

Edited by
F.R.N. Nabarro and M.S. Duesbery

Dislocations in Solids

Volume 10

$L1_2$ Ordered Alloys

North-Holland

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$L1_2$ Ordered Alloys

Edited by

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Preface

Volume 10 of this series is the first to appear under the joint editorship of E. R. N. Nabarro and M. S. Duesbery. It contains a symposium on the behaviour of dislocations in alloys with the L12 structure typified by Ni₃Al. These structures are of engineering importance because they form an essential constituent, and, in modern alloys, the major constituent, of superalloys. They also present scientific problems in the behaviour of dislocations which are still not fully resolved. Unlike most metals and alloys, they have a flow stress which increases with increasing temperature over a wide range. Unlike most metals and alloys, they behave very differently in tensile tests and in creep tests.

The first paper in the L12 symposium is a historically-oriented article by Westbrook, who observed the anomalous temperature dependence in 1967, and remarked that "Although several possible sources of this anomaly were investigated no unequivocal explanation could be established. Further study is indicated".

Then Sun and Hazzledine report studies by transmission electron microscopy of the behaviour of dislocations in these alloys, while Caillard goes further in relating the structure of dislocation cores in these and other alloys to the anomalous temperature dependence of the flow stress.

Vitek, Pope and Bassani, from the group which first expanded the ideas of Takeuchi and Kuramoto on the anomalous temperature dependence into a detailed theory, show how their theory is modified in the light of recent experimental evidence. This theory considers the way in which dislocations in L12 become pinned at certain points, and the way in which these pinning obstacles can be overcome. Chrzan and Mills carry the analysis further by considering not only the individual pinning and unpinning events, but also the way in which the overcoming of one obstacle can trigger the overcoming of neighbouring obstacles. This leads them to an important link with the modern theory of phase transitions. The symposium ends with a rather controversial article by Veyssi re and Saada, claiming that the model which Vitek, Pope and their colleagues have developed so successfully puts too much emphasis on the anisotropy of the flow stress and too little on other observations. They concentrate on the importance of the viscous motion of dislocations on the cube planes.

The first chapter outside the symposium is by Takeuchi and Maeda on the effects of electronic excitation on the plasticity of semiconducting crystals. The effects are well documented, but their mechanism is not clear. The authors support a "phonon kick" interpretation. Finally, Joos examines the role of dislocations in melting, exploiting the old idea that the presence of small dislocation loops in thermal equilibrium reduces the energy required to form more loops, so leading to a first-order phase transition.

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Superalloys (Ni-base) and Dislocations – An Introduction

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1. Background

A superalloy has been defined as “an alloy developed for elevated temperature service, usually based on Group VIIIA elements, where relatively severe mechanical stressing is encountered and where high surface stability is frequently required” (Sims and Hagel [1], p. ix). Compositionally superalloys are perhaps the most complex alloys ever developed in that they typically contain eight to twenty controlled alloying elements, the proportions of which must be exquisitely balanced in order to optimize their properties. Structurally, they are equally complex in that, unlike such common alloys as brass or Monel which are single-phase in character, superalloys have multi-phase microstructures in which the identity, size, shape, and disposition of each of the secondary phases must also be carefully managed for the best performance.

Still further complications arise from the fact that superalloys typically are required to operate at temperatures of the order of $0.8T_{\text{mp}}$ or higher in aggressive atmospheres. Under such conditions most microstructures are unstable; new modes of deformation appear; and constituent elements can react with the environment. Small wonder, then, that understanding of how these alloys respond to mechanical stressing at high temperatures has evolved slowly.

Most deformation of crystalline solids is now known to involve dislocations; thus, their structure, number, disposition, mutual interaction, and interaction with solute atoms and microstructural features all become critical. A large proportion of the content of the volumes in this series over the past 16 years has been devoted to such topics but generally with reference to other classes of materials. In order to understand how we arrived at the present state of the science of dislocations in nickel-base superalloys, we need to look at the separate historical development of superalloys and of dislocations, and then turn to the interaction of these two themes. Finally, we will attempt to project likely directions of future development, both in understanding and in application.

