, as a conventional method, particles are classificated simultaneously sedimentation, due to the action of gravitational forces. Our experiments have been carried out in a graduated cylinder (10ml) to determine the relationship between settling velocity and particle size in setted time, in this method, the best antihydration additive is to known, which RSV is least.

RESULT AND DISCUSSION

3.1 MgO suspensions in ethanol and in water





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Fig.1 Surface morphology of MgO

Fig.2 MgO particle distribution in ethanol and water

Several experimental and theoretical studies have investigated the properties of the water/MgO interface, the diversity in the data probing the nature of this interface indicates MgO is a "structure sensitive"material whose properties are very dependent on the experimental approach and sample preparation procedures used. In our experiment, light burned magnesia is used(Fig.1), which particle size is very fine, only several µms, and its D50 is 6.67µm. According to the MgO surface model, there is inevitably straight steps, normal corners, and simple kinks in the MgO surface, a roughly 2.5-fold volumetric expansion appear followed by MgO surfaces interactions with water(Fig.2), when the MgO particle size distribution is determined in water, the hydration of MgO is carried out by the contact of this oxide with liquid water, so the reaction of MgO +H₂O \rightarrow Mg(OH)₂ is happened, that is to say, MgO undergoes an expansive hydration reaction as a result of the different densities between the magnesium oxide (ρ = 3.5 g/cm3) and the corresponding hydroxide formed (ρ = 2.4 g/cm3), Mg(OH)₂, also known as brucite[4-6] In fact, however, MgO grains used as determined sample are polycrystalline and could generally be described as several single crystals bonded together. Nevertheless, any reaction will not be carried out when MgO particle dispersed to the ethanol, so the MgO particle size become bigger in water than in ethanol.

3.2 MgO suspensions hydration in different antihydration additive

The different additives to inhibit MgO hydration we chosed are a group of molecules which have various negative sites in the same molecule and due to this, could be adsorbed onto the positively charged MgO surface[7]. Moreover, these molecules are characterized by their high affinity for metal ions (such as Mg^{2+}), forming complexes with them. Thus, these Mg^{2+} complexes in a solution could inhibit the hydroxide precipitation step, so in our experiment, molecules of citric acid(CA), sodium pyrophosphate(SP), trimeric sodium phosphate(TSP), EDTA-2Na are chosed.



Fig.3 The relationship of different antihydration additive to relative sedimentation volume(RSV)

As soon as MgO comes in contact with water, surface protonation takes place. At the same time, OH⁻ ions are released to the aqueous medium Eq.1. MgO_(solid)+H₂O \rightarrow MgOH_(surface)⁺+OH_(aqueous)⁻ Eq.1

In the presence of antihydration additive, two dissociation reactions occur simultaneously in the suspensions, that are water and antihydration additive dissolution Eq.2 and Eq.3.
$H_2O \rightarrow H_{(aqueous)}^+ + OH_{(aqueous)}^-$ Eq.2 Eq.3

Antihydration additive $\rightarrow nH^++n$ Antihydration additive⁽ⁿ⁻⁾

Protoned MgO particles' surfaces by H⁺ ions from water and antihydration additive dissociation approach the negative ions from water dissociation and the antihydration additive⁽ⁿ⁻⁾ released from the antihydration additive. so Mg^{2+} ions can be trapped by the antihydration additive, the antihydration additive could:

Antihydration additive⁽ⁿ⁻⁾ +Mg²⁺ \rightarrow Mg_nAntihydration additive_{(insoluble)2} Eq.4 $MgOH_{(surface)}^{+}+Antihydration additive (n-)_{(aqueous)} \rightarrow [MgOH^{+}Antihydration additive]^{(n-1)}_{(surface)}$ Eq.5 If the Eq.4 prevails, the more Mg²⁺ions consumed in the reaction, the higher the hydration degree of MgO, on the other hand, if the Eq.4 prevails, less Mg²⁺ disperse to the solution, protective coating formed on the MgO particles will stop the dissolution reaction of MgO ulteriorly. According to the result of Fig.3, the amount of each kind of antihydration additive(EDTA-2Na, TSP, SP, CA) has a RSV optimal. Antihydration additive, EDTA-2Na, SP and TSP can generates the most stable complex on the MgO particle surface, whereas CA additive has the highest capability to adsorption on the MgO surface, for the chemical stability constant for the MgO-CA complexes is 6.31×10^{-4} . The adsorption leads to the neutralization of the positive charges on the MgO surface.

From the Fig.4, we can see that on the conditions of the best dosage of each additive(EDTA-2Na, SP ,TSP and CA), the value of RSV are 6.5ml, 5.9ml, 5.7ml and 5.3ml,respectively.Otherwise, when MgO disperse to ethanol solution, the RSV of MgO suspension is only 4.8ml for MgO particle dose not react with ethanol, so the best antihydration additive is which RSV value is proximal the RSV value of MgO dispersing in ethanol, and CA is the best choice to inhibit magnesia hydration in our experiment, which RSV is only 5.3ml when its dosage is 0.3%wt



Fig.4 Comparison among different antihydration additive with Ethanol

Conclusions

Antihydration additive of MgO, EDTA-2Na, sodium pyrophosphate(SP), trimeric sodium phosphate(TSP) and citric acid(CA) have different extent to inhibit magnesia hydration, among all of them citric acid (CA) additions minished the negative effects of MgO hydration in refractory suspensions. By the relative sedimentation volume(RSV) measurements during the antihydration experiment, the addition of CA can reduced the MgO hydration extent under the experiment conditions (4 h at 25°C, the dosage of 0.3%wt). Compared to other antihydration compounds used in our experiment, the CA has a more efficient performance to inhibit MgO hydration.

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Influences of processing factors on pore structure of aluminum foams

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Keywords: aluminum foams; PCM process; process parameters; pore structure

Abstract. Orthogonal experiments were employed to confirm the interactive effect of the addition of magnesium powder, milling time of aluminum powder, oxidization time of TiH2 on the pore structure of aluminum foam, which was prepared by PCM method. The results show that the three factors was arragned in important order as the follows: oxidization time, milling time, and the quantity of magnesium powder. The high quality aluminum foam samples, with average porosity of 84.2%, average equivalent circle diameter of 1.9 mm and average circularity of 0.754, were made on the condition of milling time as 85 minutes, oxidization time as 10 minutes and magnesium powder content as 0.5 wt%.

Introduction

Aluminum alloy foam has been an attractive material to be used in many engineering applications due to its advantages of high mechanical strength, large specific surface areas and high porosity.

Powder compact melting (PCM) technique has attracted much attention and given arise to a series of research efforts thanks to its diversified virtues in manufacturing closed cell Al foams in recent years at home and abroad. More and more attention had paid for the reasonable processing parameter to obtain the aluminum foam with large porosity and homogeneous distribution of the utilizable pores. Therefore, the work presented is aimed at studying the interactive effect of accession amounts of the three factors on the pore structure, such as the addition of magnesium powder, milling time of aluminum powder, oxidization time of TiH_2 .

Experimental principle

It was found that the melt viscosity and the amount of TiH_2 addition were the key factors determine the pore structure [1].

At present, the main stabilizing mechanism of metal foam is stabilizing mechanism of particles from DUDKA [2], it means that the addition of ceramic particles to the precursor gathering at the interface of gas-solid, increasing the viscosity of the melt apparent, significantly reduces drainage effect and leads to a table cellular structure during the whole process, to keep different pressure between Brad boundary supply and the wall pressure. The reaction of Mg powder and oxide film at the Al powder surface formed of MgAl₂O₄, and destructed the oxide structure, in the end promoted the sintering of Al powder. In the paper, the suitable Mg powder contend as an additive was used to the precursor of aluminum foam which were prepared by powder metallurgy to stabilizing the cellular, the addition is determined by own experimental data and the literature. Milling on Al powder means to increase the oxygen content of the Al powder surface, the time of milling is determined by own experimental data and the literature [3].

Aluminum foams were prepared by melt casting or powder metallurgy using TiH₂ as a blowing agent, the foaming temperature is above 700°C (The melting point of aluminum alloy is above 600°C). Decomposition of TiH₂ begins at a temperature around 350°C at atmospheric pressure, and continues up to 600°C~750°C. When the TiH₂ particles without coating added to the liquid aluminum, a large number of hydrogen decomposed with no time stirring to evenly disperse in the liquid, the bubbles merge floating, or even overflow, the pore structure is uneven in the aluminum foam. Maybe gas decomposition too fast will cause air bubbles merge and lead to non-uniform pore structure and even

foam failure. How to control the TiH_2 decomposition in effect has been the key difficulty problem. Oxidation processing of TiH_2 heated in air leads to formation of a dense oxide film, thereby slowing the release of H_2 . TiH_2 oxidation time is determined by own experimental data and the literature [4].

Experiment procedures

Here, these powders have been used of particle size lower than $450 \,\mu$ m, namely powder of pure aluminum and magnesium (0.4wt%, 0.5wt%, 0.6wt %) with the addition of TiH₂ power as the blowing agent.

Arranged the tests based on L9 (3/4) orthogonal test table, orthogonal tests with three factors (addition of magnesium powder, milling time of aluminum powder, oxidization time of TiH_2) shown in table 1, the orthogonal test program shown in Table 2.

	Table 1 Factors and levels of orthogonal test						
				Factors			
Level		$\frac{A}{a_{\text{atime of } A1}}$	1 Addition	5 n of Ma	Ovidization tin	no of	D
	powder [min]		powder	[wt %]	TiH ₂ [min]	le of	
1		65	0.4		10		
2		75	0.	5	15		
3		85	0.	.6	20		
		Table	e 2 Orthogor	nal test sch	neme		
No		А	В	С	D	P	lan
1		1	1	1	1	A1E	B1C1
2		1	2	2	2	A1E	32C2
3		1	3	3	3	All	B3C3
4		2	1	2	3	A2H	B1C2
5		2	2	3		A2E	32C3
6		2	3	1	2	A2E	33CI
/		3	1	3 1	2	A31	31C3
8		3	23	1	5	A3B2C1	
		J T 11 2 C		 ·	1 14	AJI	<u>55C2</u>
		Table 3 C	rthogonal e	xperiment	al results		
Content Class	$P_0[\%]$	D_{α} [mm]	C_{lpha}	L_{P_0}	L_{Da}	L_{c_a}	Combined score
1	82.5	1.913	0.641	0.29	0.47	0	0.29
2	82.4	1.539	0.68	0.25	0	0.35	0.20
3	84.2	2.255	0.666	1	1	0.22	0.84
4	81.8	2.02	0.732	0	0.67	0.81	0.36
5	84	2.069	0.725	0.92	0.74	0.74	0.83
6	82.8	1.791	0.684	0.42	0.35	0.38	0.39
7	83.1	1.988	0.696	0.54	0.63	0.49	0.56
8	84.2	1.931	0.753	1	0.55	0.99	0.86
9	83.1	1.901	0.754	0.54	0.51	1	0.62
K ₁	1.33	1.21	2.23				
K ₂	1.58	1.89	1.18				
\mathbf{K}_{2}^{2}	2 04	1.85	1.54				
Range R	0.71	0.68	1.05				
the order of importance	CAB		1.00				
Optimal Scheme	C1A3B2						

Quality Indicators. Three indicators, the quality of foam samples of aluminum foam: porosity, the average equivalent circle diameter, the average circularity. They are defined as follows.

Porosity (P_0) : The ratio of the volume of all the pores in a material to the volume of the whole. $D_{\alpha} = \frac{\sum D_i}{N}$ (1)

Average equivalent circle diameter circularity $({}^{D_{\alpha}})$: The ratio of the sum ${}^{\sum D_i}$ of the equivalent diameter of cross-section and the number of holes N;

$$C_{\alpha} = \frac{\sum C_i}{N}$$
(2)

Average equivalent circularity $({}^{C_{\alpha}})$: The ratio of the sum ${}^{\sum C_i}$ of the equivalent diameter of cross-section and the number of holes N;

More convenient, the three indicators are converted to their membership (L), the calculation method of the degree of membership is as follows:

$$Membership (L) = \frac{[Number] - [Mix]}{[Max] - [Mix]}$$
(3)

Visible Max (L) = 1, Min (L) = 0, so $0 \le L \le 1$. Three indicators of the importance of this test is not the same, according to the actual requirements, the weight factor of the porosity P_0 , the average equivalent circle diameter D_{α} and the average circularity are 0.5,0.3 and 0.2, respectively, so the overall score for each experiment L= $P_0 \times 0.5 + D_{\alpha} \times 0.3 + C_{\alpha} \times 0.2$, The maximum score is 1.

Result and discussion

Orthogonal Experimental results and analysis. The orthogonal experiment results shows that the factor affecting the test primary and secondary (see table 3), respectively: C (the oxidation time of TiH₂) \geq A (the milling time of Al powder) \geq B (the addition of Mg powder). Optimal solution C1A3B2, namely, the eighth group of test: the oxidation time of TiH₂ was 10min, the milling time of Al powder at 0.5 wt%. The test of aluminum foam specimen porosity was 84.2%, the average equivalent circle diameter at 1.901mm, the average round is 0.754. The cross-section photographs of sample are shown in Figure 1 (8).

Cross-sectional face structural analysis. From the Figure 1, the obvious big holes in the cross section of the sample for 1, 2, 3, 6, and 7 are shown, which not we want; the other groups of the experiment, are not homogeneous pore structure of the eighth group, it is accorded with the results of the above orthogonal test table. Fig.2 is the cross sectional structures of the eighth group, (a) is the sample photo, (b) is the cross sections structures by the binarization processing, (c) Circularity distributions evaluated by equivalent circle diameter.

A suitable melt viscosity and foaming agent were critical to the cell wall. The sequences of factors influencing the foam quality the effluent: C (oxidation time of TiH_2) \geq A (milling time of Al powder) \geq B (addition of Mg powder). It is obtained from the experimental analysis that the effect of the oxidation treatment of the blowing agent on the pore structure is relatively large in forming technology parameters; the influence of melt viscosity followed, the influence of the milling time of Al powder and the addition Mg powder on pore structure less, which provided the right path to the further experiment.

Conclusion

The results show that the three factors is arranged in important order as the follows: oxidization time, milling time, and the quantity of magnesium powder.

The milling time for 85 minutes and the oxidization time for 10 minutes using the magnesium powder for 0.5wt% can get the good quality aluminium foam, achieving the average 84.2 percent porosity and the average equivalent circle size of 1.901mm and the average circularity 0.754mm in diametre.



Fig.1 Images from cross-sectional structures of the orthogonal experiment results



Fig. 2 Cross sectional structures of the eighth group, (a) the sample photo, (b) the cross sections structures by the binarization processing, (c) Circularity distributions evaluated by equivalent circle diameter.

Acknowledgements

This work was financially supported by Shanxi Scientific Research Foundation for the Returned Overseas Chinese Scholars (2011081), Doctor Subject Foundation of Taiyuan University of Science and Technology (20102029).

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Effect of deformation ratios on microstructure and mechanical properties of ZK60 magnesium alloy by hydrostatic extruded at room temperature

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Key words: ZK60 magnesium alloy; hydrostatic extrusion; deformation twinning; microstructure; mechanical properties

Abstract: The effect of different hydrostatic extrusion ratios on the microstructure and mechanical properties of the ZK60 magnesium alloys were investigated. The results showed that, the major deformation mechanism of the alloy is twinning at room temperature, which resulted in that the tensile strengthen and hardness of the extruded alloy improved greatly. With deformation ratio increasing, the ultimate tensile strengthen and hardness are linearly increased, with the functions of Y=4.2X+358.3 and Y=2.3X+73.69, respectively. And the maximum tensile strength and hardness of the extruded alloy are 383 MPa and 87HB, respectively. But the elongation decreases obviously, the minimum decreasing degree is 50%. With the deformation ratio increasing, the tendency of elongation rate increased as an "M" model.

Introduction

In recent years, magnesium alloys have attracted great attention because of the requirement of lightweight, environment and energy sources. The applications of the magnesium structural components with high properties were increased rapidly in the motor industry, aviation and space flight industries. Just as the other materials, the wrought magnesium alloys have higher strength and better ductility than the as-cast alloys. The plastic deformation process is an effective way to improve the mechanical properties of the magnesium alloy [1-3]. While the deformation capability of magnesium alloy is poor, and the deformation mechanism for the magnesium deformation is not clear, so the conventional deformation technique can not catch up with the growing need of the excellent properties of magnesium alloy [4, 5].

The hydrostatic extrusion process is one of the most effective methods for strengthening the material with poor deformation capability alloy. Such as the hydrostatic extruded tungsten alloy, the strength of material could be raised by 50% through one deformation cycle. The material after deformation still retained excellent toughness property [6]. Comparing with the traditional extrusion process, the hydrostatic extrusion has a lot of advantages as following [7-9].

Firstly, because pressure transfers on billet by liquid medium, so the deformation of the billet is very uniform. And during the hydrostatic extrusion deformation process, there is no upsetting stage or crack occurred due to circumferential pull press.

Secondly, there is little friction between the billet and the deformation cabin. Lubricated by the liquid with high pressure, the extrusion force is decreased obviously. The surface of extrusion product is good.

Finally, the deformation speed of hydrostatic extrusion is quick. It is easy to realize extrusion with high velocity.

Presently, it is well known that the study of tungsten alloy with hydrostatic extrusion at room temperature, but up to now the research focusing on magnesium alloys is still scarce [10]. This article explored hydrostatic extrusion forming process for ZK60 magnesium alloy to improve the mechanical properties. And the effect of deformation ratio on the mechanical properties and microstructure of the alloy were investigated.

Experimental

The purpose of this experiment was to investigate the deformation microstructure and mechanical properties by hydrostatic extrusion process at room temperature. In this work, ZK60 rods were manufactured by hot extrusion process for hydrostatic extrusion deformation, and the compositions of the as-fabricated ZK60 alloy were listed in Table1.

Table1 The components of ZK60 Mg alloy (wt%)					
Zn	Zr	extaneous	Mg		
5.5	0.5	≤0.30	Bal.		

The tensile tests were carried out on the CMT-4105 testing machine at room temperature and at a cross head speed of 10^{-2} mm·s⁻¹. The hardness tests were carried out with the HB3000 testing machine. The Germany Laika MEF4 optical microscope was used for microstructural examination before and after extrusion.

The billet for the hydrostatic extrusion was the hot extruded rod with the diameter of 20mm. The deformation ratios of the hydrostatic extrusion were designed as a series of 20%, 30%, 35%, 40%, 45% and 50%. The rod length was 200mm. The hydrostatic extrusion was carried out at room temperature. The experimental equipment of hydrostatic extrusion was shown in Fig.1.



Fig.1 Scheme of hydrostatic extrusion equipment

Microstructure

The ZK60 rod was manufactured by hot extrusion, and the optical micrograph of the rod before hydrostatic extrusion deformation was shown in Fig.2. It can be seen that different sizes grains scattered along with the extrusion direction. The microstructure of the alloy by hydrostatic extruded with the different deformation ratios in Fig.3.

With the deformation ratios increasing, from (a) to (f), the extent of stress concentration nearly the grain boundary become more severe, the deformation bands have been distorted, and many twins can be found within the hydrostatic extruded alloy.

This indicates that the deformation twinning was the major deformation mechanism of ZK60 magnesium alloy at room temperature.



Fig.2. Optical micrograph of before hydrostatic extrusion deformation (500×)



Fig. 3.The microstructure photos with the different deformation ratios of hydrostatic extrusion $(800 \times)$

(a-20%; b-30%; c-35%; d-40%; e-45%; f-50%)

Because of hexagonal structure of magnesium alloy and only three glide systems, it's difficult for dislocation to slide for plastic deformation. When the deformation ratios increased from 20% to 50%, the secondary twin-crystal could also be observed clearly in the master twin. The shapes of secondary were different from ratios and the shapes of the secondary twin-crystal were varied from stick-shape to specula-shape. Some secondary twin-crystals had been distorted in the larger deformation ratio. Dynamic recrystallization was not observed in the Fig.3.

3.2 Mechanical properties

Before hydrostatic extrusion deformation, the mechanical properties of the ZK60 alloy were listed in table 2.

UTS(MPa)	Elongation (%)	Hardness (HB)
280	18	58

Table 2 The mechanical properties of the ZK60 alloy before extrusion

After deformation, the relationship between the mechanical properties and deformation ratios was shown in Fig. 4.

Comparing with the ingot before deformation, the ultimate tensile strengthen and hardness are improved, the maximum tensile strength is 383 MPa, the maximum hardness is 87 HB. But the elongation rate decreases obviously, the minimum decreasing degree is 50%. Due to different deformation twinning interaction, the linear relationship between ultimate tensile strengthen and deformation ratios can be addressed as a function of Y=4.2x+358.3, and the linear relationship between hardness and deformation ratios is can be addressed as a function of Y=2.3X+73.69. With the deformation ratios increasing, the tendency of elongation rate increases as an "M" model, as shown in Fig. 4(c). When deformation ratios were less than 45%, the alloy elongation was changed between 3% and 5%. When deformation ratios were more than 45%, the alloy elongation was improved obviously between 8% and 12%.



(a) tensile strength-defomation ratios (b) elaongation-defomation ratios (c) hardness-defomation ratios Fig. 4. The relationship between the mechanical properties and deformation ratios

Conclusions

This work explored the hydrostatic extrusion for the ZK60 magnesium alloy, and the deformation microstructure and mechanical properties of the hydrostatic extruded ZK60 alloy were investigated. The following conclusions are obtained in the present investigation.

(1) The ultimate tensile strength and hardness of the alloy after hydrostatic extrusion was increased linearly with the deformation ratios increasing.

(2) There was a critical deformation ratio at the hydrostatic extrusion of the Mg alloy. When the deformation ratio was less than the critical value, the alloy ductility was poor.