2. Superalloys, their history and nature

Superalloys were not invented *de novo* but came as the culmination of a series of developments over hundreds of years aimed at improved structural materials for use at high temperatures. Although the fact that metals soften with increasing temperature has been known for thousands of years, for most of this period there was no interest in materials with useful high temperature strength. Only two instances are known of very early attempts to actually use metals at high temperatures. The Chinese (475–221 BC) used cast-iron molds for casting tool shapes from non-ferrous metals (Lu Da [2]). Here it was the relatively high melting point of the mold material (and hence minimal distortion and interaction) that was exploited, rather than high temperature strength *per se*.

The next relevant development was the introduction of novel tool steels. With the advent of powered machine tools in the 19th c. and the increased use of iron and steel in machine construction, cutting materials superior to high carbon steel were badly needed. Perhaps the first of these was Robert Mushet's Special, introduced in 1868 and containing 1 wt.% Mn and 8–10 wt.% W. Although, as described by Keown [3], this was not a true high-speed steel, it did permit a 50% increase in cutting speed. The first real break-through in this type of material came in 1898 when Taylor and White [4] developed a tungsten steel with a 3.8% Cr content and a special heat treatment. At its first public demonstration at the Paris World Exposition in 1900, it was observed that both the tool tip and the chips coming from the workpiece were "red hot" at a cutting speed of 150 ft/min. (about 10× that possible with Mushet's Special). It was thus clear that the high temperatures generated in high-speed cutting required a tool material which softened substantially less than did the workpiece. Taylor and White's alloy was the forerunner of the 18W-4Cr-1V tool steels we know today.

While casting molds and cutting tools are early instances of the need for high temperature materials, a major demand arose only with the progressive development of heat engines (Burstall [5], Ch. VI and VII, pp. 201–365). Following the invention of the first practical steam engines by Savery and Newcomen in 1700, the further improvements by Watt and Trevithick in the late 18th and early 19th c. ushered in the industrial revolution and the "steam power age". It was appreciated that both the boiler and the engine itself required structural materials which would operate at elevated temperatures – the higher the temperature and pressure, the greater the efficiency. However, the early steam engines were materials-limited, not so much by inadequate high temperature strength as by poor materials quality control, poor construction techniques, and lack of pressure measurement and control.

At a later point, Charles A. Parsons in 1884 patented his design for a steam turbine that was an immediate commercial success and a further driver for improved high temperature materials. Design improvements over the next 40 years resulted in steady increases in size and efficiency. Over the same period, internal combustion engines, both gasoline and Diesel, were developed. For both the steam turbine and the internal combustion engine, the increases in power and efficiency that were achieved were aided in no small way by concurrent, evolutionary improvements in alloy steels (Dulieu [6])¹. A greater incentive to the development of high temperature alloys was provided by superchargers intended for both piston engines and gas turbines (Moss [7]). However, only with the advent of the turbojet aircraft engine in the late 1930s, as a result of independent work by Whittle in England and von Ohain in Germany, did the higher temperatures and stresses encountered demand a truly discontinuous change in materials (Somerscales [8], Sims [9]).

In answer to this challenge, metallurgists turned to some specialty alloys, originally developed for quite different purposes as summarized in table 1 (Westbrook [10]). Fifty

¹For example, Ni-Cr-Mo steels were introduced in 1924 for steam turbine rotors; about the same time certain stainless steels for blades, and low C, 0.5 wt.% Mo steel for steam tubing with capability to 500°C, and after 1930, Cr-Mo-V steel for a variety of applications. It is nonetheless remarkable that neither the ASM Handbook of 1930 nor the SAE Handbook of 1933 contain any data on the temperature dependence of mechanical properties!

Table 1
Origins of the superalloy families (after Westbrook [10]).

Class	Progenitor system	Original application	Early superalloy descendant
Fe-base	Fe–Cr stainless steel with/without Ni* (1914)	cutlery steel	16-25-6 (1940s)
Co-base	Co–Cr–W–C**	cutting tool and hard facing	Haynes 23 (1946)
	Co–Cr–Mo** (1929)	surgical and dental alloy	Vitallium (1950's)
Ni-base	Ni–Cr*** (1906)	resistance heating element	Nimonic 80 (1940's)

* Truman [11]
** Fritzlen [12]
*** Marsh [13]

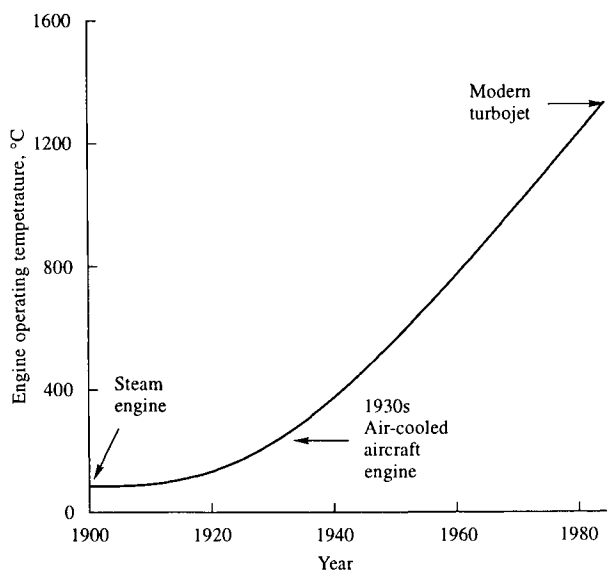


Fig. 1. 20th c. increases in engine operating temperature made possible by new materials [14].

years of largely empirical work resulted in the families of superalloys we know today. This has been a truly remarkable achievement! The Ni-base alloys in particular are able to sustain stresses of 170 MPa for thousands of hours, running at temperatures of the order of $0.8T_{mp}$, sometimes even higher. Another measure of the advance in high temperature structural materials since the days of the steam engine is shown in fig. 1. In parallel with materials development, processing of these materials became extremely sophisticated. Scientific understanding of the superalloy family also improved markedly, not just with respect to their phase constituency and the roles of individual alloying

elements, but also with respect to strengthening mechanisms, deformation mechanisms, and oxidation behavior.

In this paper we will restrict our attention to the history of a single family of superalloys, the nickel bases hardened principally by Ni_3Al (γ'), not only for reasons of space but also because that family is the focus of most of the other papers in this volume. Although many of these alloys contain very small volume fractions of carbides and borides that play a significant role with respect to mechanical properties, we will concentrate on the characteristics of the Ni_3Al phase and its relation to the solid solution matrix. Similarly, we will not treat oxide dispersion strengthened superalloys, a powder metallurgy product.

The fact that aluminum conferred age hardening behavior to a Fe–Ni or Fe–Ni–Cr base composition was deduced very early by Chevenard [15] from dilatometric and hardness tests. These effects and similar ones due to titanium and silicon additions were confirmed by a number of different workers during the 1930s, but results were inconsistent and confusing. In the late 1930s, at the beginning of World War II, when the aircraft gas turbine established an unprecedented requirement for strong high-temperature alloys, a broad systematic attack to generate precipitation-hardenable alloys from a Ni–Cr base was launched at the Mond Nickel laboratories in England (Pfeil et al. [16] and Betteridge and Bishop [17]). This research produced the famous Nimonic series of alloys of which Nimonic 80, introduced in 1941, and later Nimonic 80A, were the first high temperature alloys² to be intentionally hardened by precipitation of a $\text{Ni}_3(\text{Al}, \text{Ti})$ compound. Nimonic 80 was thus the forefather of all the “Inconel”, “René”, “Udimet”, and similar alloys of today. Yet, while precipitation hardening was undoubtedly occurring, was responsible for the outstanding high temperature properties, and was associated with the Ti and Al additions, no precipitates could be seen. Ni_3Al or γ' was not identified as the precipitate until about 1950 (Hignett [21]) with the aid of careful X-ray diffraction and electron microscopy, and the phase diagrams of the pertinent regions of the Ni–Cr–Al–Ti system were not published until 1952 (Taylor and Floyd [22, 23]).