(3) Twinning was the main deformation mechanism of ZK60 magnesium alloy during hydrostatic extrusion process at room temperature. While the deformation ratio was improved, the shape of the second twin-crystal varied from stick-shape to specula-shape.

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Mechanisms and Application on Reduction Leaching

of Pyrolusite by Cellulosic Biomass

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Keywords: Cellulosic biomass; Degradation ;Reductive leaching

Abstract: Reduction leaching of pyrolusite by cellulosic biomass, due to its good performace, low cost, renewable and environmental friendliness, has received increasing attention in recent years. In this work, the advances on reduction leaching of pyrolusite by cellulosic biomass are reviewed. The degradation mechanisms of cellulosic biomass and reduction leaching applicat- ions of pyrolusite by degradation products are analyzed. Finally, further study of the proposed reduction leaching of pyrolusite by cellulosic biomass are discussed.

Introduction

Pyrolusite (main ingredients: MnO2) is an important manganese ore resources, and raw materials of 80% electrodeposited manganese are from pyrolusite. As manganese dioxide ores are stable in acid or alkaline oxidising conditions, the extraction of manganese must be carried out in reductive conditions. In aqueous reduction, SO2, FeSO4, charcoal, coal and lignite and pyrite, etc, can be used as reducing agents. But these kinds of reducing agent have brought out plentiful negative problems, such as pyrite mine bringing large amount of existing slag and impurities, ferrous sulfate leading leaching difficulties for solution to filter and SO2 doing harm to atmospheric environment, and so on[1]. Therefore, the scientific and technical workers have tried to find efficient pollution-free reductant to instead of inorganic reductants.

Cellulosic biomass is a rich renewable biomass resources, which is mainly refers to stalk and woodiness cellulose (for short lignin) in agriculture and forestry production process, except food and fruit of straw, the processing industry of agricultural scrap products in the process of agriculture production, and so on. Although its sorts are various, cellulosic biomass is mainly composed of cellulose, hemicellulose and lignin compositions. To make it more easy to use cellulose biomass, it must be preprocessed to reduce the crystallinity of cellulose and destroy mesh structure of hemicelluloses and lignin. Degradation is a pretreatment process that covalent bond of macromolecular organics are broken down into smaller segments. Nowadays, degradation of cellulosic biomass generally focus on the following aspects: physical and chemical treatment, steam blasting, hot water treatment, dilute acid treatment, alkali treatment, low temperature ammonia blasting processing, wet oxygen method, organic solvent processing, and supercritical water treatment. Their degradation products containing reducing activity groups, such as glucose and

formic acid, have been used as reducing agents for manganese extraction from pyrolusite. The degradation mechanisms of cellulosic biomass and are reviewed, and reduction leaching pyrolusite mechanisms by cellulosic biomass and their relevant applications are summarized in this paper.

Degradation mechanisms of cellulosic biomass

2.1 Structure and characterization of cellulosic biomass

Cellulosic biomass are mainly composed by cellulose, hemicellulose and lignin, which are collectively called as lignocellulose. Hemicellulose is as molecules binder, which combines with cellulose and lignin. Lignin is of mesh structure that serves as a support skel- eton surrounded and strengthening cellulose and hemicelluloses[2].

Cellulose is a kind of macromolecular polysaccharide, which come from glucose dehydration and through the beta 1, 4-glycosidic bond connected to the amylose polymers. Its chain of both ends is different, one aspect of the matter being the reduction, the other side being no reduction. Cellulose molecules can be expressed as the simple (C6H10O5) n, n (n = 3000-10000) for the degree of polymerization, being the number of cellulose units.

Hemicellulose is a mixture made of different polysaccharide constitute, whose structures and composition are greatly various and no general formula. Low degree of polymerization, the sugar unit number in 60-200, arrangement loose, and no crystal structure, these facters make hemicellulose hydrolyze easily.

Lignin is a 3d space structure polymer compound by phenyl propane unit through carbon connected to carbon. Its molecular formula can be expressed as the simple (C6H11O2) m. The basic component units are syringyl, guajacyl, and p-hydroxy phenyl propane units. Molecules of lignin contain rich active functional groups, such as cyclobenzene, -C=C-, ether key, carbonyl,carboxyl, hydroxyl and phenolic group, etc,which provide lignin diversified chemical modification, like oxidation, reduction, hydrolysis, and alcoholysis and acid hydrolysis. Reducing products can be obtained through these reactions.

2.2 Dilute acid hydrolysis mechanisms of cellulose and hemicellulose

Acid hydrolysis is a kind of important technology of processing utilization of cellulose biomass. According to acid concentration, acid hydrolysis is divided into dilute acids and strong acid hydrolysis. Dilute acid hydrolysis is commonly used treatment method.

The beta 1, 4-glycosidic bond of cellulose molecules is a kind of acetal keys and sensitive to acid. In the presence of appropriate hydrogen ions concentration, temperature and function time, glycosidic bonds rupture, along with the degree of polymerization decline. Deoxidization and ability enhancement. Acid solution products for cellulose are glucose. The reaction is as follows:

$$(C_6H_{10}O_5)_n + n H_2O \longrightarrow (C_6H_{12}O_6)_n$$
 (1)

Hemicellulose molecule chains contain free hydroxyl what is of hydrophilic, thus hemicellulose being soluble. The more branch chains contain, the higher solubility is in water. Dilute acid hydrolysis mechanism of hemicelluloses is similar to that of cellulose: hydrogen ions coming from acid dissolving in the water to generate water hydration (H3O+), it can make it protonate oxygen of glycosidic bond in the cellulose or hemicellulose molecule quickly, and form conjugate acid, and then glycoside bond engery weakens and bond breaks. Carbon ions at end of bond react with water to produce glycose eventually. At the same time, the protons are released. The proton reaction with water to generate hydrogen ion, continue to participate in the new hydrolysis reactions[3].

In the usual hydrolysis conditions (80-200°C, acid concentration 0-6%), hemicelluloses hydrolysates are xylose and Arabia sugar and a small amount of six carbon sugars, xylose accounting for more than half generally. The hydrolysis by-products are mainly furfural, 5–hydr- ox hydroxymethyl furfural, acetic, formic acid and propionic acid[4-7]. Fig.1 is simplified reaction network for dilute acid hydrolysis of hemicelluloses.



Fig.1 Simplified reaction network for dilute acid hydrolysis of hemicellulose

2.3 Alkali treatment mechanisms of lignin

Acid parts lignin molecules, such as segments containing carboxyl and phenol, make its ether key fracture and macromolecular fragment in alkaline conditions, which promote lignin dissolving; at the same time, this lead cellulose to inflate , hemicellulose to dissolve, hydrogen bond cellulose and hemicellulose to weak, and the ester key between cellulose and lignin to saponify[8-9]. Usually, the oxygen can not oxidize lignin structure. In alkaline conditions(O₂- NaOH), however, phenolic groups of lignin's phenolic structure dissociation, quinoidstructure or will open benzene structure to generate sticky furfural. The alkaline nitrobenzene oxidation of lignin can generate vanillin, syringaldehyde and p-hydroxyl phenyl formal ehyde.

Reduction leaching mechanisms of pyrolusite by cellulosic biomass

To sum up, these degradation products containing reducing activity groups, such as glucose and formic acid,make manganese of pyrolusite be reduced from Mn4+ to Mn2+ in an acidic conditions. For example, when glucose-sulfuric acid is used, the proposed reactions are: C6H12O6 + 12 MnO2 + 24 H+ \rightarrow 6CO2 + 12 Mn2 + + 18 H2O+ organic acid (minor) (2)

Applications of reduction leaching of pyrolusite by cellulosic biomass

Cheng[10] used biomass straw as reducing agent, with the dominated combined with wet to reduce leaching oxidation manganese ore. The results show that under 500 °C, oxidation manganese ore: straw (quality)10:3, roasting 80 min, and in the 50 °C, 400 r•min⁻¹, acid concentration 3 mol•L⁻¹, and then leaching reaction 40 min, manganese leaching rate is 90.2%. The change trend of manganese oxidation state are pointed out normal forms of manganese combined are as follows : $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$.

Study[11] on reductive leaching of manganese from Hunan low-grade manganese dioxide ores using corncob as reductant in sulfuric acid solution, the results show that under 85 °C, oxidation manganese ore: corncob (quality)10:3, leaching reaction 60 min, 92.8% of manganese was leached. Sawdust as a reductant to leach manganese ores using in Hariprasad^{,s} research[12], the recovery of 98% Mn is attained under the leaching conditions of 90 °C, manganese ore: sawdus (quality)2:1, Sulfuric acid (volume) 5%, pulp density 10%, and leaching 8 h.

Sugarcane molasses leaching local oxidation manganese ore process in Su^s research[13], the result showed that leaching 97% of manganese and iron and aluminum leaching rate of only 32.4% and 21.5% when the reaction conditions are as follow: 90 °C, mineral grain size being less than 0.147 mm, 60 g·L⁻¹sugarcane molasses, 1.9 mol·L⁻¹acid,and 120 min. Research on molasses alcohol wastewater for reduction leaching oxidation manganese ore research has made the good effect, that is,manganese extraction rate amounting to 93%. The leaching process is controlled by by internal diffusions of inertia layer composed of associated minerals and it may solve the difficult problem of waste treatment[14-15]. In addition, rutin in leaching process is studied and the consequence are found: 90 °C, 25 g·L⁻¹ rutin, sulfuric acid initial concentration of 2.4 mol·L⁻¹, 90 min, manganese extraction rate 94% [16]. Molassess used reduction leaching oxidation manganese ore in nitric acid solution are investigated by Lasheen. They find manganese extraction rate may be 98% when the condition is as follow:95 °C ,20% molasses, 2.7 mol·L⁻¹ nitric acid, the liquid-solid ratio 12:1, leaching reaction 2 h, but the iron leaching rate is no more than 12.9%, and the reaction activation energy is 25.7 KJ· L⁻¹ [17-18].

Conclusion and prospect

Reductive Leaching of pyrolusite by cellulosic biomass has some advantages such as high leaching rate, less environmental pollution, renewable and low cost producing. There are some some progress in the mechanism to make research and application, but as a new technology, using cellulosic biomass to reduce leaching manganese from pyrolusite in the initial stage. There are some problems and prospect in the cellulosic biomass to reduce leaching manganese: reduction leaching process and mechanism of manganese oxide ore by cellulose biomass further is needed to study; organic material of solution influences on the process of manganese electrodeposition are unclear; how to electrodeposit no selenium high purity manganese is necessary to investigate.

Acknowledgements

This work was financially supported by Major Project of Hunan Science and Technology ,China (No: 2010 FJ1011) .

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Mechanical performance and fracture of 3-ply Cu/Al/Cu clad metals

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Keywords: Heat treatment, Interfacial fracture, Copper, Aluminum, Clad.

Abstract. The mechanical performance and fracture of roll-bonded Cu/Al/Cu clad metal were investigated after heat treatment in the temperature range $200 \sim 500^{\circ}$ C. In the roll-bonded 3-ply Cu/Al/Cu clad metal, no visible interfacial reaction compound and defects were observed at the interfaces, ensuring the well-bonded Cu/Al interface until the final moment of fracture in tension. The reaction layer was observed at the Cu/Al interface after annealing at and above 400° C, which deteriorated the ductility of clad metals. The thickness of the reaction layer increased with increasing heat treatment temperature. The periodic cracks were formed perpendicular to the tensile direction due to the strain mismatch between metal layers and the reaction compound layer in the clad heat treated at high temperatures at 500°C. The slip localization and delamination induced premature crack formation in Cu and Al layer, resulting in the decreased clad metal fracture strain, especially after heat treating at 500°C.

Introduction

As the technology advances, the demand for advanced materials with enhanced properties and functions increases. It is getting more difficult to satisfy the combination of various properties such as superior mechanical and thermal properties in a single material. To meet these demands, clad composite material in which different metals and alloys with various properties were joined have been used in various industrial fields. The clad metals, consisting of two or more metals, have been developed because of their unique combination of properties. The properties of clad composite material are determined by the selection of component materials to be joined, the stacking structure of different materials with various thicknesses and interface structure and properties between different materials. Several method such as extrusion, rolling, electro-plating, overlay welding and explosive welding have been used for the clad materials production. Among these methods, the rolling is one of the useful processes because of its low-cost and good productivity [1-6].

In recent years, the roll bonding technique has been widely applied to fabricate many kinds of multi-layer clad materials, such as Cu/Al, STS/Al/Cu, Al/Mg/STS and Ti/STS. [7–10]. Copper and aluminum clad composites have been widely studied, because of their advantages associated with low density and cost-effectiveness over copper and copper alloys. For example, a two-layer clad sheet of aluminum/copper can almost reduce 40% in weight, with the equivalent electrical and thermal conductivity as a copper alloy. But the cost can be reduced to the 60% of a copper alloy. For these reasons, Al/Cu clad is frequently used for armored cables, yoke coils in TV sets, air-cooling fin and bus-bar conductor joint. However, producing Cu/Al clad sheet is a great challenge due to the different chemical and physical characteristics of component metals. The formation of brittle Cu_xAl_y intermetallic compound at elevated temperature weakens seriously the interfacial bonding. The investigations on the effect of interfacial intermetallics on the mechanical properties of Al/Cu composite fabricated by cold rolling are still few [2, 11].

In this study, 3-ply Cu/Al/Cu sheets were fabricated by a roll-bonding process. The roll-bonded Cu/Al/Cu clad metals were annealed up to 500°C for 3hrs in order to induce the formation of the interfacial reaction layer intentionally. The mechanical and fracture properties of clad metal were investigated, as a function of annealing temperature. The objective of this research was to examine the mechanical properties of annealed clad metals in relation to the interfacial properties.

Experimental

The Cu/Al/Cu clad-metal was fabricated using roll bonding of copper and aluminum of the commercial purity. Cu/Al/Cu clad-metal used in this study have a total thickness of 2.0mm and that of Cu and Al layer was 0.2mm and 1.6mm respectively (Fig. 1). The clad metal was annealed at temperatures from 200° C to 500° C for 3hrs. To examine the mechanical and fracture properties, the tensile test were performed using a Universal Materials Testing Machine (UNITED, US/SSTM) at room temperature. The gauge length was 15mm and the gauge width was 3.4 mm. The cross-head speed was 0.9 mm/min, corresponding to an initial strain rate of $1 \times 10-3$ /sec. Microstructures at the Cu/Al interfaces in clad metals were observed by an optical microscope (OM) and a scanning electron microscope (SEM). The chemical compositions of intermetallic compounds formed at the Cu/Al interface were examined by an energy dispersive X-ray analysis (EDX). To examine the variation of the hardness across the interface, the Vickers micro-hardness measurements were made by a Vickers hardness tester (AKASHI JP/HM-122).



Fig. 1. Schematic representation of the cross section of the Cu/Al/Cu clad metal.

Results and discussion

Fig. 2 shows the optical micrographs of Cu/Al interfaces for clad metals, as-rolled (a) annealed at 200° C (b), 300° C (c), 400° C (d) and 500° C (e) for 3 hrs. As-rolled and annealed clad metals exhibited no interfacial cracks and flaws, suggesting the bonding interface between Al and Cu is intact. When annealing temperature was at and above 400° C, intermetallic reaction layers were observed at Cu/Al interfaces as shown in Fig. 2(c~e). For annealing temperature of 400° C, a reaction layer with a thickness of about 11.4 µm is developed as shown in Fig. 2(d). As the annealing temperature increases to 500° C, the reaction layer continues to thicken to a thickness of 29.2 µm and a visible multi-layered structure can be observed as shown in Fig. 2(e).



Fig. 2. Optical micrographs of Cu/Al interface region in a 3-ply Cu/Al/Cu clad metals (a) as-roll-bonded Cu/Al interface (b)~(e) Cu/Al interface annealed at 200^oC for 3 hrs (b), 300^oC for 3 hrs (c), 400^oC for 3 hrs (d) and 500^oC for 3 hrs (e).

Vickers micro hardness values of the clad metal at Cu plate, Al plate, Cu/Al interface and intermetallic reaction layer are shown in Fig. 3. On annealing at and below 300^oC, the micro hardness at the Cu/Al interface is the average of those at the Cu and Al layers. Fig. 3 also shows that the micro hardness in Cu and Al layer decreases by annealing at and above 300^oC. This is mainly due to the recovery/ recrystallization of Al and Cu plates. The reaction layer generally possesses higher hardness values than those of corresponding base metals of Al and Cu. The hardness values in reaction layer increased with increase of the annealing temperature.

Fig. 4 shows the stress-strain curves of as-rolled and annealed clad metals at various temperatures. The as rolled clad metal and that annealed at 200^oC showed the similar behavior, high yield stress followed by a rapid strain softening. On annealing at and above 300^oC, the decreases of the yield strength and the increases of fracture strain can be attributed to the softening associated with recovery /recrystallization in Cu/Al/Cu clad metals. On annealing at and above 400^oC, the lower yield strength and the gradual work hardening were observed. The fracture strain decreased with increasing annealing temperature from 400^oC to 500^oC, suggesting the increased intermetallic layer has a harmful effect on the ductility.



Fig. 3. Vickers micro hardness of component layers (Cu, Al) and interface layers (Cu/Al) for as-rolled and annealed clad metals.



Fig. 4. Stress-strain responses of as-roll-bonded clad metals and those annealed at various temperatures.

Fig. 5 shows the SEM images of the fractured tensile specimens, (a) as-rolled and (b~f) annealed at $200^{\circ}C \sim 500^{\circ}C$ for 3 hrs. Despite the formation of neck for the overall specimen, Cu layer at the outer surfaces did not detached from the Al plate, indicating an excellent bonding between Al and Cu in the as rolled and annealed clad metals at and below $300^{\circ}C$. This result is consistent with the observation that no intermetallics were formed after annealing at and below $300^{\circ}C$. Therefore, the Cu and Al layers behave as if they are a single material. This may be due to the enhanced bonding between Cu and Al in the clad annealed at $300^{\circ}C$. The delamination was observed at the Cu/Al interface of the clad metals annealed at and above $400^{\circ}C$, and it initiated from the intermetallic reaction layer formed at the Cu/Al interface. The length of the delaminated region increased with increasing heat treatment temperature, consistent with the increase of the intermetallic layer with increasing heat treatment temperature. The intermetallic reaction layer has a detrimental effect on the bonding strength of the Cu/Al/Cu clad metal.

Fig. 6 shows the cross-sectional images of Cu/Al interface parallel to the stress axis of clad metals annealed at 300° C for 3hrs. Fig. 6 exhibits the Cu/Al interface region of un-deformed (a), and deformed specimens strained to 5% (b), 10% (c), 15% (d) and 25% (e). Fig. 6(a)~(e) were taken from

the central region of tensile specimen gage. It is apparent that the deformation of the Cu layer increased as the strain increases from 5% to 25%, as indicated by the increasing degree of wrinkles on the surface. On the other hand, the surface of Al layer was not greatly modified the strain. The difference of surface morphology can be associated with that of stacking fault energy between Cu and Al. The stacking fault energy in Al is much higher than in Cu, promoting easier cross slip and dislocation cell structure formation much finer slip, which can be resulted from [12]. The intact interface between Cu and Al after straining to 25%, suggest that the bonding strength between Cu and Al layer was high enough to sustain high strain. The similarity of the ductility in Cu and Al is thought to promote the rather homogeneous deformation and may have contributed to the intact interface after 25% strain.



Fig. 5. SEM images of the tensile specimens after fracture in tension.



Fig. 6. Cross-sectional images showing Cu/Al interface parallel to the stress axis of clad plates annealed at 300° C for 3hrs. un-deformed (a), and deformed to 5%(b), 10%(c), 15%(d) and 25%(e).



Fig. 7. Cross-sectional images showing Cu/Al interface parallel to the stress axis of clad plates annealed at 500° C for 3hrs. un-deformed (a), and deformed to 5%(b), 10%(c) and 15%(d) and 25%(e).

Fig. 7 shows the cross-sectional images of Cu/Al interface parallel to the stress axis of clad metals annealed at 500° C for 3hrs. Fig. 7 exhibits the Cu/Al interface region of un-deformed (a), and deformed specimens strained to 5% (b), 10% (c), 15% (d) and 25% (e). At the 5% strain (b), the periodic cracks were formed perpendicular to the tensile direction due to the strain mismatch between metal layers and the reaction compound layer. The strain concentrated slip lines developed in the localized region both in Cu and Al. The more pronounced slip lines developed in the vicinity of cracks

in Cu also can be attributed to the lower stacking fault energy in Cu than in Al. The easier cross slip in the slip planes in Al may diffuse the localized strain near cracks, resulting in the less clear slip traces in Al. The slip localization intensified and the number cracks apparently increased with strain(c~d). A long crack parallel to the stress axis developed at 10% strain at the interface between two different intermetallic layers as indicated by an arrow and widen with increasing strain. These slip localization and delamination is likely to induce premature crack formation in Cu and Al layer, resulting in the decreased clad metal fracture strain, especially after heat treating at 500°C.

Summary

As a result of the study on the deformation and fracture of the roll-bonded 3-ply Cu/Al/Cu clad metal, the following conclusions were obtained;

- 1) In the roll-bonded 3-ply Cu/Al/Cu clad metal, no visible interfacial reaction compound and defects were observed at the interfaces, ensuring the well-bonded Cu/Al interface until the final moment of fracture in tension.
- 2) After the heat treatment at 300 ^oC, Cu/Al/Cu clad metal exhibited a good combination of strength and ductility with inappreciable debonding along the interface even after the final fracture.
- 3) The intact interface between Cu and Al after straining to 25 % in the as-rolled clad suggests that the bonding strength between Cu and Al layer was high enough to sustain high strain. The similarity of the ductility in Cu and Al is thought to promote the rather homogeneous deformation and may have contributed to the intact interface after 25 % strain.
- 4) The reaction layer was observed at the Cu/Al interface after annealing at and above 400^oC, which deteriorated the ductility of clad metals.
- 5) The periodic cracks were formed perpendicular to the tensile direction due to the strain mismatch between metal layers and the reaction compound layer in the clad heat treated at high temperatures above 400°C. The strain concentrated slip lines developed in the localized region both in Cu and Al.
- 6) A long crack parallel to the stress axis developed at 10% strain at the interface between two different intermetallic layers in the clad heat treated at high temperatures above 400°C.
- 7) The slip localization and delamination induced premature crack formation in Cu and Al layer, resulting in the decreased clad metal fracture strain, especially after heat treating at 500°C.

Acknowledgements

This work was supported by the by the Fundamental R&D Programs for Core Technology of Materials funded by Ministry of Knowledge Economy, Republic of Korea (10037275).

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The effects of micro-hardness of Cu based friction materials to wear rates and the wear rates ratio of the pair and the friction materials

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Keywords: Cu based friction material; WRRPF; TiC; wear and friction.

Abstract: The four kinds of Cu based friction materials with different micro-hardness were fabricated by sintering method, the Ti content of four kinds of Cu based friction material is 8%, 12%, 16% and 20%, respectively. The tribological properties were carried out on ring-to-block tester. The results show that the wear rates and the wear rates ratio of the pair and the friction material with lower micro-hardness were lower than that of friction material with higher micro-hardness, and lower wear rates ratio of pair and friction materials (WRRPF) is very helpful for protecting pair of friction materials.

Introduction

The friction materials, which provides clutch adhesion or brake force for machine through itself wearing, is a necessary function materials of clutch and brake. As friction materials, the main function parameters were friction coefficient and wear rates. The friction material with modest friction coefficient is crucial to a smooth and efficient brake of machine [1], and low wear rates of friction material has a direct effect to prolong service life of friction material. In addition, there are requirement for friction materials such as mechanical properties, high-temperature behavior, low cost, environmental protection, and so on. Although there are requirement to friction materials for little damage to pair, the literatures [2-5] is more focused on the main parameters of friction materials, namely, friction coefficient and wear rate, and there are little report about the wear rate of pair. The friction material is wearing part for machine and it would be replaced when used to a certain degree, and it is not hope to replace the pair. The micro-hardness of friction materials is affecting not only itself wear rate but also the pair's. The article will focus on the effects of micro-hardness of friction materials (WRRPF).

Experiment

Source powders include electrolytic Cu powder (75-150 μ m; 99.7% purity), Ti powder (75 μ m; 99.9% purity), and graphite powder (30 μ m; 99% purity). The content of Ti in Cu based composites is at a weight fraction of 8%, 12%, 16%, 20% (named as 8#, 12#, 16#, 20#, respectively), respectively, and the content of the graphite was fixed as 12 wt%. The composition of four Cu based friction materials are listed in Tab.1.

Tab. 1 Composition of Cu based friction materials (wt. %)					
name	Ti	Graphite	Cu		
		- " <u>r</u> · ·			
8#	8	12	Balance		
12#	12	12	Balance		
16#	16	12	Balance		
20#	20	12	Balance		

The ingredients were mixed for 8 hours by a mixer. Then the powders were hot pressed in a graphite mold in a vacuum sintering furnace. The hot press pressure was 5MPa at 300°C, 10MPa at 500°C, and 20 MPa at 780°C for 1 hour, the heating-rate was about 10 °C /min. The samples were machined into rectangular block of 12 mm × 12 mm × 19 mm for tribo-testing. The micro-hardness was measured by a Vicker's micro-hardness tester at a constant load of 200gf and dwelling time of 10s. The hardness values were the average of ten times tests of each sample.

Wear tests were conduced on a MRH-3 block-on-ring wear tester (made by Jinan Testing Machine Factory, China). The schematic of the block-on-ring pair is described in detail elsewhere [6]. The ring is made of AISI52100 bearing steel with hardness of HRC62-63 and the outer diameter of 49.24 mm. The wear loss was weighed by an electronic balance with accuracy of 0.1 mg. The tests were carried out at load of 75~150 N, sliding speeds of 1.04~2.60 m/s (400~1000 rpm) and the sliding time of 40 min. Before each test, the samples was abraded with 900 abrasive papers and then cleaned with accuracy. Each specimen was weighed before and after test.

Wear rate was calculated by following formula:

w = v/pl

(1)

Where w is the wear rate; v is the worn volume of the specimen, which can be calculated with wear mass loss and the density of the specimens; p is the normal load applied; l is the sliding distance of specimen.

Scanning electron microscope (SEM) was carried out for viewing the worn surfaces and microstructure, and the phases of composites were characterized by XRD.

Results and Discussion

The micro-hardness and density of Cu based friction materials are listed in Tab.2. It can be seen that the micro-hardness of friction materials is increased while density is decreased with the Ti content increased. The density of Ti is only 1/3 of Cu, but its strength is high, so the micro-hardness of friction materials is elevated and its density is decreased with the increasing of Ti content. The micro-hardness of 8# is 45 and the micro-hardness of 12# and 16# only has a little increment, but the micro-hardness of 20# is 112 which was a great increment to that of 8#. Fig.1 is the XRD patterns of 20# material. It can be seen from Fig.1 that peaks of TiC were discerned. Obviously, TiC was formed through the reaction of Ti and graphite [7]. With increasing of Ti content, there is more TiC synthesized which has high micro-hardness, so the micro-hardness of friction materials was increased and the micro-hardness of 20# is the highest.

rab.2 The intero-narchess and density of interior materials						
	8#	12#	16#	20#		
Micro hardness(HV)	45	56	70	112		
Density(g/cm^3)	5.09	5.04	4.90	4.71		

Tab.2 The micro-hardness and density of friction materials



Fig. 1 XRD patterns of 20# material

Fig.2 shows the variation of wear rates of friction materials and the pair with sliding speeds under a load of 100N. From the Fig. 2a it can be seen that the wear rates of the pair and friction materials are all increased with the increasing of sliding speed, and the wear rates curves of the pair and friction materials are very similar. It can be seen from Fig. 2b that the WRRPF of 8# material is the lowest. The WRRPF value of 8# material is 1/9 at sliding speed of 2.08m/s, that of 12# and 16# is 1/5, and that of 20# is 1/3 which is the highest. The trends of WRRPF at other sliding speeds are similar to at sliding speed of 2.08m/s. From Fig.2, it can be seen that the low micro-hardness of friction materials is helpful to low the wear rates of the pair and friction materials, and the wear rates of the pair is far more less than that of the friction materials, this is very important to prolong the service life of the friction material.



Fig. 2 The variation of wear rates with sliding speeds under a load of 100N: a) of friction materials,b) of pairs (the fractional number marked in Fig. 2b are the WRRPF, and the 'P' of 8#P, 12#P, 16#P and 20#P is presented the pair.).



Fig. 3 The variation of wear rates with load under a sliding speeds of 2.08m/s: a) of friction materials, b) of pairs (the fractional number marked in Fig. 3b are the WRRPF, and the 'P' of 8#P, 12#P, 16#P and 20#P is presented the pair).

Fig. 3 shows the variation of wear rates of the friction materials and the pairs with loads at sliding speed of 2.08m/s. From Fig.3a, it can be seen that the wear rates of friction materials is increased with the increasing of loads, and the wear rates of the 8# friction material which has the lowest micro-hardness is the lowest. It can be seen from Fig. 3b that except the wear rates of the pairs of 16# materials the wear rates of other friction materials' pairs are increased at load increased from 75N to 125N, then decreased with load increased to 150N. The wear rates of the pair of 16# friction material are decreased with the load increasing. It also can be seen from Fig.3b that the WRRPF is much low at high loads, and the WRRPF of 8# friction materials is the lowest and the highest WRRPF of 8# friction materials is helpful to low the wear rates of the pair and friction materials and WRRPF so prolong the service life of the pair.

Fig. 4 shows the variation of friction coefficient of the pair and friction materials with loads and sliding speeds. It can be seen that the friction coefficient of 8# friction material which has a lowest micro-hardness is the lowest. From Fig. 4a it can be seen that the friction coefficient of pair and friction materials are low at the load of 75N and 150N. From Fig. 4b it can be seen that the friction coefficient is increased with increasing of sliding speeds.



Fig. 4 The variation of friction coefficient of frictional couple: a) with loads at sliding speed of 2.08m/s, b) with sliding speed at load of 100N.

In the tribological process, there are wear debris produced continually due to shearing action of frictional force. Those wear debris containing much solid lubricant can reduce direct contact area between friction couple, and have a lubrication action to friction couple [8]. At the condition of the same load, wear debris produced from friction materials with low micro-hardness is much more than that of from friction materials with high micro-hardness, so the friction materials with low micro-hardness has low coefficient (Fig. 4) as well as low wear rates. With increased sliding speed, the number of shearing action in per unit time is also increased, so the wear rates of friction materials is increased accordingly (Fig. 2).

With load increased, the shearing action between friction couple become more intense, and there is more wear debris produced, so the wear rates of friction couple is elevated (Fig. 3a). At the high loads, there is more wear debris produced result in reduced direct contact area between friction couple, so the wear rates of the pair is decreased obviously (Fig. 3b). The WRRPF of friction materials with low micro-hardness at high load is the lowest, this is very important for prolonging the service life of the pair.

Fig. 5 shows the worn surfaces of 8# and 20# friction materials at sliding speed of 2.08m/s. It can be seen that the wear mechanism of friction materials is dominated by adhesion. There are more cracks in the worn surfaces of 8# friction material which has low micro-hardness, while there are irregular grooves in the worn surfaces of 20# friction material which has high micro-hardness. With increased Ti content, there are more TiC synthesized which resulted in high micro-hardness of friction materials, and the brittleness of friction materials with high micro-hardness is increased accordingly. Under shearing action of friction force, the cracks in worn surfaces of friction materials which have low micro-hardness became larger and larger and dropped to form wear debris finally, and the wear rates of friction force, and mainly produced wear debris due to high brittleness under shearing action of friction force, and mainly produced wear debris through digging the surfaces of pairs by hard particles (grooves were produced by hard particles digging). So the wear debris is too little to lubricating, and the low micro-hardness.

The low micro-hardness of friction materials bring about not only low wear rates but also low WRRPF. It can be seen from Fig. 3b that the lowest WRRPF of the 20# friction material which has high micro-hardness is 1/12, and the highest WRRPF is 1/3, namely, the wear rates of the pair and the friction materials are very close to each other, so it is difficulty to protect the pair. On the contrary, the highest WRRPF of 8# friction material which has the lowest micro-hardness is only 1/9, namely, the wear rates of friction couple is not in the same order of magnitude, so the pair can be protected effectively.





Fig. 5 SEM micrographs of the worn surfaces of friction materials at sliding speed of 2.08m/s[9]: (a) 8# and (b) 20# friction material at load of 75N, (c) 8# and (d) 20# friction material at load of 125N.

Conclusions

The effects of the micro-hardness of four Cu based friction materials with different micro-hardness to the wear rates of friction couple and the WRRPF were investigated and the important results as follow:

1. The wear rates and the WRRPF of friction materials with low micro-hardness are low, so it can prolong the friction couple service life and protect the pair effectively.

2. The wear rates and the WRRPF of friction materials with high micro-hardness are too high to protect the pair.

3. The WRRPF is low at high loads.

Acknowledgments

This investigation was supported by Natural Science Foundation of Gansu province of China (1107RJZA119) and Gansu province high school graduate tutor research project funding(1114-01).

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Influence of Mn and Heat Treatment Technology on Microstructure and Mechanical Properties of a low-alloy Wear-resistant Cast Steel Shovel tooth

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Keywords: Wear-resistant Cast Steel, Mn, Heat treatment, Mechanical Properties

Abstract. The influences of Mn and heat-treatment technology on microstructure and mechanical properties of medium-carbon-low-alloy wear-resistant cast steel were investigated. The results show that the hardness first increases and then drops down with the increase of Mn content, and the best hardness is 54HRC with Mn content 1.5%. The impact toughness first increases and then drops down with the increase of Mn content. The hardness and impact toughness first increase and then drop down with the increases of quenching temperature. The optimal impact toughness can be obtaind by quenching at 920°C and tempering at 200°C. Part of lower bainite and residual austenite and mass of tempered martensite are obtaind after tempering.

Introduction

Excavator shovel tooth is on one of the major wear parts with large consumption [1-5]. As the traditional high-manganese steel shovel tooth material can not fully play the role of work hardening in low-impact load working conditions, the wear resistance is not high.

In this paper, the influences of Mn and heat-treatment technology on microstructure and mechanical properties of ZG40CrMnSi low-alloy wear-resistant cast steel were investigated which were aiming mainly at shovel teeth working conditions. New excavator shovel tooth material and new production technologies of low cost, simple technology and high wear resistance were explored.

Materials and methods

Experimental Materials and Methods. The chemical composition of experimental steels in Table 1.

Table1 Chemical compositions of wear-resistant steel ωt (%)						
С	Mn	Si	Cr	RE	S	Р
0.40~0.45	1.1 ~ 1.8	0.8 ~ 1.4	0.6~1.2	tiny	≤ 0.05	≦0.05

Modelling with sodium silicate sand, melting molten steel by intermediate frequency furnace, adding rare-earth silicon inside package. Then pouring into 10.5mm × 10.5mm × 55mm unnotched specimens at 1500° C. Heat treatment process is shown in Figure.1. Impact toughness was tested by ZBC-300 type impact testing machine. Hardness was tested on the HR-150A Rockwell hardness tester, microstructure was observed by Olympus optical microscope.



Fig.1 Heat treatment process curve of experimental steel

Experimental results and analysis

Mechanical Properties Testing and Analysis. Figure.2 has shown mechanical properties of different Mn contents of the experimental steel after 920 °C quenching and 200 °C tempering. The hardness first increases and then drops down with the increase of Mn content (1.3% to 1.7%), The impact toughness first increases and then drops down with the increase of Mn content, and reached (223.5J/cm²) in the w (Mn) = 1.5%. This is because parts of the Mn solute in the ferritic (or austenitic), the others formate manganese alloy cementite (Fe, Mn) 3C, which increase the hardenability and strength of the steel. However, as Mn can enhance the bad tendency of grain coarsening and temper brittlement, the austenite grain growing up with further increased of Mn content, and cause the change of impact toughness [5].

Figure.3 has shown the mechanical properties of steel after different quenching and 200 °C tempering. It can be seen that hardness and impact toughness increase at first and then drop down with the increases of quenching temperature. This is because with the increase of austenitizing temperature, in the same holding time conditions, the content of alloy elements and carbon dissolving in the austenite and the austenite composition uniformity increased, the content of lath martensite after quenching relative increased. In addition, hardness and toughness increased as the enhancing of austenite stability and eventually increasing of residual austenite content [6-7]. However, lower hardness and toughness were obtained at 970°C quenching for the austenite grain growth getting easier and the ultimate microstructure coarse. In this study, the best fit of hardness and toughness were obtained after 920°C quenching and 200 °C tempering.

Figure.4 has shown the hardness and impact toughness after different quenching process. It can be seen that the hardness was maximum after water-cooled, then the isothermal, air-cooled the last. The variation of impact toughness was the opposite. The microstructures were different after treatment. Water-cooled microstructures were $F + A_r + M$, air-cooled microstructures were $P + F + A_r$ and isothermal microstructures were $B_l + F + A_r$.



Microstructure observation and analysis

Manganese Steel of the experimental. Figure 5 shows microstructures of different manganese contents after 920 °C austenitic and water quenched. It can be seen that water-cooled microstructures after tempering were $F+A_r+M_t$. M_b content and the hardness of steel significantly increased with Mn concent increasing. Manganese can reduce the critical cooling rate and promote the formation of M,

therefore, M content increased with the gradually increasing of Mn. Manganese impacted toughness of steel because its increasing reduced the Ms point and affected the M substructure, which tallies with variation trend of mechanical properties of experimental steel.



Fig.5 The influences of Mn content on structure of experimental steel a) $\omega_t(1.3\%) \times 500$ b) $\omega_t(1.5\%) \times 500$ c) $\omega_t(1.7\%) \times 500$

Austenitizing temperature on the impact of experimental steel. Figure.6 has shown the microstructures of experimental steel with ωt (Mn) 1.7% after water quenching by different austenitizing temperature. The microstructures was mainly tempering M by water treatment and tempering. When the quenching temperature was low, stability of high temperature austenite was low due to less Cr, Si, Mn and other elements dissolving in austenite. The austenite hardenability rised, and the hardness and toughness of experimental steel increased with the quenching temperature rising, since more and more Cr, Mn, Si and other elements dissolved into high-temperature austenitic. However, the stability and grains size of austenite significantly increased and also the retained austenite content increased when the quenching temperature was high.



Fig.6 The influence of austenitizing temperature on structure of experimental steel a) 870°C×500 b) 920°C×500 c) 970°C×500

Steel quenching methods on the impact of experimental. Figure.7 shows the microstructures after different ways of quenching at 870°C austenitizing. You can see that isothermal microstructures were B_l+F+A_r+M , air-cooled microstructures were P+F and water-cooled microstructures were M_b+F+A_r .

Alloy elements' adding can make the C curves to move right, reduce the critical cooling rate at 870° C austenitizing with small amount of alloys dissolving. Isothermal process B_l+M were obtained in the microstrucrures, air-cooled were mainly P and a small amount of F due to slow cooling rate in this process, and water quenched steel microstructure was mainly M, since the experimental cooling rate increased and the stress of austenite increases, which promoted the formation of M.



Fig.7 The influence of quenching way on structure of experimental steel a) isothermy×500 b) air-cooling×500 c) water-cooling×500

Heat Treatment of shovel teeth. The heat treatment process of shovel teeth was determined as follows according to the experimental results and the working conditions of shovel teeth, austenitizing at 920 $^{\circ}$ C for 1h, sharp teeth to adopt water bathe quenching or salt bathe quenching, and the tooth root by dry quenching. The hardness was HRC 36-47-58 from the tooth root to the tip respectively according to experimental performance test results of parts.

Conclusions

Through different manganese contents and different heat treatment processes, the mechanical properties and microstructure comparative analysis of the samples, we can draw the conclusions as following:

(1) The hardness and impact toughness first increases and then drops down with the increase of Mn content, and the best hardness is 54HRC with Mn content 1.5%.

(2) The hardness and impact toughness increase at first and then drop down with the increases of quenching temperature. The material's mechanical properties were better when austenitizing temperature was at 920°C than that of 870°C and 970°C.

(3) The mainly obtained microstructures were respectively lath-martensite and low-bainite, pearlite and a small amount of ferrite, water has been microstructures primarily lath martensite and small amount of ferrite and residual austenite after isothermal treatment, air-cooled and water-cooled.

(4) The best mechanical properties were obtained at 1.5% Mn content, 920°C austenitizing for 60min isothermal, impact toughness reached 223.43J/cm², hardness HRC49.6.

Acknowledgements

This work was financially supported by Heilongjiang province ZD200909 fund, Heilongjiang ministry of education project 11221476,12521519 and Jiamusi university innovation subject.

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Fabrication of Nb-based Alloy via Spark Plasma Sintering

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Abstract. Nb-5 at.% W-5 at.% Mo-2 at.%Zr-2 at.% C (Nb5522) bulk alloys were prepared using blended powders or ball-milled powders via spark plasma sintering. The differences between blended powder compacts and ball milled powder compacts with respect to their density, microstructure and mechanical properties were studied. The results showed that ball milling enhances the sinterability of Nb5522 powders. After sintered by SPS at 1873 K, the milled powders achieved a near-full densification density. The SPS process favors the precipitation of (Nb, Zr)C particles.

Introduction

Niobium, with a density of 8.57 g/cc, is the lightest refractory metal [1]. Nb-based alloys have been considered as one of the most promising refractory structural materials in place of Ni-based superalloys, which have a maximum operating temperature of about 1273 k [2]. Because the strength of Nb decreases significantly at temperature above 1200 K, some refractory elements such as W, Mo, Ta, Zr and V have been reported to be used in the solid solution strengthening of Nb-based alloys [3]. All of the Nb-based alloys in production today were produced by traditional metal working processes such as melting, forging, extrusion, spinning, annealing and welding [4]. This method was either beset by the undesirable segregation and grain growth during melting and annealing or frequently limited by the ultrahigh processing temperature and the time-consuming complicated process.

The powder metallurgy process can usually obtain alloys with uniform composition and morphology, preventing recrystallization and severe grain growth [5].Ball milling is a solid state powder processing method for attaining homogeneous ultrafine particles with high activity. During milling process, powder particles are trapped between colliding balls, undergo severe plastic deformation followed by work hardening, and fracture into ultafine powders containing high strain energy[6,7,8] Spark plasma sintering (SPS), a novel consolidation process that combines plasma generation with resistance heating and pressure application, can densify materials at a lower temperature in a very short time. This short-time sintering process favors the preparation of metals with small grain size [9].

In the present study, Nb-5 at.% W-5 at.% Mo-2 at.%Zr-2 at.% C alloys were prepared via SPS process. The differences between blended powder compacts and ball milled powder compacts with respect to their density, microstructure and mechanical properties were investigated.