The further development of this class of alloys, via variations in composition and heat treatment, has again been largely empirical. Improved processing techniques, most importantly *vacuum melting* (permitting higher Ti and Al contents and Nb and Hf additions without formation of deleterious oxides and nitrides) and *directional solidification*, introduced by Ver Snyder [24] (eliminating grain boundaries transverse to the stress axis or altogether, and allowing higher contents of refractory metal solutes) have brought about a 200°C increase in the permissible operating temperature and greatly improved reliability (10,000 hrs time between overhauls of jet engines).

However, the reasons for all of these improvements were often in doubt despite the opportunities offered for “cleaner” experiments by the availability of superalloy single crystals. It has been observed (usually *after* the development of superior alloys) that: the solution hardening of the matrix was increased, the volume fraction of γ' increased, and the presence of deleterious phases avoided; but the more subtle and perhaps more important aspect – the development of an optimal compositional relationship between matrix and γ' remained poorly understood and hence not realized.

²ICI Metals Division in England, now IMI, developed age-hardenable copper-base alloys, named Kunial, in the early 1930s. The hardening compound was later shown to be Ni_3Al [18–20].

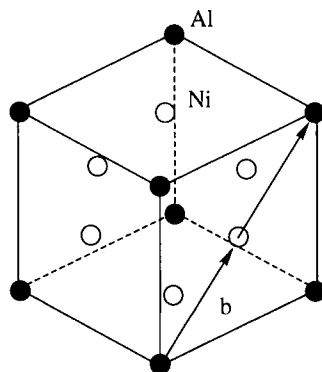


Fig. 2. The $L1_2$, cP4 structure of Ni_3Al . Note that the $\frac{1}{2}(110)$ vector, which is the perfect dislocation in the disordered f.c.c. γ phase, becomes a superpartial dislocation in the ordered γ' phase. Thus movement of a pair of such partials is required to restore order (after Sun [25]).

We must next digress briefly to consider what γ' is and why it is important to Ni-base superalloys. Ni_3Al (γ') possesses a f.c.c. structure (hence the γ in reference to the usual nomenclature in Fe-based systems) and is ordered (indicated by the prime symbol) as shown in fig. 2. Intermetallic compounds have been recognized as such only since the work of Karsten [26]. The idea of atomic ordering was introduced by Tammann [27] and confirmed by the X-ray diffraction studies of Bain [28]. The first determination of the ordered f.c.c. arrangement of Ni_3Al ($L1_2$, cP4) was by Westgren and Almin [29]. In contrast to many other cases (e.g., Cu–Au) where this structure forms on cooling from a disordered solid solution at high temperatures, Ni_3Al remains ordered to its solution temperature or melting point, forming directly by peritectic reaction between the disordered Ni solid solution and the liquid, as shown in fig. 3.³ This circumstance is itself indicative of the strong bonding between nickel and aluminum atoms at this composition.

The surprisingly high hardness characteristic of compounds formed, even between two relatively soft metals, was recognized early on, e.g., Martens [31], but studies of the temperature dependence of mechanical properties of intermetallics were not undertaken until much later. Tammann and Dahl [32] studied over 30 intermetallics and found that while all were brittle in the macroscopic sense at room temperature (albeit, some showed slip lines in individual crystals) macroscale plasticity could always be observed at sufficiently elevated temperatures. In the 1930s Shishokin and co-workers [33–36] studied the temperature and compositional dependence of hardness and flow stress (extrusion pressure) of a number of intermetallics and found a minimum in the temperature dependence of these properties at a composition corresponding to the ideal stoichiometry of any intermetallic formed, thus foreshadowing their potential as high temperature

³The peritectic and eutectic reaction temperatures for the binary are very close as seen in fig. 3 as also are the compositions of γ' and eutectic liquid. These relationships may well be altered with ternary and higher alloys. There is reason to believe that in practical multicomponent superalloys the eutectic composition lies between γ and γ' , rather than between $NiAl$ and γ' as seen in fig. 3.