Experimental procedures

The alloy powders were prepared with nominal composition of Nb-5 at.% W-5 at.% Mo-2 at.%Zr-2 at.% C (Nb5522). Elemental Nb (\geq 99.8 %; \leq 44 µm), W (\geq 99.9 %; \leq 3 – 5 µm), Mo (\geq 99.9 %; \leq 1 – 2 µm), Zr (\geq 99.99 %; \leq 4 - 6 µm), and C (\geq 99.9%, \leq 1µm) powders were used as received without any further purification. Blended powders were prepared in an argon-filled 3D mixer (ZJH-I), while ball milling of powder mixture was carried out in argon atmosphere for 18h by using a QM-QX4L type planetary mill machine with the selected velocity of 250 rpm. Stearic acid was used as a process contral agent in order to prevent secessive cold welding of these powders during mixing and ball milling. Hardened chromium steel vial containing WC hard metal balls (6, 8, and 10 mmin diameter and 20%, 50%, and 30% in weight, respectively) was used for ball milling, and the ball-to-powder weight ratio was 20:1.

These powders were consolidated to the size of 20 mm diameter and 10 mm thickness by a SPS machine (DR SINTER - 1050) at temperatures between 1473 and 1873 K under a pressure of 40 MPa in a vacuum of 2 Pa for 5 min. The heating rate was 100 K/min and the temperature was measured at the surface of a carbon mold during sintering.

The microstructure and resultant phases were studied using a scanning electron microscope (SEM-ZEISS ULTRA 55) and an X-ray diffraction (XRD-MAC Science M21X). The density of sintered samples was measured by Archimedes' principle. Hardness was measured using Vicker's microhardness tester (HVS-5/10/30/50), with sample size of 3 mm \times 5 mm \times 10 mm.

Results and discussion

Fig. 1 shows the morphologies of the blended powder and milled powder, respectively. It is noticed that the blended powder consists of large irregular shaped particles of various sizes (Fig.1 (a)), while the milled powder exhibits homogeneous ultra fine particles with sizes of about less than 10 μ m (Fig.1 (b)). It can be concluded that milled powder suffered serious colliding during ball milling process. Because of the high-energy crashes between particles and balls, the raw powder experienced plastic deformation followed by work hardening, and then fractured into fine particles.



Fig. 1 SEM micrograph of Nb5522 powder after (a) blending, and (b) ball milling

Fig.2 shows the evolution of sintered densities as functions of temperature. It is vividly discernible in Fig. 2 that the density of compacts increases with increasing sintering temperature. The milled compacts have higher densities than that of blended bulks. The relative density of the milled compact sintered at 1773 K is about 98 %, achieved near-full densification. Increasing sintering temperature to 1873 K leads little increase in density for milled bulks. However, the blended powders are not well densified even at temperature of 1873K, with a relative density of about 93 %. The above results suggest that the sinterability of Nb5522 powders is greatly enhanced by ball milling process. The poor sinterability of blended powder can be attributed to its relatively coarse particle size. The effect of milling may be partially ascribed to the de-agglomeration of particles, in addition to continued refining of particles and grain sizes of the powder [10].



Fig.2 Relative density of Nb5522 compacts.

Fracture surfaces of samples sintered at 1873 K are shown in Fig. 3. Cleavage planes and small quantity of glide steps are obtained in the surface of the blended compact (Fig.3 (a)). It suggests that brittle transgranular failure was the dominant failure mode. Fig.3 also demonstrates that the blended bulk has coarse grains with some holes among them, while the milled compact exhibits a dense fracture surface with tiny grains, which consistent with the relative densities observed in Fig. 2. The difference of fracture surfaces between blended bulk and milled bulk might be caused by the different particle status of the as-sintered powders. Due to the ball milling process, the ultra-fine milled powders have abundant surface energy and grainboundary energy, which can provide a large driving force for sintering [11]. Additionally, the tiny, dense microstructure makes the milled compact reveal a higher microhardness (485 Hv) than that of blended compact (446 Hv).



Fig. 3 SEM photographs of (a) blended compact, and (b) milled compact sintered at 1873 K.

The XRD patterns of compacts sintered at 1873 K are presented in Fig. 4. It is noticeable that blended bulk has the similar pattern with milled compact. No W or Mo peak is observed in Fig.4, indicates the solid solution of W and Mo elements at 1873 K. The appearance of ZrC, $ZrC_{0.7}$, and Nb₂C peaks demonstrates the C element combines with Zr atoms and part of Nb atoms, forming second phase particles. Researches have reported that the precipitation of (Nb, Zr)C particles are difficult in Nb-based alloy ingot, needing long-term annealing at temperatures between 1273 K and 1673 k[12]. The results obtained in Fig. 4 manifests that the SPS process favors the precipitation of (Nb, Zr)C particles.



Fig. 4 XRD patterns of (a) blend compact and (b) milled compact sintered at 1873 K

Conclusions

A near-full densification of Nb-5 at.% W-5 at.% Mo-2 at.%Zr-2 at.% C alloy compact was prepared via ball milling followed by SPS processes. It is found that the sinterability of Nb5522 powders was greatly enhanced by ball milling process. After sintered by SPS at 1873 K, the milled powders achieved a relative density of about 98%, exhibiting a dense morphology with fine grain size. The SPS process favors the precipitation of (Nb, Zr)C particles.

Acknowledgement

This work is financially supported by the National 973 Program (2011CB606306), National 863 Program (2009AA033201) and National Natural Science Foundation of China (No. 50974017).

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An investigation of mechanical properties of Al-Mg porous materials with cell wall strengthening

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Keywords: AI-Mg porous material; mechanical properties; cell wall strengthening

Abstract. Mechanical properties of Al-Mg porous materials which were made by self melting reactions at low temperatures are investigated in this work. The results showed that the yield strength of Al-20%Mg was up to 240 MPa, and this is the compressive characteristics of brittle porous materials. The excellent of mechanical properties of Al-Mg porous material was analyzed and the reason was ascribed to the homogenous distributed pore with cell wall strengthening.

Introduction

Metallic porous materials are one kind of materials which are prepared by sintering metal powder, metallic fiber or metal wire network. Metallic porous materials have interpenetration structure in 3D space. The main fabrication methods are foaming method, powder compact melting, powder metallurgy method, metal deposition, sintering powders or fibers and so on [1-4]. Metallic porous material has the characteristics of the material from which it is made. Also, metallic porous material has low density, combining with excellent properties of absorption and vibration damping, and is widely applied in petrochemical, metallurgical and mechanical industries [5-7]. With the increasing range of application, metallic porous materials are developing towards integration of structure and function. The mechanical problems gradually attracted the attention of the researchers in the entire world [8,9].

For the traditional methods to make metallic porous materials, there are addictives existing on the cell wall which are difficult to be get rid of, and this will affect the mechanical properties. We synthesized Al-20wt.%Mg porous materials using the self melting technology at low temperatures, and the mechanical properties are also studied.

Experimental

Al and Mg powders were baked at 200 °C x2h, and 120°C x1h, respectively. Then 20 % (in weight percent, hereinafter) and 80 % Al were mixed in SYH-5 mixer for 40 min., and after that the compact was obtained under a pressure of 400 MPa. Finally, the porous material was isothermally kept at

470°C for 10 min. using SPS sintering system. The morphology was observed by JSM-840 SEM, cell wall phases were analyzed by Rigaku D/MAX2400, and the mechanical properties were measured by Instron-1195 testing machine.

Results and discussions

Fig.1 showed the morphology of Al-20wt.% Mg porous materials. The pore is nearly spherical with a diameter of 50 μ m which is surrounded by a homogenous wall with a thickness of 15 μ m. And, the pores are not connected to each other. Fig. 2 gave XRD patterns of Al-20wt.%Mg porous material. It can be seen from the XRD patterns that this porous material is composed of α -Al and β (Al₃Mg₂). And the EDX (energy dispersive x-ray spectrum) also conformed that B area was pure α -Al and cell wall (A area) was composed of Al-rich compounds containing Mg content. According to the binary phase diagram, the Al-rich compounds should be α -Al and β (Al₃Mg₂). There was no impurity found at cell wall because of no addictives containing in the raw materials which were used to make porous materials.



Fig.1 SEM morphology of Al-Mg porous material (500x)



Fig. 2 XRD patterns of Al-20.wt. % Mg porous material

Fig. 3 gave compressive stress-strain curves of both Al-Mg porous material and pure Al. By comparison of the compressive behavior of pure Al, Al-Mg porous material has the following characteristics: 1) In a wider elastic range, Al-Mg porous had a linear relationship between stress and strain, while pure Al only has about 1% elastic range; 2) Al-Mg porous material has a distinct yielding point; 3) After yielding, the stress-strain relationship became complex and shows a wave-like type and hardly showed strain-hardening.

Fig.4 gave an illustration of compressive curves of both porous Al alloy with Ni-P as addictives and foamed Al-Mg alloy. Comparasion with Fig. 3, the similarity can be seen that there are an obvious long yielding plateau for both alloys. And, this is indeed one energy absorption ability for porous material. Al-Mg porous material with cell wall strengthening effect has a yield strength of no less than 200 MPa, while Al porous alloy with Ni-P as addictives and foamed Al-Mg alloy only have



Fig. 3 Comparison of compressive stess-strain curves of pore wall strengthened porous material with pure Al



Fig. 4 Al porous material with Ni-P as addictives and foamed Al-Mg alloy. (a) Ni-P porous Al alloy and (b) foamed Al-Mg alloy

a yield strength of no higher than 50 MPa. Meanwhile, the compressive plot of Al-Mg porous material changes in a wave-like mode and no increasing intendency. For the latter one, there is an increasing tendency for the compressive strength.



Fig. 5 Ideal compressive curves for elasti-plastic and elastic-brittle porous materials. (a) elasti-plastic porous material. (b) elastic-brittle porous material.

Fig. 5 gave the ideal compressive plot of ealstic- plastic and elastic-brittle porous materials. It can be seen from the figures that both materials have three regions: linear elasticity, plateau and desification. The obtained Al-Mg porous material in this work has lower porosity rate than that of foamed materials. But, their compressive curves are similar to each other, and then only difference is that our porous materials didn't reach the densification stage. Our Al-Mg porous material with cell

wall strengthening effect is composed of Al matrix and brittle strengthening layer, and Al matrix belongs to elstic plastic meterial. Form the perspective of microstructure, Al matrix can be considered as a confinement because the pores are not connected to each other while they are surounded by the strengthening layer. The strengthening phase in porous Al-Mg material is intermetallic compound (s), and there is less sliding systems, so sliding deformation is difficult to happen. Also, during compressive process, Al matrix first deforms and stress concentration can be transfered to the strengthening layer. Even though, the applied stress is far below the destroying strength of these strengthening phases, the micro zone stress concentration is high enough to destroy the compound layer. The sign of destroy happening is the yielding point of Al-Mg porous material with cell wall strengthening. From Fig. 3, the macroscopic yielding in the present Al-Mg porous material was accompanied by a steep but smooth drop in flow stress, followed by an extended "plateau" region, consisting of periodic increases and decreases in flow stress punctuated by numerous sharp "serrations". Because of the confinement of Al matrix, the bearing loading ability loss of porous material was made up by Al matrix. Therfore, no intensive drops happened for stress-strain curves like that of brittle-elastic porous material (see Fig.5(b)). Also, this behaviour is different to that of elastic-plastic porous materials (Fig. 5(a)) because of no long yielding pleatau happed for Al-Mg porous material. Thus, it is concluded that the compresiive behaviour of our Al-Mg porous material with cell wall strengthening is the compressive property of elastic-elastic porous material under confinement condition.

Conclusions

1. There are cell wall strengthening layer existing in Al-Mg porous material which was made by self melting reaction method at low temperatures. The strengthening layer is composed of Al-rich compound(s).

2. Al-20 wt.%Mg porous material has a yield strength of 240 MPa which is higher than that of other porous materials.

3. The main reasons for the excellent mechanical properties of Al-Mg porous material are ascribed to small pore size, higher relatively density and homogenous distributed and cell wall strengthening pores.

4. The compressive behavior of Al-Mg porous material is a typical property of brittle-elastic porous material under confined condition.

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The effect of the preparation conditions of Al₂O₃ support to catalysts for diesel particulate removal from exhaust gases

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Keywords: Diesel engine exhaust treatment; Particulate matter; Modified support; Preparation condition;

Abstract. A study has been conducted on the preparation conditions of Al_2O_3 for the catalysts for diesel particulate matter. The results show that the preparation conditions of Al_2O_3 support had great contribution to performance of Sn-Cu-K-V/Zr0₂-Al₂O₃ catalyst. The conditions of precipitant, pH value and calcination temperature were investigated. The experiment results show that the suitable precipitant was Na₂CO₃, the pH value of the solution was 9 and calcination temperature was $1000^{0}C$. The catalyst which active components were loaded on the modified support by immersion method showed better catalytic activity.

Introduction

As the standards to control the emission of diesel engine exhaust becoming more and more stringent, after-treatment for exhaust is required. Particulate matter, which is one of the main pollutions of the diesel engine exhaust and the hardest one to reduce, is hazardous to human health due to its potential mutagenic and carcinogenic activity^[1]. Several different after-treatment to reduce exhaust have been suggested. Particulate traps is considered to be one of the best after-treatments. The development of a filter with catalyst coverage that combines retention and oxidation of the emitted particulate matter has drawn wide attention^[2,3]. The catalyst used in the trapper should decrease the ignition temperature of particulate matter to typical exhaust temperature of diesel engine vehicles. The particulate matter could be moved on time^[4, 5]. In this paper, the work was based on the previous work and effect of preparation condition of Al₂O₃ support to catalyst for diesel particulate matter was studied^[6, 7, 8].

Experimental

1.1 Catalyst preparation

The modified Al_2O_3 were prepared by co-precipitation of an aqueous solution of suitable metal nitrates with an aqueous solution of precipitant. The two solutions were mixed under vigorous stirring at 75 0 C at different pH. The resulting slurry was aged in the mother liquor at 75 0 C for 3 h. It was then filtered and washed with distilled water until the pH of the filtrate was around 7. The precipitate was then dried at 120 0 C for 12 h and then calcined at 1000 0 C. The catalyst was prepared by impregnation which active components were loaded on the modified support.

1.2 Catalyst activity test

The catalytic activity for the combustion of particulate matter was determined by temperature-programmed oxidation (TPO). This TPO equipment mainly consists of a fixed bed inserted in a quartz micro-reactor. The fixed bed was prepared by mixing 555 mg of a 1:9 by weight mixture of soot (Printex-U) and catalyst. And then the catalyst/soot mixture was inserted in the reactor and confined between two layers of quartz wool. The tests were carried out by heating the sample up to 700 0 C at a 3 $^{\circ}$ C /min rate, with a mass flow meter delivering a gas flow (composition: 5%O₂,

95%He (balance)) toward the micro-reactor (150 ml/min), after an initial 30 min stay at 473K under He flow as a common pre-treatment. The outlet gas was analyzed via an on-line gas chromatograph (Shanghai Kechuang, GC900A) with columns of TDX-01, equipped with thermal conductivity detector (TCD).

1.3 Catalyst characterization

Scanning electron microscopy (SEM, Leo-1530VP) was used to observe the microstructures of catalysts

Results and discussion

2.1 Effects of precipitants on the performance of catalysts

In the precipitation process, using different precipitants, the growth of grain and the speed of growth were different; thus, the particle size of alumina catalyst carrier was different, resulting in a change of the surface area. The effects of different precipitants for the modified Al_2O_3 were shown in Fig. 1



Fig. 1 Effects of precipitants on the performance of catalysts

In the Fig. 1, used the NaOH and $(NH_4)_2CO_3$ as precipitants, The ignition temperature of particulate matter was about 390 0 C. While used Na₂CO₃ and NH₄OH as the precipitant, the ignition temperature was about 350 0 C. Na₂CO₃ reflect the relatively narrow combustion interval.

2.2 Effects of pH value on the performance of catalysts



Fig. 2 Effects of pH value on the performance of catalysts

Modified support Al_2O_3 was prepared by co-precipitation. In the precipitation process, the pH of the solution impacted greatly on the precipitate composition and morphology, thereby affecting the activity of the catalyst composition and crystalline structure, thus the catalyst activity and thermal stability change a lot.

In the Fig. 2, when pH value was 7, the ignition temperature was the lowest, about $355 \, {}^{0}$ C, however, the combustion interval was relatively wide. When the pH value was 8, 10, 11, the effects were no different. When pH value was 9, the ignition temperature was about $370 \, {}^{0}$ C, higher than the temperature when pH was 7, but lower when they were other pH values, while the combustion interval was the narrowest when the pH value was 9. So, keeping the pH value at 9 was the best.

2.3 Effects of calcined temperature on the performance of catalysts

Fig. 3 showed that the catalytic activity increased with the increase of the modified support Al_2O_3 calcination temperature. The higher calcination temperature, the better catalytic activity.





When the calcination temperature was 600 0 C, the activity of the catalysts for the carrier was relatively low. the ignition temperature of particulate matter was 370 0 C. At 700, 800, 900 0 C, the activity had been improved, but not significantly. When the calcination temperature reached 1000 0 C, the catalyst activity had been greatly improved, the ignition temperature of particulate matter was 345 0 C. In all the calcination temperature range, the combustion interval of the particulate matter were not significant change.

The active components of catalyst were the same and excluded the interference of other factors. The calcination temperature proved to be the cause in catalytic activity change. Therefore, the optimum calcination temperature of modified support Al_2O_3 which prepared by co-precipitation was 1000 ^{0}C .

2.4 Characterization of catalysts

The impact of the precipitant and calcination temperature on the catalyst surface morphology were tested by the SEM test analysis



(a) NH₄OH, calcined at 700 ⁰C
 (b) Na₂CO₃, calcined at 700 ⁰C
 (c) Na₂CO₃, calcined at 1000 ⁰C
 Fig. 4 SEM spectra of catalysts support on Al₂O₃ prepared by different precipitants and calcined temperature

Fig. 4 (a) showed that when the precipitant was ammonia, metal active on the support surface was granular, and distribution-intensive, distributed more evenly.

Fig. 4 (b) and (c) showed the support with different calcination temperature of the same precipitant, and then on through a step-by-step impregnation method of catalyst.

Fig. 4 showed the support was calcined at 700 6 C, the active component on the distribution of state was very different with the distribution of ammonia as the precipitant. On the surface of the carrier distribution was not uniform, the large particles, particles of different sizes. Catalyst carrier in 1000 6 C calcined alumina, the active component on the distribution pattern of calcined at 700 6 C the very different was flocculent crystal, a very low degree of crystallinity of the active component dispersed relatively uniform.

In the Fig. 4, the type of precipitants affected the surface properties of the catalyst support to a certain extent. When Ammonia as the precipitant, the distribution of metal active component on the carrier density, small particle size. While Na₂CO₃ as precipitant, the metal active component showed flocculent crystals and highly dispersed on the surface of the catalyst carrier. Calcination temperature impacts the catalyst particle size and surface morphology relatively large. The calcination temperature was relatively low, the metal active component on the catalyst support particles were relatively large, and unevenly distributed. When calcination temperature was high, the additive and Al₂O₃ had a coordination effect and then changed the nature of the surface of alumina, the metal active component in the catalyst support on the morphology and distribution of the great changes. Although the specific surface area size of the catalyst support has a certain influence on the performance of the catalyst, but as long as its specific surface area reaches a certain level the surface properties of the catalyst, but become an important factor to affect the catalyst performance.

Conclusions

(1). The calcination temperature affects catalyst performance relatively large. In the temperature range we investigated, the catalytic activity increases with the calcination temperature. The catalyst do good in the burning activity of particulate matter when reach 1,000 0 C.

(2). With the four precipitants, the effect of Na_2CO_3 is the best, which regulate the ability of the solution pH value moderately, and while caused the nitrate completely precipitated, the size of the grains formed are not so large, and easy to wash.

(3). Controlling the pH value at 9 through the process, the precipitation is complete, and the grain growth rate is moderate. So, not only obtained a relatively high specific surface of the modified Al_2O_3 , but also improved the catalyst activity.

Acknowledgements

This work was financially supported by the Guangdong Natural Science Foundation (S2011010003492).

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Study On Accelerated Corrosion Test Environment Spectrum of Aluminum Alloys in a Typical Marine Atmosphere

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Keywords: Aluminum alloys; corrosion; equivalent environment spectrum

Abstract. With the increasing effects of a corrosive environment on aluminum alloys, the corrosion of aluminum alloys has become a severe problem. In this paper, the accelerated corrosion test environment spectrum and corrosion equivalent relationship was systematically studied. The Accelerated Corrosion Test Environment Spectrum of aluminum alloys under a typical marine atmospheric environment was established. The Spectrum is composed of three parts, namely, a periodic infiltration test, a UV irradiation test, and a salt spray test. The Spectrum can well simulate aluminum alloy corrosion in a typical marine atmospheric environment.

Introduction

Aluminum alloys are widely used in aerospace and other fields because of their low density, excellent mechanical properties, and good processability. As the most widely used aircraft structural materials, aluminum alloy consumption has increased. However, the quantity of aluminum alloys exposed to the atmosphere in recent years has increased [1]. Therefore, the corrosion behavior of aluminum alloys has become a research hotspot. Upon exposure to the atmosphere, pollutants significantly affect the corrosion kinetics of these alloys, forming less compact and more soluble corrosion products. Consequently, the materials undergo localized attack with significant loss of mechanical resistance. This phenomenon leads to premature failure, even in materials with good mechanical properties. Thus, maintenance and repair costs are greatly increased, and the life of aluminum alloys is shortened, thereby causing huge economic losses [2].

Therefore, the corrosion behavior, patterns of use, and practical significance of aluminum alloys under a typical atmospheric environment are studied. Natural environmental exposure tests are a true reflection of the corrosion resistance of materials in a typical climate area of the environment. Such tests are an important means of evaluating the quality of a material. However, studies on accelerated corrosion laboratory tests have only begun to develop due to long test cycles and other reasons. One commonly used accelerated test methods is the salt spray test, which has great defects in simulation [3, 4]. The continuous salt spray test has been developed into the cyclic salt spray test. However, studies on the Accelerated Corrosion Test Environment Spectrum have had little progress [5]. An important reason is the inconsistency between the accelerated corrosion and actual exposure results.