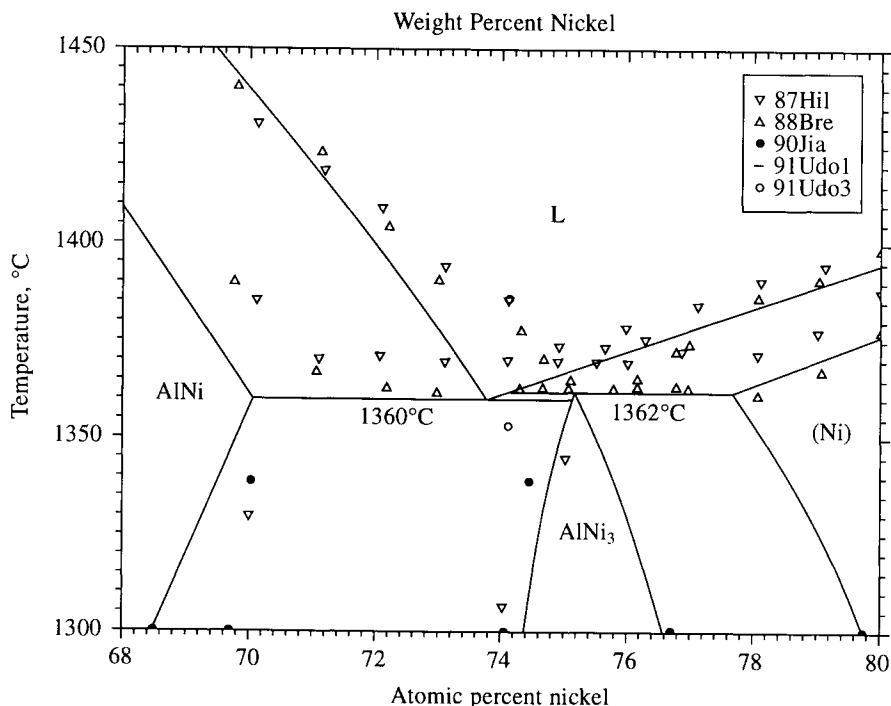


Fig. 3. Partial Al-Ni phase diagram for the 68–80 at.% Ni region between 1300 and 1450°C (after Okamoto [30]).

structural materials. Other aspects of the history of intermetallic compounds have been previously reviewed by the author [10, 37–40].

In the early post-World-War-II period, research in this area took two general paths. On the one hand there was continued empirical development in alloying of superalloys and improvements in their processing, accompanied by increased effort to understand their behavior; and, on the other, some pioneering work was begun to see if intermetallics themselves might be exploited as a new class of high-temperature materials, rather than simply as constituents of more conventional alloys. In connection with the first theme, an appreciation of the uniqueness of Ni₃Al began to be realized. No aluminide with comparable structure occurs in Fe- or Co-based systems. While in the Ni–Al binary the compositional range of Ni₃Al is quite restricted, it can accommodate considerable solid solution alloying by ternary additions on both the Ni and Al sites, leading to both significant hardening and the ability to adjust the lattice mismatch between Ni₃Al and the matrix. Thus, the improved scientific understanding led to concentration on Ni-base superalloy development rather than on Fe- or Co-based alloys.

With respect to the second theme, single phase intermetallics or alloys with very high volume fractions of intermetallic were increasingly seen as having attractive potential for high temperature applications from a fundamental point of view because of several factors:

Mechanical:

- high intrinsic yield strength at high fractions of the melting point;
- deformability at low homologous temperatures (at least for some compounds, especially as single crystals);
- high strain hardening rate.

Kinetic:

- low diffusion rates (relative to metals of comparable melting point) contributing to microstructural stability;
- low diffusion rates that slow degradation by oxidation or corrosion or by diffusive deterioration of coatings;
- low diffusion rates retarding atomic deformation processes.

Matrix compatibility:

- equilibrium or quasi-equilibrium structures;
- compositional similarity between compound and matrix;
- adjustable coherency.

In an early instance of this type of observation, Westbrook [41] found that two-phase Ni–Cr–Al alloys, consisting of a high volume fraction of γ' in a γ matrix, exhibited an unusual combination of low temperature toughness and high temperature strength.

We conclude this summary of the history of superalloys by referring the reader to two sets of conference proceedings: the Seven Springs Superalloy Conferences (1968, 1972, 1976, 1980, 1984, 1988 and 1992) sponsored by TMS/ASM cover developments in superalloys, and the Materials Research Society Symposia (1984, 1986, 1988, 1990, 1992 and 1994) treat high temperature ordered intermetallic alloys. More focussed reviews of the mechanical properties of γ' are given by Pope and Ezz [42], Stoloff [43], Suzuki et al. [44], and Liu and Pope [45]. Nembach and Neite [46] and Anton [47] have supplied reviews of the role of γ' in superalloys. Later we will review some particular observations relevant to the interaction between superalloy structure and dislocations. Now we trace the history of our understanding of dislocations.

3. Dislocations in intermetallics and superalloys

There have been several recent histories of the development of dislocation concepts, most notably those of Hirth [48] and Schulze [49], and it would be pointless to recapitulate them here in any detail. A convenient summary is given by tables 2a, b and c, taken from Schulze. As is well known, the modern conception of the dislocation theory dates from the independent publications of Orowan, Polanyi and Taylor in 1934. Their model successfully accounted for the low shear strength of real crystals and for the strain hardening of crystalline materials. A flood of papers appeared over the next 20 years by authors from all over the world elaborating the basic concepts and interpreting a wide variety of experimental results in terms of the generation, motion, and interaction of dislocations, both with themselves and with other microstructural features and atomistic defects.

Table 2

Key points in the evolution of dislocation theory: a) first period, 1892–1920; b) second period, 1921–1934; c) third period, 1934–1958 (after Schulze [49]).

a) First period		
Event	Year	Authors
"strain-figure" in a granular medium as a modification in the structure of mechanical aether	1892	C.V. Burton
"intrinsic strain-form" in a medium showing strictly linear elasticity – constituting an electron – moving in the stagnant aether	1897	J. Larmor
Observation of "slip steps" on Pb; PRIORITY?	1900	J.A. Ewing, W. Rosenhain
First observation of slip lines (NaCl; CaCO ₃); origin of terms "slip plane", "direction of easiest translation" and "weak positions" in crystals	1867	F.E. Reusch (Poggendorfs An.) (once again brought to view by G.E.R. Schulze)
• Really first observation of slip lines in metals (Au, Cu, ...); • Determination of slip systems; • Originator of term "translation"	1899	O. Mügge (once again brought to view by G.E.R. Schulze)
Theory of self-strain states in an elastic continuum ("distorsioni")	1901	G. Weingarten,
	1907	V. Volterra,
	1912/15	C. Somigliana
Theory of hysteresis in a lattice of rotating dipoles with slipable regions of abnormal alignment	1907	J.A. Ewing
"I have ventured to call them Dislocations"	1920	A.E.H. Love
b) Second period		
Event	Year	Authors
Proposed notch effect by internal cracks in order to overcome the contradiction between theoretical and measured critical shear stress	1921	A.A. Griffith
Systematic measurements of stress-strain curves with Polanyi-apparatus using single and polycrystalline metals	twenties	M. Polanyi, E. Schmid, W. Boas, G. Sachs et al.
Shear stress law	1926?	E. Schmid
Model of flexural slip ("Biegegleitung")	1923	G. Masing, M. Polanyi
Interpretation of mechanical hysteresis on account of translation periodicity of crystal lattice	1928	L. Prandtl
Model of "Verhakung"	1929	U. Dehlinger
Observation of decorated dislocations; not interpreted as such	1905	H. Siedentopf,
	1932	E. Rexer,
	1932	A. Edner
"Lockerstellen"	about 1930	A. Smekal
Model of local slip	1934	E. Orowan

Table 2
(Continued)

c) Third period		
Event	Year	Authors
Models of edge dislocation	1934	E. Orowan, M. Polanyi, G.I. Taylor
First estimation of critical stress		
Model of screw dislocation	1939	J.M. Burgers
Idea of partial dislocations	1948	W. Shockley
Influence of screw dislocations on crystal growth	1949	W.K. Burton, N. Cabrera, F.C. Frank
Pictures and energy estimations of small angle boundaries	1949 – 1953	W. Shockley, W.T. Read
Model of dislocation multiplication (Frank-Read-source)	1950	F.C. Frank, W.T. Read
Imaging of an edge dislocation in lattice fringes of platinum phthalocyanine	1956	J.W. Menter
Evidence of real existence of dislocations in metals by electron diffraction contrast	1956	P.B. Hirsch, R.W. Horne, M.J. Whelan
Work hardening theories		
(I) Glide-zone model	1957/58	A. Seeger
(II) Forest-theories	1958/60	{ P.B. Hirsch Z.S. Basinski
(III) Jog-dragging theory	1960	P.B. Hirsch
(IV) Mushroom theory	1962	D. Kuhlmann-Wilsdorf
"The dislocation is the elemental residual-stress source"	1958	E. Kröner