Aluminum alloy atmospheric corrosion characteristics

The atmospheric corrosion of aluminum alloys by electrochemical destruction due to the combined effects of moisture, oxygen, and corrosive media contained in the atmosphere is a special form of electrochemical corrosion. The corrosion behavior occurs on the metal surface under the thin layer of electrolyte. The anode and cathode reactions are as follows:

Anode reaction: $Al - 3e^- \rightarrow Al^{3+}$

(1)

Cathodic reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in neutral or alkaline solution) (2) Or: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (in acidic solution) (3) The passive film of aluminum alloys in the general indoor environment is not destroyed because it is corrosion resistant. However, in the outdoor atmosphere, aluminum corrodes. The main form of this corrosion is localized corrosion such as pitting, which sometimes occurs as intergranular corrosion and delamination corrosion.

Aluminum alloy atmospheric corrosion factors

Aluminum alloy corrosion includes many natural factors, such as temperature, rainfall, as well as biological and atmospheric pollutants. The influence levels of corrosive factors also vary under different environments. Some are altered with changes in area and time, and a certain correlation exists between these factors.

(1) Impact of relative humidity

The relative humidity in air is one of the most important factors affecting atmospheric corrosion. In the atmospheric environment, a greater humidity more likely results in metal surface condensation; a longer exposure time of the electrolyte membrane surface to humidity leads to increased material corrosion rate.

(2) Surface wetting time

The surface wetting time is the time from the atmospheric corrosion of the electrolyte membrane to adsorption and coverage on the metal surface. The surface wetting time actually reflects the electrochemical corrosion process of the metal surface. The metal surface wetting time is also an important indicator of the corrosion classification of the atmospheric environment. A longer metal surface wetting time for determining metal corrosion corresponds to a greater overall corrosion.

(3) Ambient temperature

The ambient temperature is an important factor affecting atmospheric corrosion. Changes in ambient the temperature affect not only water film formation on the metal surface, but also the corrosion reaction speed of the anode and cathode processes of primary cells. When the ratio of the relative humidity in air to the critical relative humidity of the metal is high and the ambient temperature is pronounced, as a general chemical reaction, the temperature increases by 10 °C and the reaction rate increases by about twofold. This case is true for the humid tropics in China, and the high temperature causes severe corrosion.

(4) Rainfall

Rainfall has two main effects on atmospheric corrosion. On one hand, rainfall increases the relative humidity in the atmosphere. Consequently, the metal surface becomes wet, the metal wetting time is extended, and the atmospheric corrosion of the metal is accelerated. On the other hand, rainfall can wash off pollutants on the metal surface, thereby slowing corrosion in the marine atmosphere [6]. In industrial atmospheres, rain dissolves the pollutants in air, such as of SO₂, Cl⁻, etc.. These pollutants promote metal corrosion in acid rain regions in China.

Preparation of Accelerated Corrosion Test Environment Spectrum

4.1 Analysis of Accelerated Corrosion Test Environment Spectrum

The factors affecting marine atmospheric corrosion include salt fog, solar radiation, temperature, humidity, and so on. The main characteristic of oceanic and atmospheric air is the Cl⁻ content. The Cl⁻ content is sensitive to the temperature, humidity, waves, sea breeze, and other factors. On one hand, due to the presence of Cl⁻ in the oceanic atmosphere, the relative humidity is high. Thus, condensation easily occurs on the aluminum surface, forming a thick liquid film. The liquid film dissolves oxygen and other corrosive substances, further accelerating the corrosion of aluminum alloys. Also, if Cl⁻ is deposited on the aluminum surface, destruction is inevitable because Cl⁻ is highly corrosive. Sunshine is also an important factor affecting the atmospheric corrosion of materials. Sunshine promotes the corrosion reaction of the aluminum surface, whose photosensitivity enables pollutants to dwell on the aluminum alloy surface, thereby accelerating aluminum alloy corrosion.

To determine environmental factors in a typical Xisha ocean atmosphere environment, the Accelerated Corrosion Test Environment Spectrum is used to simulate the influence of $C\Gamma$ ion under light, temperature, humidity, and the marine environment. The Spectrum constitutes UV irradiation, infiltration of the salt spray test, and cycle test

4.2 Basic components of Accelerated Corrosion Test Environment Spectrum

The three environmental accelerated corrosion modules constitute a form of imposed components, namely: (1) cycle infiltration test, (2) UV irradiation test, and (3) salt spray test. Designed to test the conditions for a period of one year to accelerate the Spectrum, the three environmental accelerated corrosion modules are described as follows:

(1) Cycle infiltration test

Taking into account the effects of the actual Xisha environmental factors on aluminum alloy corrosion, 5% NaCl solution is used to simulate the Xisha atmospheric environment salt spray. Moist air and condensation effects, as well as the baking process of the surface solution under different temperature and humidity environments are used to simulate the environmental conditions. The temperature *T* is40 °C, the relative humidity RH is 90%, and the infiltration cycle is 60 min. The specimen infiltration duration is 15 min in the solution and 45 min outside the solution.

(2) UV irradiation test

Based on the average annual UV radiation in the spectrum of the Xisha test atmospheric environment, the test conditions of UV irradiation were developed. The chamber UV radiation intensity Q is (500 ± 10) W/m², the irradiation temperature T is 55 °C, and the exposure time is 166 h.

(3) Salt spray test

The salt spray test duration depends on the climate and environment. According to literature, the general time of the spectrum of accelerated salt spray test conditions for aluminum alloys is 168 h. Based on a comprehensive analysis of industrial pollution in China, in the typical coastal humid areas, the acid rain ratio is close to 40% salt spray environment using standard 5% NaCl as neutral salt spray. The ambient temperature *T* is (35 ± 2) °C.

The accelerated testing of the Xisha marine environment spectrum for one cycle reveals an approximate equivalent to the field of actual exposure. In contrast, according to the accelerated corrosion test sample field and laboratory exposures, the equivalent relationship is determined and the extent of corrosion contrast is further amended.

4.3 Equivalent verification of Accelerated Corrosion Test Environment Spectrum

To determine the aluminum alloys that can accelerate the effectiveness of the environmental spectrum, after a cycle of aluminum alloys and actual field exposure, the aluminum alloy specimens were compared. The maximum pitting corrosion depths are first compared. The basic idea is to select a direct measure of the amount of corrosion of the corrosion damage, such as the pit depth and corrosion area, and establish the equivalent accelerated relationship. The specific process is observation of the aluminum alloys during the external field exposure. The extent of corrosion is evaluated by statistical comparative analysis using scanning electron microscopy and X-ray diffraction. The equivalent accelerated relationship is determined, and the effectiveness of the Accelerated Corrosion Test Environment Spectrum for aluminum alloys is evaluated.

Conclusion

The study of the acceleration environment of aluminum alloys under a typical marine atmospheric environment has a great significance in understanding the structural life of aluminum. In this paper, the Accelerated Corrosion Test Environment Spectrum for aluminum alloys is introduced. The spectrum simulates the Xisha atmospheric environment and enables systematic analysis.

Acknowledgements

This work was financially Supported by National Science and Technology Infrastructure Platform funded projects(No.2005DKA10400), and this work was Supported by Scientific Research Fund of Hebei Provincial Education (No.Z2009301)

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Effects of melt superheating holding time on solidification structure and mechanical property of AZ31B magnesium alloy

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Keywords: AZ31B magnesium alloy; melt superheating holding time; solidification structure; mechanical property

Abstract. Effects of melt superheating holding time on microstructure and mechanical properties of AZ31B magnesium alloy were studied. The results show that the grain size of AZ31B magnesium alloy is gradually increased with the elongation of holding time. The grain is the finest without insulation work, and the increase amplitude of grain size is the most when holding for 20 minutes in this experiment. The higher is the melt superheating temperature, the larger the increase amplitude of grain size when holding for 20 minutes is. The tensile strength, yield strength and elongation percentage of AZ31B magnesium alloy specimens are small declined with the elongation of holding time under lower melt temperature. At 850°C or 900°C, the mechanical properties are rapidly declined with the elongation of holding time when holding time is less than 20 minutes, whereas the mechanical properties are slight increased when holding time is more than 20 minutes. DSC analysis shows that the elongation of holding time causes the increase of solidification onset temperature and the augment of solidification range, so the undercooling degree and nucleation rate are decreased in the melt, which result in the grain coarsening and the mechanical properties decrease.

Introduction

AZ31B magnesium alloy is a widely used wrought magnesium alloy. The close-packed hexagonal structure of magnesium results in the deformation difficulty at room temperature. In order to get the large deformation without cracks, thermal processing is commonly used [1,2]. The most effective way enhancing the plastic deformation of magnesium alloy at room temperature is to refine the grain [3,4]. The most common methods refining cast structure of magnesium alloy include adding alloy elements [5,6], inoculation [7], outfield application [8,9], melt superheating. Among these methods, melt superheating treatment has the advantages of simple operation and low cast. Si N C et al [10], Zhou Z et al [11] research the effects of melt superheating on the microstructure of Al alloy. Zha M et al [12] points that the primary Mg_2Si size is obviously decreased with increasing the melt superheating temperature. The research about melt superheating are focused on the effects of superheating temperature and use alloys, whereas the influences of melt superheating holding time on magnesium alloy have not been reported. It is found in the experiment that holding time after melt superheating has a great impact on the refinement effect.

The effects of melt superheating holding time on the microstructure and mechanical properties of AZ31B magnesium alloy.

Experiment materials and methods

The commercial AZ31B magnesium ally is used, which includes 3.1 pct Al, 1.2 pct Zn, 0.3 pct Mn, 0.03 pct Fe, 0.02 pct Cu, 0.02 pct Ni, the rest Mg. The casting longitudinal surface and sampling location is shown in Fig. 1. AZ31B magnesium alloy is melted in a home-made electric resistance furnace with a mild steel crucible, and the melt is protected by the gas mixture of 0.5 pct SF₆ and 99.5 pct CO₂. The schematic of melting device is shown in Fig. 2. The dried AZ31B is put

into the crucible preheated to 300 degrees and is heated to 750, 800°C, 850°C and 900°C, respectively, then the melt is held for 0 min, 10 min, 20 min and 30 min at every temperature, respectively. The crucible is removed from the electric resistance furnace after reaching the predetermined experimental condition, and then the crucible is put into a decay tank and is compulsively cooled. The cast ingots are cut along the longitudinal surface and the macrostructures are observed. The metallographic specimens are etched with a solution containing 5.5 g picric acid, 5 ml glacial acetic acid, 90 ml alcohol and 10ml water after grinding and polishing. The microstructure is observed with Axiovert200MAT metallurgical microscope. The tensile samples with $\Phi 8 \text{ mm} \times 40 \text{ mm}$ were cut at every casting, respectively, and the room tensile tests are performed using an electron universal testing machine (CMT5305) with a crosshead speed of 2mm/min. The grain sizes are measured adopting the average intercept. The differential thermal analysis experiment is put up with an integrated thermal analyzer (Setaram).



Fig. 1 Schematic of cast ingot shape and sampling location



Fig. 2 Schematic of melting device of magnesium alloy 1-furnace lid 2-heat electric couple 3-refractory brick 4-mineral flax 5-gas-guide tube 6-internal furnace 7-crucible 8-resistance wire

Experimental results and analysis

Effects of melt superheating holding time on the macrostructure of AZ31B

When the melt temperature is 850°C, the macrostructures of AZ31B magnesium alloy under different holding time are shown in Fig. 3.It can be seen that the grains are relatively fine in the solidification structure as a whole, and the equiaxed grain becomes coarse firstly, then the coarseness extent is decreased with the elongation of holding time. The grain is the finest without thermal retardation, and the grain coarseness is the most serious holding for 20 min. The grain holding for 30 min is finer than the grain holding for 20 min. It is found that the variation is the same under different superheating temperature.



Fig. 3 Macrostructures of AZ31B magnesium alloy under different holding time (850°C) (a) 0 min (b) 10 min (c) 20 min (d) 30 min

Effects of melt superheating holding time on the microstructure of AZ31B

The microstructures of AZ31B magnesium alloy are shown in Fig. 4 when the holding time at 850° C is 0 min, 10 min, 20 min and 30 min, respectively. It can be found that the grain is relatively fine without holding, the grain is gradually coarsened with the elongation of holding time, as shown in Fig.4(b) \sim (c). When holding time reaches 20 min, the grains become very coarse, that is to say the increase amplitude of grain is the biggest when holding for 20 min in this experiment. The grain is again refined when holding time reaches 30 min, whereas the grain is still larger than the grain without holding.

The effects of melt superheating holding time on the grain size of AZ31B are shown in Fig. 5. It can be found that the change rules of equiaxed grain size are the same with the elongation of holding time under different melt superheating temperature. Namely the grain sizes are increased as the holding time on the whole, and the increase amplitude is the most when holding for 20 min. The grain size at 750°C is increased of 3%, 26% and 6% after holding for 10 min, 20 min and 30 min, respectively. When the melt temperature is enhanced to 850°C, the grain size is increased of 3%, 26% and 6% after holding for 20 min. The higher is melt superheating time, and the increase amplitude is most when holding for 20 min. The higher is melt superheating temperature, the larger the increase amplitude of grain size holding for 20 min is.



Fig. 4 Microstructures of AZ31B magnesium alloy under different holding time (850°C) (a) 0 min (b) 10 min (c) 20 min (d) 30 min



Fig. 5 Effects of melt superheating holding time on grain sizes of AZ31B

Effects of melt superheating holding time on mechanical properties

The effects of melt superheating holding time on the tensile strength, yield strength and elongation percentage of AZ31B magnesium alloy are shown in Fig. 6 (a) \sim (c). It can be found that the change rules of the tensile strength, yield strength and elongation percentages of AZ31B magnesium alloy are the same. They are declined with the elongation of holding time. The decrease extents of tensile strength, yield strength and elongation percentage are relatively small at 750°C or 800°C, while the decrease amplitudes of tensile strength, yield strength and elongation percentage are obviously increased at 850°C or 900°C, and the decrease amplitudes are especially large when holding time is 20 min.

The tensile strengths of AZ31B at 750°C are respectively decreased by 0.2%, 2.7% and 1.3% comparing with without holding, and the yield strengths are respectively decreased by 2%, 4% and 5%, and the elongation percentages are respectively decreased by 0.2%, 11.2% and 18.6%. The tensile strengths of AZ31B at 850°C are respectively decreased by 10%, 14% and 10% comparing with without holding, and the yield strengths are respectively decreased by 5%, 10% and 6%, and the elongation percentages are respectively decreased by 32%, 39% and 33%. These data suggest that the mechanical properties of magnesium alloy are the best without holding time. The higher is the melt superheating temperature, the more significant the effects of holding time on the mechanical properties are, and the larger the decrease amplitude of mechanical properties with the elongation of holding time is.



Fig. 6 Effects of holding time on tensile strength (a), yield strength (b) and elongation percentage (c) of AZ31B

Discuss

AZ31B magnesium alloy is heated from 400°C to 850°C at a heating rate of 10°C /min and held for 0 min or 20 min, then it is cooled at a cooling rate of 5°C /min, DSC curves of the specimen are shown in Fig. 7. It can be deduced from Fig. 7 (a) and (b) that the holding time has a great influence on the solidification process of the specimen. The solidification onset temperature of the specimen without holding is 612°C and the solidification termination is 595°C, the solidification range is 17°C. The solidification onset temperature of the specimen holding for 20 min is increased by 33°C and the solidification range is increased by 5°C. This shows that the nucleation supercooling is decreased with the elongation of holding time. It is analyzed that there exist clusters of different sizes in the melt, and it is possible that some small clusters are gathered with the elongation of holding time, so the clusters quantity is decreased. Because the nature of magnesium is more active, the inclusions MgO, Al₂O₃, Al₄C₃ can be easily generated in the melt. In the subsequent solidification process, these large size clusters can easily be absorbed on the non-metallic inclusions to form the critical nucleation. So the solidification onset temperature is enhanced and the nucleation supercooling is decreased, which results in the decrease of the nucleation rate. The decrease of the nucleation rate makes the solidification structure of AZ31B to become coarse and the mechanical properties to be declined.



Fig. 7 DSC curves of AZ31B magnesium alloy holding for 0 min (a) and holding for 20 min (b) at 850°C

Conclusions

The grain size of AZ31B magnesium alloy is gradually increased with the elongation of holding time. The grain is the finest without holding, and the increase amplitude of grain size is the most holding for 20 minutes in this experiment. The higher is the melt superheating temperature, the larger the increase amplitude of grain size holding for 20 minutes is. The tensile strength, yield strength and elongation percentage of AZ31B magnesium alloy specimens are declined with the elongation of holding time. The higher melt superheating temperature, the larger the decrease amplitude of mechanical properties. The elongation of holding time causes the increase of solidification onset temperature and the augment of solidification range, so the decrease of the nucleation rate make the solidification structure of AZ31B to become coarse and the mechanical properties to be declined.

Acknowledgements

This work was financially supported by the Liaoning Natural Science Foundation (20092197), the Education Department of Liaoning Province (2007T078).

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Microstructure and Tensile Property of NiAI-Cr Alloyed with Zr

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Keywords: NiAl; microstructure; BDTT; tensile property

Abstract. The microstructure of as-cast NiAl-33.5Cr-0.5Zr alloy is the eutectic colonies of NiAl and Cr phase with non-continuous Heusler (Ni₂AlZr) phase segregating at the cell boundaries. After hot isostatic press (HIP) processing at 1573K, 100MPa for 2h, the Ni₂AlZr phase changes into Zr-rich phase. The elevated temperature tensile strength and elongation of the HIP-ed alloy are much higher than those of as-cast alloy. It was noted that this alloy either as-cast or HIP processing exhibits a brittle to ductile transition behavior, which is difference between as-cast and HIP-ed alloy. HIP processing decreases the BDTT of the alloy, especially in high strain rates, and lower the range of BDTT. When the strain rate increases by two orders of magnitude, the BDTT has an approximate increase from150K for as-cast alloy to 100K for HIP-ed alloy. The mechanism responsible for elevated temperature deformation has also been discussed.

Introduction

Recent improvements in elevated temperature strength have made NiAl-based alloys an even more attractive candidate for elevated temperature structural materials[1]. But the low tensile ductility or toughness of these alloys at low temperature has not still been overcome. This lack of ductility at low temperature has been attributed to an insufficient number of slip systems due to the operation of <100> {hkl}slip, which provides only three independent deformation mechanism[2, 3]. Fortunately, the promising creep properties that can compete with current Ni-based superalloys have been achieved through precipitation of an ordered Heusler phase in NiAl single crystals. However, the precipitation of the Heusler phase made such NiAl single crystals more brittle than binary NiAl[4]. It has been reported that processing multiphase alloys may be one way of toughening these kinds of materials[5]. Therefore, a NiAl-34Cr eutectic alloy was selected as base and small amounts of Zr element was substituted for Cr element in order to strengthen this alloy with Heusler phase.

Experimental procedure

The NiAl-33.5Cr-0.5Zr (at. %) alloy used in this study was prepared by induction melting in vacuum from starting materials of 99.9% Ni, 99.9% Al, 99.5% Cr and 99.0% Zr. Some of the casting rods were processed by hot isostatic press (HIP) at 1573K /100MPa for 3h. The tensile specimens with a gauge section of $2 \times 2.5 \times 16$ mm³ were electro-discharge machined from the rods. Tensile tests were performed to fracture in a Shimadzu AG-2500KNE test machine equipped with a furnace in air. Specimens for microstructure observation were electropolished in a solution containing 25% perchloric acid and 75% glacial acetic acid. Morphology and the tensile fractographs observations were performed using a JSM-6301F scanning electron microscope.

Results and discussion

Microstructure

The microstructure of the cast alloy is typically eutectic colonies of NiAl and Cr phase with non-continuous Heusler (Ni₂AlZr) phase segregating at the cell boundaries. At the center of the colony, Cr phase is fine, but the Cr dendrites at the colony boundaries lost its regular morphology and became somewhat coarse in size (Fig.1a). After HIP processing, the size of the eutectic colony is nearlly the same as that in casting state, but the Heusler phase became a Zr-rich phase (Fig.1b). The possible reason of that is the effect of Cr elements. During the HIP processing, Cr elements diffuse into the Heusler phase, which can lower the order degree of the Heusler phase, and make the Heusler phase unstable. Consequently, the Heusler phase converts into NiAl and Zr-rich phases. This is consistent with the identity of more Cr element in Zr-rich phase by the energy dispersive spectrum (EDS).



Fig. 1 Microstructures of the NiAl-33.5Cr-0.5Zr alloy (a) the as-cast alloy; (b) the HIP-ed alloy

Tensile properties

The typical true stress-true strain curves of as-cast and HIP-ed alloys tested at 1273K are shown in Fig.2. After deforming, the alloys reach the peak stress rapidly, and followed by strain softening. Whether at as-cast state or HIP-ed state, as the initial strain rate increases, the yield strength increases and the elongation decreases. The HIP processing make the material more densely, so the yield strength and ultimate strength are larger than that of as-cast, especially the increase of the elongation is more significant.



Fig. 2 True stress-strain curves at 1273k for as-cast alloy and HIP-ed alloy

Fig.3 shows the plot of elongation versus temperature at the strain rate of 1.04×10^{-4} s⁻¹, 1.04×10^{-3} s⁻¹, 1.04×10^{-2} s⁻¹ for as-cast alloy, exhibiting the effect of strain rate and temperature on the tensile ductility of the present alloy. The data at higher strain rates resemble the data at a strain rate of 1.04×10^{-4} s⁻¹, but the ductility versus temperature curves are displaced to a higher temperature as the strain rate increases. A brittle to ductility transition temperature (BDTT) value of approximate 1200K is determined at the strain rate 1.04×10^{-4} s⁻¹, and 1300K at 1.04×10^{-3} s⁻¹, and 1350k at 1.04×10^{-2} s⁻¹. Thus BDTT of NiAl-33.5Cr-0.5Zr alloy shifted up about 150K because of two orders of magnitude increasing in strain rate.

Fig.4 shows the plot of elongation versus temperature at the strain rate of 1.04×10^{-4} s⁻¹, 1.04×10^{-3} s⁻¹, 1.04×10^{-2} s⁻¹ for HIP-ed alloy, and the tendency of the plots is the same as that of as-cast alloy. However, there are still three differences. The first one is that the HIP processing make the BDTT decrease, such as a BDTT value at the strain rate 1.04×10^{-4} s⁻¹ is approximately 1173K, which is lower than that of as-cast alloy. The second one is the range of BDTT reduces, which is BDTT shifted up about 100K because of two orders of magnitude increasing in strain rate. The third one is that the decreasing of BDTT is more significant at the fast strain rates, the BDTT value at 1.04×10^{-2} s⁻¹ is 1273K. The reasons are that the HIP processing made the material more densely, i.e. depressed the micro-defect, which is beneficial to accommodate the deformation.



Fig. 3 The effect of strain rate and temperature onFig. 4 The effect of strain rate and temperature elongation for as-cast alloy on elongation for HIP-ed alloy

Besides the change of the BDTT, a significant change in fracture morphology is observed around the BDTT. The tensile rupture mode of HIP-ed alloy is predominantly debonding along phase boundaries at a strain rate of $1.04 \times 10^{-4} s^{-1}$ and below 1173K. Above 1173K, the fracture morphology changes to a combination of debonding along phase boundaries and ductile fracture within its constituent phases, the percentage of debonding along phase boundaries decreases as the temperature increase. At 1223K and with a strain rate of $1.04 \times 10^{-4} s^{-1}$, the fracture morphology is predominantly ductile. However, the fracture behavior changes predominantly to debonding along phase boundaries at 1223K and with a strain rate of $1.04 \times 10^{-3} s^{-1}$. At 1273K and with a strain rate of $1.04 \times 10^{-3} s^{-1}$, the fracture morphology has changed to predominantly ductile (Fig.5a). At the fastest testing rate of $1.04 \times 10^{-2} s^{-1}$, limited ductility and predominantly debonding along phase boundaries are observed once again at the temperature of 1273K (Fig.5b). Therefore, the fracture mode of this alloy changed from debonging along phase boundaries below BDTT to completely ductile fracture above the BDTT.

Since the BDTT of this alloy is sensitive to the strain rate, the mechanism responsible for transition from brittle to ductile should be the combination of gliding and climbing of <100> type dislocation[6, 7]. When the strain rate imposed upon the sample is greater than what can be accommodated by climbing, the material would fail in a brittle manner due to the cell boundaries incompatibility. A thermally activated deformation process can also be reasonably anticipated to participate in the BDTT process[8, 9]. In addition, the solute addition can affect the onset of climb by forming solute atmospheres around the dislocation[8], which is probably another evidence that BDTT of this alloy is so high. Bowman et al[10] pointed out that the addition of Zr has also been shown to enhance the transgranular fracture mode and increase the strength and BDTT of NiAl.



Fig. 5 The fractographs of HIP-ed alloy tested at 1273K (a) initial strain rate of 1.04×10^{-3} s⁻¹; (b) initial strain rate of 1.04×10^{-2} s⁻¹

Conclusions

(1) The as-cast NiAl-33.5Cr-0.5Zr alloy consists of NiAl, Cr and Heusler (Ni₂AlZr) phases. After the HIP processing, there is no change of eutectic morphology, but the Heusler phase segregation in the cell boundaries converts into Zr-rich phase.

(2) The brittle to ductile transition temperature (BDTT) of as-cast alloy was determined to be approximately 1200K at the strain rate of $1.04 \times 10^{-4} \text{s}^{-1}$ and typically dependent on strain rate. Two orders of magnitude increase in strain rate resulted in an approximate 150K increase in BDTT.

(3) The HIP processing decreases the BDTT, and reduces the range of BDTT. BDTT value at strain rate of 1.04×10⁻⁴s⁻¹ is approximately 1173K, and two orders of magnitude increase in strain rate resulted in an approximately 100K increase.

Acknowledgement

The authors would like to acknowledge the program of science research of Liaoning Office of Education (No. L2011100) for the financial support.

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Electrochemical corrosion characterization of as-cast Mg-7Li alloy

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Keywords: Mg-7Li alloy, Electrochemical corrosion, Polarization curve, Impedance

Abstract. The electrochemical corrosion behavior of as-cast Mg-7Li alloy in 3.5wt% NaCl aqueous solution was investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electrochemical workstation. Results showed that the E_{corr} and the I_{corr} of Mg-7Li alloy were -1.5857V and 2.235×10⁻⁴A/cm², respectively. The cathode process was chiefly the hydrogen evolution reaction, and the corrosion rate of Mg-7Li alloy was mainly controlled by anode dissolution. The corrosion products on the alloy surface consisted of Mg(OH)₂, Li₂O₂ and Al(OH)₃. The electrochemical impedance spectroscopy (EIS) of Mg-7Li alloy contained two capacitive loops and one inductive loop. The inductance value increased to 250 ohm cm⁻² with a rise in frequency at low frequency. The capacitive reactance maintained the value of 50 ohm cm⁻² with increasing frequency at high frequency region.

Introduction

Mg-Li alloys, one of the lightest metal structure materials, have attracted great attention in recent years. They have became promising materials for many applications in aerospace, military, automobile, and electronics due to their excellent properties such as super strength to weight ratio, high Young's modulus , good damping characteristic and cold-workability [1-2]. With the addition contents of Li from 5% to 11%, Mg-Li alloys are composed of α phase and β phase, this dual phase structure contributing to the extra-low density and excellent formability of the alloy [3,4].

However, the extremely high chemical reactivity of Li will make Mg-Li alloys suffer from severe electrochemical corrosion in the moist air and the industry atmosphere, which restricts their widespread use [5,6]. Therefore, it is necessary to discuss the corrosion characterization of Mg-Li alloys to develop more effective protection methods. At present, many research work about the corrosion behavior of Mg alloy have concentrated on such alloy as Mg-Al, Mg-Zn and Mg-Cd [7-9], whereas there is less study on Mg-Li alloy [10-11]. In this study, the electrochemical corrosion behavior of as-cast Mg-7Li alloy in 3.5wt% NaCl aqueous solution was investigated.

Experimental

The polarization curves were obtained in 3.5wt% NaCl solution at room temperature using a CHI 604c electrochemical station (Chenhua instrument Co. Shanghai, China). A classical three electrode cell was used with Pt as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the samples as a work electrode. The scan voltage ranged from -2 to -0.8V at a constant scan rate of 10 mV/s. The surface morphology of the electrochemical corrosion was observed by scanning electronic microscope (JSM-6360LV, Japan). The phase composition of the corrosion products was identified by X-ray diffraction (BRUKER, D-8 Germany) with Cu-Ka radiation at a scanning rate of 4°/min from 10 to 100°.

Electrochemical impedance spectroscopy (EIS) measurement was performed at an open-circuit potential using an electrochemical station (ZENNIUM IM6ex, Germany) with the same electrodes and solution as those for polarization curves tests. The scan frequency ranged from 0.01Hz to 100 kHz and the perturbation amplitude was 10mV. The initial retard of 1800s was set to obtain a stable testing system.

Results and Discussion

The polarization curve of as-cast Mg-7Li alloy. A corrosion system forms in NaCl solution with pure Mg or Mg-7Li alloy as an anode and Pt as a cathode. Fig.1 shows Tafel potentiodynamic polarization curves of pure Mg and as-cast Mg-7Li alloy in 3.5wt% NaCl solution. The electrochemical corrosion occurred when pure Mg and Mg-7Li alloy under the action of impressed

current. The figure of cathode and anode polarization curve is similar, indicating that both two metals are not resistant to the corrosion in NaCl solution. During the reaction process, the cathode process was chiefly the hydrogen evolution reaction. Anode polarization curve shows the active dissolution of pure Mg and Mg-7Li alloy, namely the process of Mg ions migrating from the matrix to the aqueous solution and forming aquo-metal ions. It was the anode process that mainly controlled the corrosion rate of pure Mg and Mg-7Li alloy. Since the loose oxide film and the corrosion products on the surface of pure Mg and Mg-7Li alloy can only partially restrict the corrosion reaction, there are no passivation region and pitting potential appeared on the anode polarization curve.



Fig.1 Tafel curves of pure Mg and Mg-7Li alloy

Table 1 shows the fitting results of the polarization curve by extrapolation method of Tafel, where E_{corr} and I_{corr} denote self-corrosion potential and self-corrosion current density of pure Mg and Mg-7Li alloy in NaCl aqueous solution. The symbol of b_a and b_c characterize Tafel slope coefficient of cathode and anode, respectively. R_p represents polarization resistance.

Sample	$E_{\rm corr}({\rm V})$	$I_{\rm corr}({\rm A}\cdot{\rm cm}^{-2})$	$b_{\mathrm{a}}\left(\mathrm{V}\right)$	$b_{\rm c}\left({ m V} ight)$	$R_{\rm p}(\Omega \cdot {\rm cm}^{-2})$
Mg-7Li	-1.5857	2.235×10 ⁻⁴	0.0139	0.0235	16.97
Pure Mg	-1.5377	1.555×10 ⁻⁴	0.0224	0.0176	27.52

Table 1 Fitting Results of the polarization curve

According to Fig.1 and Table 1, the cathode potential of pure Mg and Mg-7Li alloy was approximate from -2 to 1.5377V and from -2 to -1.5857V, respectively. The corrosion current density decreased with a rise in potential, implying that the hydrogen evolution rate gradually diminished. When the potential reached the E_{corr} of -1.5377V and -1.5857V, the curve entered the region of anodic polarization. The corrosion current increased rapidly with increasing anodic potential. When the potential exceeded -1.3V, the corrosion current density increased slowly. From above fitting result, the E_{corr} of pure Mg and Mg-7Li alloy was 1.5377 and 1.5857V with a discrepancy of about 500mV. The I_{corr} of two metals was 1.555×10^{-4} and 2.235×10^{-4} A/cm² with a discrepancy of about 1.5 times. Accordingly, the R_p was 27.52 and 16.97 $\Omega \cdot \text{cm}^{-2}$. It indicated that the corrosion resistant of pure Mg was higher than that of Mg-7Li alloy at initial stage, and the corrosion rate of two metals was the same when the potential exceeded -1.2V.

Phase composition and morphology of the alloy after electrochemical corrosion. Fig.2 presents the surface phase composition and morphology of Mg-7Li alloy after electrochemical corrosion. The whole corrosion took place on the surface of the alloy.

From Fig.2(a), it is observed that the surface corrosion products consisted of Mg(OH)₂, Li₂O₂ and Al(OH)₃. In addition, α -Mg and β -Li were the composition from the matrix. As shown in Fig.2(b), there were corrosion crack, corrosion pit and punctiform protuberance on the alloy surface, where the corrosion crack propagated along the top of protuberance to the bottom.



Fig.2 Surface phase composition and morphology of Mg-7Li alloy after electrochemical corrosion (a) XRD pattern; (b) Morphology

The impedance measurement of as-cast Mg-7Li alloy. The corrosion behavior of Mg-7Li alloy in 3.5wt% NaCl aqueous solution was investigated by EIS measurement at open circuit potential. The Nyquist and Bode plots of Mg-7Li alloy contained three loops, namely one high frequency capacitive loop, one medium frequency capacitive loop and one short low frequency inductive loop, as shown in Fig.3 and Fig.4.



The Nyquist plot of Mg-7Li alloy is presented in Fig.3. When Mg-7Li alloy was immersed in NaCl solution, the atom of magnesium, lithium and aluminum combined with water molecule forming aquo-positive ions through the porous oxide film on the alloy surface. After the alloy aquo-positive ions directly went into the solution by anodic dissolution process, an electric double layer quickly formed at the interface between the matrix and the solution. There existed two dynamic processes for the oxide film in the solution, namely simultaneous stage of the dissolution and the growth. At the film/ solution interface, the dissolution process of the oxide film made the film thin. Meanwhile, a potential difference between the interface of metal/film and film/solution drove the metal cations to transfer from the inside of oxide film to the outside or the anions moving toward the opposite direction, which resulted in the thickening of the oxide film. At high frequency region, since the oxide film couldn't act as a resistance, the charge and discharge of the double layer generated a high frequency capacitive loop. At medium frequency region, the ions of magnesium, lithium and aluminum at the matrix/solution interface as well as the ions in surface film dissolved in the solution, forming the medium frequency capacitive loop. At low frequency region, with the oxide film as a resistance, the diffusion of ions inside the film was inhibited by the solution penetration and current disturbance, resulting in the dissolution rate of surface film higher than its thickening speed. Subsequently, the surface film became thinner and burst quickly, following the exposure of a new surface of magnesium, which was related to the formation of the low frequency inductive loop.

Fig.4(a) presents the relation between the impedance and the frequency of Mg-7Li alloy. At low frequency range from 10^{-2} to 1 Hz, the inductance value increased to 250 ohm cm⁻² with a rise in frequency. The increasing inductance value was attributed to the cracking of more oxide film caused by the main dissolution of new magnesium alloy surface and the corrosion products on the surface as a resistance. At medium frequency range from 1 to 10^{-2} Hz, the entrance of metal ions into the solution reduced the number of positive ions on the substrate surface, so the value of capacitive reactance decreased with increasing frequency. At high frequency range from 10^2 to 10^5 Hz, as the electric double layer was thinner, the capacitive reactance maintained the value of 50 ohm cm⁻² when the frequency increased. The relation between the phase angle and the frequency of Mg-7Li alloy is shown in Fig.4(b). The phase angle didn't vary in the form of a sine wave at low frequency region, while it exhibited a sine change at medium frequency region and a linear change at high frequency region.

Conclusions

The E_{corr} and the I_{corr} of Mg-7Li alloy in 3.5wt% NaCl aqueous solution were -1.5857V and 2.235×10^{-4} A/cm², respectively. The cathode process was chiefly the hydrogen evolution reaction, and the corrosion rate of Mg-7Li alloy was mainly controlled by anode dissolution, namely the process of Mg ions transfering from the matrix to the aqueous solution and forming aquo-metal ions. The corrosion products on the alloy surface consisted of Mg(OH)₂, Li₂O₂ and Al(OH)₃. The EIS of Mg-7Li alloy contained two capacitive loops and one inductive loop. The inductance value increased to 250 ohm·cm⁻² with a rise in frequency at low frequency region. The value of capacitive reactance decreased with increasing frequency at medium frequency. The capacitive reactance maintained the value of 50 ohm·cm⁻² with increasing frequency at high frequency region.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No.31070859) and Biomaterial Key Laboratory Foundation of Jiamusi University of China (L5309). The authors thank the Engineering Center for Wear Resistant Materials and Surface Technology of Ministry of Education (Jiamusi University) and the Key Laboratory for Super Light Materials and Surface Technology of Ministry of Education (Harbin Engineering University). The authors also thank Prof. T. Zhang for the assistance of corrosion test and impedance analysis.

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Microstructure and mechanical properties of horizontal continuous casting AI-18%Si alloy billets

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Keywords: Horizontal continuous casting; Al-18%Si alloy; Fine-grained structural material

Abstract: Horizontal continuous casting (HCC) Al-18%Si alloy billets were prepared with the addition of fine-grained Al-18%Si as a master alloy. The influence of cooling conditions and this fine-grained structural materials addition on the microstructure and tensile properties were studied. The uniformity of the HCC Al-18%Si alloy billets was also analyzed. The results denote that the HCC Al-18% Si alloy billets showed finer microstructure and better mechanical properties after double cooling. Fine-grained structural material addition can effectively reduce macrosegregation and make both primary and eutectic silicon much finer. The ultimate tensile strength clearly increased with an addition of 15 percent fine-grained structural material compared to the HCC alloy with no addition of fine-grained structural material. However, a small decrease occurred after an addition of fine-grained structural material.

Introduction

Hypereutectic Al–Si alloys are attractive materials for many commercial applications due to their low density, low thermal expansion coefficient and high wear resistance ^[1-3]. They are applicable for piston materials^{[4-7].} Casting of hypereutectic aluminum alloys are carried out primarily by the continuous casting process^[8]. Horizontal continuous casting (HCC) has many advantages such as a lower investment cost, greater flexibility and its longer casting times^[9]. However, casting defects such as macrosegregation and porosity are usually present in the as-cast microstructure. These flaws can lead to the deterioration of the mechanical properties^[10].

The use of grain refining is advantageous because it can resolve these undesirable effects. It reduces microsegregation, reduces hot cracking and improves the mechanical properties^[11]. Several mould technologies such as hot top casting and electromagnetic casting (EMC)^[12] are known to enable structural refinement. However, chemical inoculation is often considered as the most economical and efficient method in the casting of aluminium alloys. P is the most widely used element for hypereutectic Al-Si alloy modification^[13-16]. However, problems such as reaction with other elements in the base alloy and the introduction of casting defects can arise. On the other hand, hypereutectic Al-Si alloy with a fine microstructure can be obtained via rapid solidification. It is a suitable method for using a rapidly cooling material as a refiner for Al-Si alloy due to the inherited fine structure of the Al-Si alloy. Accordingly, in this work, the effect of this fine-grained structural material addition on the microstructure and mechanical properties of the HCC alloy billets is studied^[17]. The uniformity of the HCC Al-18%Si alloy billets is also analyzed.

Experimental

Both the base alloy and the master alloy used for HCC were binary Al-18%Si alloys in this study. The fine-grained structural material was prepared by rapid solidification process. 15 and 30 percent mixture of fine-grained structural material were added to the base alloy to compare these combinations to the alloy which contained no fine-grained structural material. The continuous casting alloys billets were prepared by HCC equipment. The inner diameter of the mould was 70mm. To consider the influence of the fine-grained structural material on the macrosegregation exclusively, throughout the process of the experiment, conventional parameters were held constant. These parameters were a casting temperature of 720° C and a casting speed of 180 mm/min.

All of the specimens for SEM observation were chosen from the center of the HCC alloy billets because the center part solidified last during the horizontal continuous casting process. This makes the center have the coarsest structure across the cross-section of the HCC Al-18%Si alloy billets. These specimens were polished and etched by a solution of 5 ml HBF₄ and 95 ml H₂O. The tensile test was performed according to the ASTM standard. Five different sections across the cross section were chosen to calculate the SDAS for studying the influence of fine-grained structural material on uniformity as shown in Fig. 1.



Fig. 1 Schematic illustration of sections from ingots selected for SDAS analysis

Results and discussion

3.1 Effect of cooling conditions

There are two cooling system in horizontal continuous casting process: single and double cooling. Alloy billets prepared by single cooling solidify in the air after drawn from the crystallizer. Thus the cooling rate is not rapid enough to make fine crystalline materials. Direct water spray method is adopted in double cooling process to obtain a greater cooling rate. The water jet can be spayed from mould to chill the alloys drawn from the crystallizer which is known as indirect chill. The temperature of cooling water used in this study is about 20°C and the water consumption is in the average of 5-15m³/h. Fig. 2 shows the microstructure of the HCC Al-18% Si alloy billets with single and double cooling processes. The primary silicon is nearly in the same size of approximately 90µm. This means the size of primary silicon is not sensitive to the cooling rate. However, the morphology of eutectic silicon has a considerable change in the greater magnified image. It changes from a coarse needle-like shape to a fine fibrous shape.



Fig. 2 Microstructure of the HCC Al-18%Si alloy billets with different cooling conditions (a) single cooling (b) double cooling

Tensile properties of Al-18%Si alloy billets with different cooling conditions are shown in Table 1. Both the yield strength (YS) and ultimate tensile strength (UTS) clearly increase after double cooling process, especially for the UTS, which increases by 56 MPa. The heat can convect rapidly in the cross-section of the billet by introducing cooling water. Thus the higher cooling rate of melt results in a bigger undercooling, which induces finer microstructure and enhance mechanical properties.

Cooling conditions	YS[Mpa]	UTS[Mpa]	Elongation[%]	
Single cooling	70	134	4.8	
Double cooling	110	190	3.5	

Table 1 Tensile properties of the HCC Al-18%Si alloy billets with different cooling conditions

3.2 Effect of the addition of fine-grained structural material

3.2.1 Effect of the fine-grained structural material addition on the microstructure and properties of the HCC Al-18%Si alloy billets

In this study, the refiner for the HCC Al-18%Si alloy is rapidly cooled fine-grained Al-18%Si raw material, as shown in Fig. 3. The microstructure is very fine with an average size of primary silicon of $20\mu m$.

Fig. 3 shows the microstructure of the HCC alloys billets with addition of different contents of fine-grained structural material. All the billets were prepared after double cooling process. Fig. 4 (a) (b) and (c) show the HCC alloy billets with 0, 15 and 30 percent fine-grained structural material while Fig. 4 (d) (e) and (f) show corresponding images at a greater magnification. The size of primary silicon decreases from 95µm to approximately 50µm with an addition of 15 percent fine-grained raw Al-18%Si material. And the eutectic silicon also becomes much finer. However, increasing the content of fine-grained structural material to 30 percent led to no great change in the size of primary silicon. It is also noted that the eutectic silicon becomes somewhat coarser, as shown in Fig. 4 (f). The tensile properties reveal the same tendency noted in the images of the microstructure. Fig. 5 shows the mechanical properties of the HCC Al-18%Si alloys billets with different contents addition of the grain-refined structural material. The yield strength increases from 120MPa to 140 MPa while the UTS increases from 190MPa to 220 MPa.



Fig. 3 Microstructure of the fine-grained Al-18%Si raw material

The relation between yield stress and grain size is described mathematically by the Hall-Petch equation:

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \tag{1}$$

Where σ_y is the yield stress, σ_0 is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), k_y is the strengthening coefficient (a constant unique to each material), and *d* is the average grain diameter. The average grain diameter *d* becomes smaller after the addition of 15 percent fine-grained structural material as shown in Fig. 4 (b). Thus, the yield stress shows an increase compared to the alloy without raw materials according to the above equation. In addition, the HCC Al-18% Si alloy with smaller grain size is able to have less dislocation to pile up leading to a smaller driving force for dislocation to move form one grain to another. Thus more force should be applied to move a dislocation from a smaller than from a bigger grain (the HCC Al-18%Si alloy without fine-grained structural material), leading the HCC alloy with 15 percent fine-grained structural materials exhibit higher yield stress.



Fig. 4 Microstructure of the HCC Al-18%Si alloy billets with different contents addition of fine-grained material (a) (d) 0%; (b) (e) 15%; (c) (f) 30%

The findings pertaining to both the microstructure and tensile properties prove that fine-grained Al-18%Si raw material addition can be used as a refiner for the horizontal continuous cast Al-18%Si alloy billets. According to Popel^[17], alloy melt will show microscopic stratification when it is close to its liquidus temperature. This can be seen as a metastable micro-emulsion layer or as group elements enrichment of suspended colloid particles. Occasionally these particles are metstable because they have excess interfacial energy which facilitates their use at a certain temperature above the liquidus temperature before irreversible damage occurs. These metastable colloidal particles inherit fine-grained material characteristics, which can be the source of the metal structural characteristics. Therefore, if a fine-grained structural material was added during the corresponding temperature range, the metastable colloidal particles will retain the fine grain characteristics. These existent microscopic substructures will serve as the nuclei during the subsequent solidification process, which enhances the nucleation rate and grain refinement.



Fig. 5 Tensile properties of the HCC Al-18%Si alloy billets with different contents addition of fine-grained structural material



Fig. 6 Temperature range of Al-Si alloy with metastable colloidal microstructure

For Al-18%Si alloy, the temperature range to generate metastable hereditary colloidal particles is $640^{\circ}C \sim 800^{\circ}C$, as determined from Fig. 6 from the literature^[17]. Therefore, the fine-grained Al-18%Si raw material was introduced in this temperature range into the horizontal continuous casting Al-18%Si alloy. The fine-grained structural material consisted of metastable colloidal Al-Si particles when heated into the temperature range of $640^{\circ}C \sim 800^{\circ}C$. These colloidal particles inheriting their fine structure became the nuclei of the HCC Al-18%Si alloy billets during subsequent solidification process, which resulted in a finer microstructure and better properties with an addition of 15 percent fine-grained structural material.

Generally speaking, a larger number of nuclei can facilitate more nucleation events. However, the addition of 30 percent fine-grained structural material does not refine the structure any further. It has been found that increasing the grain refiner amount beyond a certain level does not help in further structural refinement^[9]. This is due to the fact that as the amount of inoculant particles participating in nucleation (at given undercooling) increases, so does the latent heat release leading to recalescence with less undercooling, thereby lowering the efficiency of the grain refiner. Thus 30 percent fine-grained structural materials may release much more recalescence during solidification compared with 15 percent raw materials leading to less undercooling and a bit larger grain size. In addition, the assemble probability of nuclei increases may be another reason with 30 percent fine-grained structural materials.

3.2.2 Effect of the fine-grained structural material addition on the uniformity of the HCC Al-18%Si alloy billets

Not only do the grains in the center become finer, but the entire structure of the HCC Al-18%Si alloy billets becomes more uniform with the addition of the fine-grained structural material. Fig. 7 shows the difference in primary silicon size of the HCC Al-18%Si alloy billets with addition of different contents of fine-grained structural material. The value of the x-coordinate represents the distance from four different positions to the top point. The diameter of billet is 70mm; therefore, the point at 35mm denotes the center of the HCC alloy billets. At every same position, primary silicon size decreases with an addition of 15% fine-grained structural material. However, a small increase occurred when the fine-grained structural material addition up to 30%. The reason has been explained above. The difference of primary silicon size between center and surface in the HCC alloy billets is approximately 20µm, while the values become to be 10µm and 14µm respectively after 15 and 30 percent fine-grained structural material were added.



Fig. 7 Size of primary silicon in the HCC Al-18%Si alloy billets with addition of different contents of fine-grained structural material

There are a number of advantages of grain refinement such as reducing the degree of porosity and the number of the surface defects. The grain refiner, metastable colloidal particles, in the liquid phase generally slows the growth velocity of newly formed grains, allowing more grains to thereby nucleate. This observation can be explained by what is known as the "growth restriction" theory of grain refinement^[9]. The sample with variation in its grain morphology and size is, however less pronounced as compared to its unrefined counterpart; moreover, grain refinement makes the microstructure of the alloys less sensitive to the cooling rate. The temperature gradient of the HCC Al-18%Si alloy billets along the cross-section becomes smaller and the bottom of the sump becomes

much flatter with grain refinement. Hence, the microstructure becomes more uniform after the introduction of the fine-grained structural material into the HCC Al-18%Si alloy billets.

Conclusions

(1) Microstructure differs at different cooling conditions in horizontal continuous casting process. Al-18% Si alloys billets shows finer microstructure and better mechanical properties after double cooling process.

(2) Fine-grained Al-18%Si raw material prepared by rapid solidification can be used as a refiner for the horizontal continuous casting Al-18%Si alloy billets due to the inherited fine structure of the Al-Si alloy.

(3) With an addition of 15 percent fine-grained material, the microstructure of the HCC Al-18%Si alloy billets becomes finer and the tensile properties clearly improved. The average size of primary silicon in the center of the HCC Al-18%Si alloy billets decreases from 95µm to approximately 50µm. The morphology of eutectic silicon changes from a coarse needle-like form to a fine rod-like form. The UTS increases from 190MPa to 220 MPa. However, the effect of refinement is weakened when the amount of fine-grained material is increased to 30 percent.

(4) Grain refinement can reduce the difference between the surface and the center of the HCC Al-18%Si alloy billets, resulting in the microstructure becoming much more uniform.

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Experimental Study on the Mineral Processing of a Certain Low Grade Copper-Molybdenum Ore in XINJIANG

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Keywords: Copper molybdenum ore, Experiment study, Copper molybdenum separation, Flotation

Abstract. Aimed at the ore characteristics, the flotation flowsheet of one—stage coarse grinding bulk flotation of copper and molybdenum—regrinding of bulk concentrate—separation of copper and molybdenum was determined effected. Experiment uses the above flowsheet and reasonable conditions to process molybdenum crude ore of molybdenum and copper crude grade being 0.066% and 0.03%,and the better indexes of the molybdenum grade of concentrate is 51.68%,the copper grade of concentrate is 12.60% and molybdenum recovery is 74.33% are got.

Introduction

In recent years, molybdenum metal prices in the international market have been rising steadily. As a majorexporterof molybdenum metal, olybdenum mine ore in China has become more and more depleted, which affects molybdenum grade and recovery of concentrate of ore processing. Therefore, the rational development and utilization of the low grade molybdenum ore become an important research topic in the field of mineral processing. This article takes a certain copper molybdenum ore in Xinjiang as the research object to conduct more detailed process mineralogy and beneficiation experiment study.

Ore Property

1.1 chemical composition and mineral composition of the ore

Mineral sample multi-element analysis results are shown in Table 1; The main elements of molybdenum chemical phase analysis results are shown in Table2; The types and content of ore minerals are shown in table 3. From the mineral sample multi-element analysis results we can see that molybdenum grade of ore is 0.066%, and other metallic minerals is in low grade, only molybdenum element has a certain industrial development and utilization value. But considering the symbiosis of the two elements of copper and molybdenum is relatively close, at the same time to obtain the molybdenum concentrate needs a larger enrichment ratio, and copper may result in enrichment, therefore, we must pay attention to the recovery of copper in the experiment and verify that we can obtain the copper concentrate ,meanwhile not only avoid the copper content exceeded in molybdenum concentrate but also have the copper recovered.

Chemical Constituents	Мо	Cu	Pb	Zn	Р	TFe	As/10 ⁻⁶	S	SiO ₂
Content	0.066	0.03	0.02	0.02	0.13	4.95	84.95	0.422	45.21
Chemical Constituents	Al ₂ O ₃	CaO	MgO						
Content	16.10	14.23	2.86						

Table1 Analysis result of mineral sample multi-element (%)

1.2 major metallic mineral dissemination characteristics in the ore

Molybdenite is the main molybdenum in the ore, which content is little, particle size is small, but distribution is wide. It mainly disseminated in the gangue as idiomorphic grained, half idiomorphic grained and tabular forms. Its general particle size is less than 0.04mm and very few particles is than 0.05mm.Molybdenite crystallization has higher degree of larger а and its boundary rules straight, which largely disseminated in the gangue that near the metal-sulfide and less disseminated in the gangue that away from the metal-sulfide, in where it occasionally adjoin attachment or encapsulate with chalcopyrite and pyrite. Molybdenite is part of star spots, irregular granular disseminated in the gangue, whose boundary is generally clear and smooth.

processing experiment results and discussion

2.1 experimental scheme

Aimed at the ore characteristics that the low metal content, copper and molybdenum minerals dissemination size uneven thickness and molybdenum minerals with copper minerals and gangue minerals symbiotic close, we determine the principle flowsheet as ore coarse grinding-mixingcoarse concentrate regrinding program, that is the ore is grinded to 65% -200 mesh, and then carry out copper molybdenum bulk flotation. Coarse concentrates is regrinded to 85%-325 mesh and by once cleaning to obtain crude concentrates of copper and molybdenum. Then take copper molybdenum bulk concentrate to conduct copper-molybdenum separation, finally separate tailings after three times of scavenging to obtain copper concentrate, and molybdenum concentrate by five times of cleaning to obtain the qualified molybdenum concentrate.

2.2 flotation condition test

2.2.1 grinding fineness text

Grinding fineness is the foundation to guarantee to obtain flotation technical index ,therefore, finding a suitable grinding fineness is extremely important .Test use the flowsheet of Figure 1 and the medicament system as the original fixed conditions.

The above test results shows that under the same circumstances of the medicament system ,with the increase of grinding fineness molybdenum recovery rate corresponding increased, but the grade of molybdenum decreased gradually,which is also consistent with the general law of the flotation .Considering the grade and recovery rate, selecting grinding fineness is -200 mesh accounting for 65%.

2.2.2 dosage of lime text

Grinding fineness use -200 mesh accounting for 65%, and collector and frother use the above amount to carry out different dosage of lime of flotation tests. The test results are shown in Figure 3. The test results show that when applicating a lower dosage of lime, molybdenum concentrate has a higher grade, and molybdenum recovery is basically between 93 and 95%, which has a less influence by it. But when the dosage of lime exceeds 3000g / T, the recovery rate declines sharply to less than 90%. Analysising of the reasons ,it is caused by that the pyrite in the mineral is inhibited by lime and the molybdenum element in pyrite comes into the tailings. Therefore, determining the dosage of lime for 2000g / T in order to ensure the recovery rate.

2.2.3 dosage of sodium silicate text

Grinding fineness use -200 mesh accounting for 65%, the dosage of lime use 2000g / T and collector and frother still use the above amount to carry out different dosage of sodium silicate of flotation tests. The test results are shown in Figure 4. The test results show that with the increase of the dosage of sodium silicate, in the case of little change of molybdenum grade, the molybdenum recovery is increase firstly and then decline. Considering the grade and recovery rate to determine the dosage of sodium silicate for 1200g / T.

2.2.4 dosage of kerosene text

Grinding fineness use -200 mesh accounting for 65%, the dosage of lime use 2000g / T, the dosage of sodium silicate use 1200g / T and the dosage of 2 pine oil frother use 50 g/t to carry out different dosage of kerosene of flotation tests. The test results are shown in Figure 5. The test results show that with the increase of the dosage of kerosene, the molybdenum recovery is improved ,and when the dosage of kerosene is 150 g/t the recovery index tends to be stable. So determining kerosene optimal dosage is 150g / T.

2.3 The flowsheet of integrating open-circuit test

Using flotation conditions of the verification tests above to conduct single-stage open circuit flotation tests.Roughing, scavenging and cleaning are adopted by XFD-type single-slot 1.5,0.751 two flotation machine .Roughing pulp density 32% and cleaner concentration decreased gradually. Taking the uncertainty of the flotation test into account the text increases one times of scavenging to ensure the recovery rate. Considering when applicating a higher dosage of lime the recovery of molybdenum lement is significantly become smaller, which illustrates there is a part of molybdenum element intergrowth with pyrite.For this reason the flotation test selects small lime dosage, so there is pyrite into a coarse molybdenum concentrate. In order to obtain qualified copper concentrate at the same time the flowsheet adds regrinding test. After regrinding without inhibitors to conduct flotation separation of pyrite both to improve the molybdenum grade of coarse molybdenum concentrate and to create the conditions for the copper-molybdenum separation .The test proves that in order to obtain qualified grade molybdenum concentrate the ore must be finely ground to be able to make the copper-molybdenum separation. The test flowsheet is shown in Figure 6, and the test results are shown in Table4.

From the test results we can see that nine cleaner tailing and concentrate meet the requirement of that the grade is greater than 45%, and if the eight cleaner tailing also is counted as qualified products, so we can obtain the ideal concentration indexes that is the concentrate grade is 47.962%, the yield is 0.11% and the recovery rate is 73.325%.

Tublet The results of integrating open cheart test						
Droduct Namo	(Mo)	(Mo)	(Mo) Recovery	(Cu)		
Flouuet Maine	Yield (%)	Grade (%)	(%)	Grade (%)		
One cleaner tailing	5.50	0.022	1.681			
Two cleaner tailing	0.65	0.120	1.084			
Three cleaner tailing	0.32	0.252	1.121			
Four cleaner tailing	0.124	0.513	0.884			
Five cleaner tailing	0.074	4.68	4.810	9.23		
Six cleaner tailing	0.049	8.57	5.836	6.33		
Seven cleaner tailing	0.033	17.34	7.953	3.77		
Eight cleaner tailing	0.025	36.84	12.801	1.29		
Nine cleaner tailing	0.021	45.82	13.373	0.65		
Concentrate	0.064	53.01	47.151	0.29		
Scavenging concentrate	1.98	0.028	0.771			
Tailing	91.16	0.002	2.535			
Totle	100.00	0.073	100.00			

Table4 The results of integrating open-circuit test
Due to that the copper content in the mine is low but considering the molybdenum ore enrichment is relatively larger and the copper molybdenum mineral paragenesis is close, and also the copper minerals will be enriched, therefore it is necessary to identify the amount of copper in the molybdenum concentrate. To this end, this test does not do detailed experimental study on the type and dosage of copper-molybdenum separation inhibitors. Only based on actual production data the inhibitor of the copper minerals (sodium sulfide) takes dosage of 1000g / T in primary separation, after the primary separation adds the appropriate and the cleaning dosage of sodium dosage of supplement water which sulfide according is 50-250g to the range / t. The dosage of sodium sulfide is shown in Table5.

section	five cleanings	six cleanings	seven cleanings	eight cleanings	nine cleanings	
dosage (g/t)	1000	250	200	150	150	

Table5 Adding dosage of sodium sulfide

2.4 The flowsheet of integrating open-circuit test

Open-circuit test proves that the molybdenum concentrate grade has reached the national standard, so on the basis of the open-circuit test conduct closed circuit test. The test uses the ore samples of the very low content of copper ,when after molybdenum roughing concentrate uses sodium sulfide inhibition, the scavenging tailings should be merged into the tailings in principle. But considering the inhomogeneity of copper containing of orebody in mining area and the higher molybdenum, copper grade in tailing ,ore should be given comprehensive recycling.

Based on the above reasons, copper molybdenum separation is conducted in the test flowsheet design to the factories designed to provide a reference for the design and construction of the dressing plant . In addition, according to the situation in operation should be properly adding a certain quantity of kerosene and 2 pine oil in the scavenging after separation operation in order to reduce the loss of molybdenum in copper concentrate. The test flowsheet is shown in Figure 7, and the test results are shown in Table6.

Product Name	Yield (%)	Grade (%)	Recovery (%)	Remark
Molybdenum Concentrate	0.105	51.680	74.335	
Copper Concentrate	0.200	12.60		
Tailing	99.642	0.003	4.500	
Calculation of Ore	100.00	0.073	100.00	

Table6 The results of closed circuit test

Conclusion

(1)The main purpose mineral of the ore is molybdenite, and associated metallic minerals are chalcopyrite, pyrite, etc, all of which are failed to meet the comprehensive utilization indexes.Molybdenum in mineral is easy to grind monomer dissociate and process, but part of molybdenite and chalcopyrite symbiotic closely. In order to prevent the copper content in molybdenum concentrate to exceed the standard experiment study text conducts copper and molybdenum separation and obtains the molybdenum concentrate of better quality indexes.

(2)According to the ore characteristics, the flotation flowsheet of one—stage coarse grinding bulk flotation of copper and molybdenum(one roughing stage, four cleaning stages, one scavenging stage)—regrinding of bulk concentrate—separation of copper and molybdenum (one roughing stage, four cleaning stagesthree scavenging stages) is determined effected, and the better index of the molybdenum grade of concentrate is 51.68%, the copper grade of concentrate is 12.60%, molybdenum recovery is 74.33% are got.

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Study on Material Constant Values of Ti-6AI-4V-Rare Earth Titanium

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Keywords: titanium alloy; hot compression deformation; flow stress; constant value

Abstract: According to hot compressive test date, relationship between flow stress, temperature, strain rate and strain is studied. Material constant value is researched through single regression, such as activation energy Q, stress level parameters α and structure factor A. The results show dynamic recovery is principal in the softening process of .titanium and Ti-6Al-4V-Rare Earth Titanium is positive strain rate sensitive material.

Introduction

The titanium alloy as the significant structural materials are widely used in aviation and space, high performance engine, transportation, national defence and military industry ^[1-4]. The Ti-6Al-4V-Rare Earth titanium alloy and its material constant values were studied in this paper. Based on the hat compression deformation data, activation energy Q, stress level parameters α and structure factor A were obtained through single regression. The main components of Ti-6Al-4V-rare earth titanium alloy are shown in Table 1.

Al	V	La+Ce (30%+70%)	Ti
5.8~6.5	3.6~4.3	0.04~0.1	rest

Tab. 1The composition range of the Ti-6Al-4V-rare earth titanium alloy (wt %)

Experiments

The experiment material is Ti-6Al-4V-rare earth titanium alloy in this paper. The main parameters of hot compression deformation simulation experiment are that the temperature is 1000° C, 1050° C, 1100° C and 1150° C, and the strain rate is $0.01s^{-1}$, $0.1s^{-1}$ and $1s^{-1}$ separately. The heating rate, the holding time before compression and the total deformation is 1° C /s, 5 minute and 40%, respectively.

Results and discussion

Fig.1 shows true stress-strain curves for Ti-6Al-4V-rare earth titanium at different compressive strain rates.

Fig.2 shows true stress-strain curves for Ti-6Al-4V-rare earth titanium at different compressive temperature.



(c) $\dot{\mathcal{E}} = 1 s^{-1}$

Fig.1 True stress-strain curves for Ti-6Al-4V-rare earth titanium at different compressive strain rates



Fig. 2 True stress-strain curves for Ti-6Al-4V-rare earth titanium at different compressive temperature

It can be obtained that true stress of Ti-6Al-4V-rare earth titanium rises with the increase of true strain under the certain deformation temperatures and strain rate form fig.1 and fig.2. Increaser of true stresses is linear at the beginning stage. True stresses become gradually stable and steady rheological characteristics appear when true strains reach a certain value. True stresses decrease with the increase of temperature when other parameters are identical. It can be seen that Ti-6Al-4V-rare earth titanium is positive strain rate sensitive material and dynamic recovery is prior in its softening process^[7].

The steady stresses Ti-6Al-4V-rare earth titanium at the different deforming condition and true strains of Ti-6Al-4V-rare earth titanium alloy in the stable deformation are separately showed in Tab.2 and in Tab.3.

Tab.2 Steady stresses of Ti-6Al-4V-rare earth titanium alloy at the different deforming condition

$T/^{\circ}C$ σ/MPa $\dot{\varepsilon}/s^{-1}$	1000	1050	1100	1150
0.01	53.08	46.09	40.89	37.21
0.1	58.1	53.22	44.6	39.8
1	71.78	59.14	48.86	42.63

Tab.3 Various of true strains of Ti-6Al-4V-rare earth titanium alloy in the stable deformation

ε T/°C $\dot{\varepsilon}$ /s ⁻¹	1000	1050	1100	1150
0.01	0.028	0.016	0.011	0.008
0.1	0.04	0.024	0.018	0.012
1	0.16	0.052	0.042	0.038

Determination of material constants of Ti-6Al-4V-rare earth titanium

Many researchers brought up the following equations to describe their Mechanical behavior with regard to many metals and titanium^[5]:

$$\dot{\varepsilon} = A[\sinh(\alpha\sigma)]^n \exp(-Q/RT) \tag{1}$$

Both sides of the above equation (1) is for natural logarithm and then for partial differential obtained:

$$Q = R \left[\frac{\partial \ln \dot{\varepsilon}}{\partial \ln \sigma} \right]_{T} \left[\frac{\partial \ln \sigma}{\partial l / T} \right]_{\dot{\varepsilon}}$$
⁽²⁾

 $\left[\frac{\partial \ln \dot{\varepsilon}}{\partial \ln \sigma}\right]_{T} = n = 1/m; \text{ R: Gas constant, which is 8.31J/(mol \cdot K); n: Stress index, which physical}$

meaning is reciprocal of temperature compensation of strain rate sensitivity.

Value of n can be obtained through the slope of $\ln \sigma$ and $\ln \dot{\varepsilon}$ under contain temperature. Value of $\left[\frac{\partial \ln \sigma}{\partial 1/T}\right]_{\dot{\varepsilon}}$ can be obtained through the slope of $\ln \sigma$ and 1/T. Then, activation energy (Q) can be

obtained.

With regard to Ti-6Al-4V-rare earth titanium, the $sinh(\alpha \sigma)$ can substitute for the σ in the equation (2) because its flow stress, strain rate and deformation temperature conform to hyperbolic sine function. Activation energy (Q) can be obtained through under equation:

$$Q = R \left[\frac{\partial \ln \dot{\varepsilon}}{\partial \ln[\sinh(\alpha\sigma)]} \right]_{T} \left[\frac{\partial \ln[\sinh(\alpha\sigma)]}{\partial 1/T} \right]_{\dot{\varepsilon}}$$
(3)

 $\left\lfloor \frac{\partial \ln \dot{\varepsilon}}{\partial \ln[\sinh(\alpha\sigma)]} \right\rfloor_{T}$ can be obtained through the slope of $\operatorname{Ln} \dot{\varepsilon}$ and $\ln[\sinh(\alpha\sigma)]$; Its curve is shown in Fig.3 and Fig.4.



Fig. 3 Relation between flow stresses and temperatures of Ti-6Al-4V-rare earth titanium



Fig. 4 Relation between flow stresses and strain rates of Ti-6Al-4V-rare earth titanium

Which can be obtained from Fig.3 and Fig.4: The value of $\left[\frac{\partial \ln \dot{\varepsilon}}{\partial \ln[\sinh(\alpha\sigma)]}\right]_T$ is 5.732; the value of $\left[\frac{\partial \ln[\sinh(\alpha\sigma)]}{\partial 1/T}\right]_T$ is 13.416. The value of activation energy (Q) is 639.043(J/mol·K).

Value(β) can be obtained by the equation ($\ln \dot{\varepsilon} = \ln A_2 + \beta \sigma$). The relationship of $\ln \dot{\varepsilon}$ and σ is

shown in Fig.5:



Fig.5 Relation between $\ln \dot{\varepsilon}$ and σ

The value of β is 0.763 from Fig.5.

The value of stress level parameters ($\alpha = \beta / n$) is 0.133.

Structure factor A can be acquired through under equation: $\dot{\varepsilon} = A\sigma^n \exp(-Q/RT)$. ln A = 15.32.

Values of activation energy (Q), stress level parameters α , stress parameters *n* and structure factor $\ln A$ are shown in Tab.4.

Activation energy(Q) J/(mol • K)	Stress level parameters	Stress parameters <i>n</i>	Structure factor lnA
639.043	0.133	5.732	15.32

Tab.4 Material constant values of Ti-6Al-4V-rare earth titanium

Conclusions

(1) Dynamic recovery is prior in its softening process of Ti-6Al-4V-rare earth titanium under high temperature compression

(2) Ti-6Al-4V-rare earth titanium is positive strain rate sensitive material.

(3) Material constant values of Ti-6Al-4V-rare earth titanium: Q=639.043J/(mol • K); α =0.133; *n*=5.732; ln*A*=15.32

Acknowledgements

We are grateful to the National Natural Science Foundation of China (51075122); The State Key Program of National Natural Science of China (U1034002); National Natural Science Foundation of China (50871085).

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CHAPTER 2: Iron and Steel

The Hydrogen Blistering formed on the surface of A333Gr6 Pipeline Steel exposed to wet H₂S solution

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Keywords: A333Gr6 pipeline steel; inclusion; hydrogen blisters; H₂S.

Abstract. After Hydrogen-induced cracking (HIC) test, many hydrogen blisters appeared on the surface of A333Gr6 pipeline steel. The amount of hydrogen blistering depends on the sample location. The amount and area rate of the hydrogen blistering on the surface of A333Gr6 sample near the internal wall are more than those of the sample near the external wall. After the upper part of the hydrogen blisters were torn off, the fracture surfaces of the upper and lower parts of the blister were analyzed by scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDS). The cell segregation inclusion of alloying elements which contain Ca and Al sulfides and oxides were observed in most of the nucleation sites of hydrogen blisters. The result shows that the dislocations and the increasing vacancy concentration are the main reasons to form hydrogen cavities in the nucleation sites. The hydrogen pressure which exceeds the strength of the materials will cause the formation of hydrogen blister.

Introduction

More and more oil gas fields containing high H_2S partial pressure have been exploring and the pipeline steel used in the environments will be destroyed for the acid corrosion. When the hydrogen atoms penetrate into the steel and precipitate in the defects and secondary phases interfaces, significant cracking may occur. Such hydrogen damages were called hydrogen induced cracking (HIC) and Hydrogen blistering (HB). HIC and HB can result in premature failure of pipeline. HIC and HB are caused by inclusion distribution, especially by the elongated MnS inclusion distribution[1]. Recent investigation showed that HIC in the steels primarily nucleated at inclusions and clusters containing the Al and Ca oxides [2]. Therefore, a good understanding of the formation kinetic and mechanism of the HB and HIC is requested and the research results are useful for improving the corrosion resistance of the pipeline in high H_2S environment.

In this study, we evaluated the formation of HB on the surface of A333Gr6 specimens by immersing them into NACE A solution. The hydrogen blisters were agglutinated with the draught tool by SAg-50 (Ni) and then were separated[3]. Then the fracture surfaces of the upper and lower parts and the initiating zones of the blisters were analyzed. The formation mechanism and the influence factors were studied by the analysis of the upper and lower parts of the hydrogen blisters.

Experimental

The material used in the test was A333Gr6 steel. The chemical compositions of the steel are (wt%) C0.12, Si0.24, Mn1.10, P0.008, S0.002, Cu0.12, Cr0.02, Ni0.12, Fe,Balance. The HIC testing was performed in NACE A solution according to NACE TM 0284-2003 standard[4]. Three specimens ($100mm \times 20mm \times pipe$ thickness) were tested for each group. Before the HIC test, the surfaces were ground with SiC abrasive paper down to 400 meshes. All immersed specimens were cut and polished and then the cross-sections were examined with optical microscope after etched with 4% nital solution.

For microstructural observations, all specimens were ground up to 2000 grit paper and polished with the diamond suspension. They were degreased with acetone and etched with 4% nital solution. The microstructure was examined with optical microscope. The blisters are torn off by the method described in literature [3]. The blister caps of the specimen surface could be lifted and the fracture surfaces of blisters were examined by scanning electronic microscopy (SEM) and the chemical composition of blisters were analyzed by energy dispersive spectroscopy (EDS).

Results and discussions

In order to analyze the relationship between the formation of HB and inclusions, the test specimens were taken from the different positions. One group of test specimens were taken with the full wall thickness of the pipe only removing the oxidation layer, the other five groups are taken with the internal and external surface removed 0.2mm, 0.4mm. 0.6mm, 0.8mm and 1mm. Figure 1 shows the appearance of the specimens after 96hours exposure to sodium chloride, acetic acid solution saturated with H₂S at ambient temperature and pressure. From the figure, it was found that the amount and area rate of HB on the specimen surface are different depending on the sample positions. There are many HBs on the internal surface while no HB on the external surface. The amount and area rate of HB on the internal surface of the specimen with 0.6mm base metal removed from internal wall of the pipe are 21 and 1.43%, respectively. However, there are 43 HBs on the surface of the specimen with only oxidation layer removed and HB area rate is 2.85%.



Fig.1 The appears of the specimens exposed 96hours in NACE A solution saturated with H_2S a) 0.6mm base metal was removed from internal wall of the pipe; b) only oxidation layer was removed

Figure 2 shows the metallographic results near the inner and outer wall of the pipe. From the figure, it was found that there were obvious banded structures near the inner wall of the pipe and no any banded structure outside, which mean that the banded structure gradually disappeared from inside to outside. The difference of inclusion distribution and microstructure lead to the susceptibility of HB near internal wall is higher than that of near external wall. After exposure, each test specimen was cleaned to remove corrosion scale and deposits and the specimens were sectioned according to NACE TM 0284-2003. Each polished cross-section was examined with optical microscope and no crack was observed. Blisters presented a circular cap appeared on the specimen surface. The hydrogen-induced crack under a hydrogen blister was observed in the cross-section of the specimen and the cracks extend to the specimen surface.



Fig.2 The metallographic microstructures of different position of the pipeline. a) near external surface; b) near internal surface

Figure 3 shows the morphologies of the testing specimen after the upper part of the HBs was torn off. It was found that the HB dent appeared spherical cap shape and there were corrosion production at the bottom of the HB, which means that the saturated H₂S solution was induced into the HB when the crack extended to the specimen surface. Figure 4 shows the fracture surface of the blister on the surface of A333Gr6 steel. The upper and lower parts of the blister are shown in Fig. 4a and b. The diameter of the bigger blister is approximately 350µm while that of the smaller one is 120µm on the surface of one test specimen after exposure 96hours in saturated H₂S solution. In the bigger blister, grainy inclusions segregated at grain boundaries. The cracks of the two blisters also propagated in the quasi-cleavage mode. The EDS results show that the inclusions are Ca, Al and Mg oxides, which were also observed in HIC cracks of API X70 grade steel by Wan Keun Kim et al. [2]. So the wall of the sheet inclusions can increase the susceptibility of the cracks initiation and decrease the resistance of the development of the cracks. The nucleation site of the smaller one is near the surface of specimen, so the crack propagated quickly to the surface. Once unilateral of the crack reached the surface, the hydrogen pressure vanished and the crack growth stopped which can be certificated by the crack growth expiration at point A in the magnification of Fig. 4a. When the growth of the crack of the bigger blister propagated near the smaller blister, cracks interfered mutually and then linked up after the bigger blister's crack propagated towards the original direction. A distinct cavity, as shown at point B in the magnification of Fig. 4b, was observed around an inclusion. That proves that the cavity is necessary for the nucleation of a hydrogen blister.





In the HIC test, hydrogen atoms penetrate into specimens, but in the beginning the hydrogen atoms are not enough to induce hydrogen pressure. When the hydrogen atoms penetrated into the hydrogen-cavity or micro-cracks, the hydrogen atoms can combine into hydrogen molecules and many hydrogen molecules aggregate to form hydrogen pressure in the defects. The stress existed in the pipeline can promote the movement of the dislocations which provide the place for the aggregation of hydrogen molecules. The stress can be deduced by the differences of thermal expansion coefficient between inclusion and base metal during heat treatment and mechanical processing. Dislocations are the trap of hydrogen[5]. Dislocations can move together with hydrogen atoms and hydrogen atoms can be captured by defects when opposite sign dislocations encounter and mutually counteract. When the dislocations slipped or the dislocations were obstructed by the inclusions, hydrogen atoms were dumped in the micro-cavities around inclusions and the dislocations wind around the inclusions. So, the dislocation can also increase the local brittleness and the concentration of vacancies.

Recent studies have shown that the concentration of vacancies in some hydrogenated metals were much greater than that in hydrogen-free metals [6-8]. Hydrogen atoms are much smaller than Fe atoms and they can induce strain in metal lattices when the hydrogen atoms enter into the specimens and are absorbed as interstitial atoms. The hydrogen concentration in the interface is much higher than that in the metal matrix [3]. Chu et al [9] found that hydrogen blisters could form in second phase and on the boundary of second phase and the metal matrix by TEM observation. Some researches have

found that the plastic deformation happened and the microcrack propagated when the hydrogen pressure increased to the yield strength (σ_s) [10,11]. In order to calculate the change of the yield strength and hydrogen concentration, the yield strength of A333Gr6 was measured to be 340MPa. The basic equation for hydrogen concentration can be written in the form as follows[9]:

$$C_{H} = 33.1\sqrt{f} \exp(-3440/T)$$

where C_H is the hydrogen concentration (ppm), f hydrogen fugacity, and T the absolute temperature (K).

when the environment temperature is 323.15K, the C_H is 0.124ppm which means that the microcrack in A333Gr6 pipeline will form and propagate to form hydrogen blisters when the hydrogen concentration is up to 0.124ppm.



Fig. 4 The fracture surface of two typical hydrogen blisters on the surface of A333Gr6 specimens. (a) upper part, (b) lower part.

Conclusions

(1) Many hydrogen blisters had appeared on the surface of A333Gr6 test specimens after exposure 96hours to the wet H_2S solution.

(2) HB susceptibility is influenced by inclusion distribution and microstructure. Ca and Al sulfides and oxides were identified in the initiating zones of hydrogen blisters.

(3) The cavity was observed around the inclusions, which indicates that the cavity is necessary for the nucleation of hydrogen blisters.

(4) Intersection of dislocations and the increasing vacancy concentration are the main reasons for the cavity formation in the inclusion zone.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (No.51171208).

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Corrosion Inhibition of 2-Mercaptobenzothiazole

for Carbon Steel in Sulfuric Acid Solution

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Keywords: 2-Mercaptobenzothiazole, Corrosion inhibitor, Carbon steel, Acid

Abstract. The inhibition effect of 2-Mercaptobenzothiazole (2-MB) against the corrosion of carbon steel in sulfuric acid solution was studied by weight loss measurement and electrochemical measurements(potentiodynamic polarization techniques). The results show that 2-MB acts as a good corrosion inhibitor in sulfuric acid solution. Adsorption of 2-MB is found to obey Langmuir isotherm. Polarization curves indicate 2-MB is a mixed-type inhibitor. The effects of temperature and sulfuric acid concentration were also studied.

Introduction

Carbon steel corrosion has been the subject of many studies, particularly in acid media commonly used in several industrial fields. The use of acid in cleaning of scales, pickling of metals and acidizing of oil-well is more economical and efficient. The damage by corrosion not only generates high cost for inspection, repairing and replacement, but constitutes a public risk. The use of inhibitors is one of the most practical methods for metals protection against corrosion in acidic media. Most organic inhibitors contain nitrogen, oxygen, phosphorus and sulfur atoms. Multiple bonds can be formed between the electron pair of the donor atoms, through which they are adsorbed on the metal surface. Therefore, inhibitors can control, reduce, or prevent reactions between a metal and its surroundings. In spite of the large number of inhibitors are developed, there is always a need to develop a novel corrosion inhibitor, especially in acid media [1-5].

2-Mercaptobenzothiazole (2-MB) is used primarily as a vulcanization accelerator in the production of rubber. There are few studies have investigated the corrosion inhibition of 2-MB for metals. The present study is to investigate the inhibitive action of 2-MB on corrosion of carbon steel in sulfuric acid solution.

Experimental

Synthesis. The corrosion inhibitor (2-MB) was synthesized according to the procedures illustrated in Scheme 1.

$$NH_2 + CS_2 + S \xrightarrow{200 \sim 300 \ °C} S \xrightarrow{N} SH$$
 (2-MB)

Scheme 1. Synthetic procedures and structure of 2-Mercaptobenzothiazole

Materials preparation. Carbon steel and sulfuric acid solution were used in weight loss and electrochemical measurements. All of the electrochemical measurements(potentiodynamic polarization techniques) were carried out by using a conventional three-electrode cell consisting of a carbon steel working electrode, a saturated calomel electrode (SCE) as reference and a graphite counter-electrode. The polarization curves were obtained by changing the electrode potential automatically from (E±150 mV) at open circuit potential with a scan rate 0.5 mV s⁻¹ to study the effect of 2-MB on carbon steel corrosion.

The inhibition efficiency (IE%, electrochemical measurements.) was determined by using Eq. 1:

IE
$$(\%) = (1 - \frac{I_1}{I_0}) \times 100$$
 (1)

where I_0 and I_1 are the corrosion current densities in absence and presence of 2-MB, respectively.

The inhibition efficiency (IE%, weight loss measurements) was determined by using Eq. 2:

$$IE(\%) = (1 - \frac{W_1}{W_0}) \times 100$$
(2)

where W_0 and W_1 are the weight loss values in absence and presence of 2-MB, respectively.

Results and discussion

Type of inhibitor. As seen in Fig.1, 2-MB acts as a good corrosion inhibitor in different concentration of sulfuric acid solution. The results reveal that the 2-MB is a mixed-type inhibitor.



Fig. 1 Polarization curves for carbon steel in different concentration of sulfuric acid solution (a:1.0 M, b:2.0 M, c:3.0 M) with different concentration range of 2-MB(0, 40, 80, 100 mg·L⁻¹) at 30°C

Temperature and acid concentration. The effect of sulfuric acid concentration and temperature on corrosion behavior of carbon steel in the presence of $2\text{-MB}(100 \text{ mg} \cdot \text{L}^{-1})$ was studied. The results were shown in Fig. 2(a) and (b). The inhibition efficiency of 2-MB declines with temperature increase, and it is less affected by acid concentration.



Fig. 2 Variation of inhibition efficiency with different concentration of sulfuric acid solution(a) and different temperatures(b)

Weight loss measurements. Study results of weight loss measurements for carbon steel in 2.0 M sulfuric acid solution at 30°C (with different concentrations of 2-MB) are shown in Fig. 3(a). With the increasing of 2-MB concentration, the inhibition efficiency increases. That is up to 99.93 % at the 2-MB concentration of 100 mg \cdot L⁻¹. The results indicate that the 2-MB acts as a good inhibitor.



Fig. 3(a) Study results of weight loss measurements for carbon steel in 2.0 M sulfuric acid solution at 30°C,(b) Langmuir isotherm for adsorption of 2-MB on the carbon steel surface in 2.0 M sulfuric acid solution at 30°C

Adsorption. The adsorption of 2-MB molecules on carbon steel surface is a substitute process, during which the adsorbed water molecules on the carbon steel surface are replaced by 2-MB molecules. The data has been tested using Langmuir, Freundlich, Temkin and Frumkin isotherms. The adsorption of 2-MB on carbon steel is found to be consistent with Langmuir adsorption isotherm (R=0.99958), the results is shown in Fig. 3 (b). The equilibrium constant for adsorption process was related to the free energy of adsorption (ΔG_a^0) and can be expressed by Eq. 3 and Eq. 4:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_a^0}{RT}\right) = 5.414 \times 10^4 \; (\text{mol.L}^{-1})^{-1} \tag{3}$$

$$\Delta G_a^0 = -RT \ln(55.5K) = -37.67 \text{ kJ.mol}^{-1}$$
(4)

where 55.5 is the molar concentration of water in the solution expressed in molarity units (mol·L⁻¹), T and R are absolute temperature (K) and gas constant (8.314J·K⁻¹·mol⁻¹) respectively. The ΔG_a^0 value indicates that is the chemisorption for 2-MB on carbon steel surface.

Conclusions

- (1) 2-MB acts as a good corrosion inhibitor in different concentration of sulfuric acid solution.
- (2) Adsorption of 2-MB is found to obey Langmuir isotherm.
- (3) Adsorption of 2-MB is chemisorption.
- (4) 2-MB is a mixed-type inhibitor.
- (5) The inhibition efficiency of 2-MB declines with temperature increase.
- (6) The inhibition efficiency of 2-MB is less affected by sulfuric acid concentration.

Acknowledgment

This work is supported by School of Material and Chemical Engineering, Sichuan University of Science & Engineering.

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Effects of RE on Microstructure and Mechanical Properties of Low-alloy

Steel

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Key words: RE, low-alloy steel, microstructure, mechanical properties

Abstract. The effect of rare earth element on structure and mechanical properties of SS400 steel were studied by metallographic examination, scanning electron microscope (SEM), tensile test and impact test. The results show that rare earth can refine microstructure of SS400 steel. Fracture is changed from cleavage to ductile fracture by adding RE to SS400 steel. And the mechanical properties of SS400 are improved. The impact toughness value of SS400 steel (containing 0.02 RE) increases by 39.66% at -40°C, and at 0°C the impact toughness value increases by 31.05%, respectively comparing with that of steel without RE.

Introduction

It is no exaggeration to say that low-alloy steels play a critical role as industrial basic materials which serve the industrial and social infrastructure, beginning with shipbuilding, building construction, bridges and various types of industrial machinery [1]. And it is commonly used for manufacturing components and moderate corrosion resistance [2-6].

And it was well known that the rare earth (RE) metals are beneficial for refining microstructures and improving the mechanical performance of steels, especially for the toughness [7]. With the development of metallurgical techniques, the purity of the steels has been improved quite a lot. It is to be significant to carry out the research on the application of RE in the clean steels and to develop RE micro-alloyed steels. In this paper, the microstructure and mechanical properties of SS400 steel were studied, and the mechnism of RE on SS400 steel had been also studied.

Experimental

The compositions of SS400 steel are shown in Table 1. The test materials (the same batch of continuous casting slab) were melted by a 25kg vacuum medium frequency induction furnace. After deoxidization with Al at 1600°C, the melt was poured with addition mischmetal (Cerium-rich mischmetal, containing La, Pr, Nd, Tm) into the ladle for modification before tapping. Scanning electron microscopy(Quanta400) was used to study the fracture surfaces in the steels.

The impact samples (10mm×10mm×50mm, V-notch) were performed for determining impact toughness with a JB-300 impact test machine. And the tensile samples were performed according to GB/T228-2002 standards and requirements for determining room temperature tensile with a WDW-200 tensile testing machine. Before final machining, the following forging and heat treatment processes were performed: The starting forging temperature is 1100°C, and finish forging temperature is 900°C and air cooling, 2) heat treatment: heating to 850°C for 2h and air cooling.