Embarrassingly, as Read [50] noted, not only could any particular result be given a reasonable dislocation interpretation, but often several radically different models appeared to serve equally well. Worse still was the fact that until the end of this period no one had observed a dislocation "in the flesh", although slip lines had been seen as early as 1867 by Reusch [51]. An enormous boost was given the field in the 1950's with the introduction of techniques which permitted the observation of dislocations: etch pitting (Vogel et al. [52]), decoration (Hedges and Mitchell [53]), and especially electron microscopy (Heidenreich [54], Hirsch et al. [55] and Bollman [56]) and field emission microscopy (Muller [57]). Not only were some dislocation configurations now seen to be exactly what had been imagined, but it was finally possible to perform critical experiments, obtain quantitative data such as dislocation mobilities (e.g., Johnston and Gilman [58]), make detailed observations of dislocation core structures (down to resolutions of 1–2 nm), and even, in the case of transmission electron microscopy, observe other dynamic effects by stressing samples *in situ* in the microscope (Suzuki et al. [59, 60]).

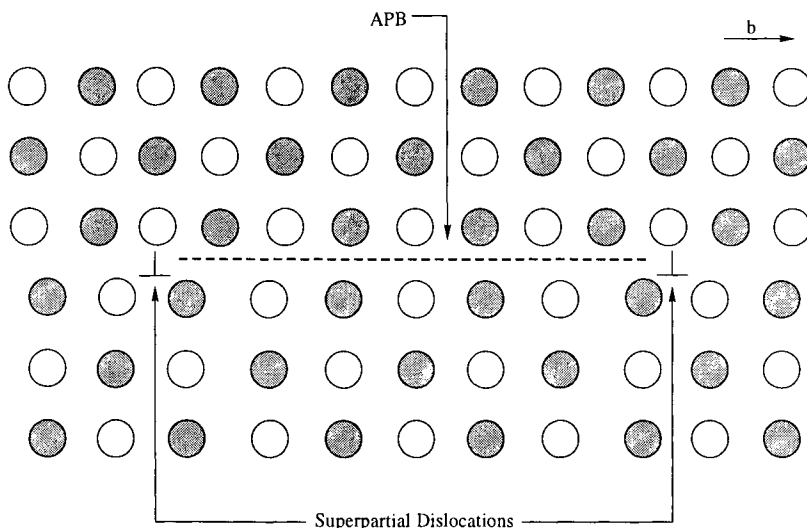


Fig. 4. Two superpartial dislocations coupled with a piece of antiphase boundary (after Sun [25]).

The improved atomistic level of understanding of plastic deformation in solids had some particular impacts on interpreting the behavior of intermetallic compounds and superalloys, and conversely experimental findings on the latter contributed to the former. An early problem was that what would have been a unit dislocation in the disordered lattice, in attempting to glide through an ordered lattice, should experience a large resistance due to the disordering effect brought about by its motion; yet some fully ordered alloys, e.g., Cu_3Au , deformed quite readily. Koehler and Seitz [61] predicted that the ordered structure of most intermetallics would require a superdislocation, i.e., a pair of partial dislocations separated by a strip of material with the ordering of the atoms exactly out-of-phase with the normal structure, a so-called antiphase boundary (APB) as shown in fig. 4. They reasoned that, in motion of this complex, the order that is destroyed by the leading member of a pair would be immediately restored by the trailing dislocation and hence would encounter much lowered resistance. At that time, however, no one had knowingly seen a dislocation, let alone a closely spaced pair of dislocations. Only a few years later, however, such superdislocations were first revealed by Marcinkowski et al. [62] by electron microscopy. More recently weak beam electron microscopy was employed by Crawford and Ray [63] to demonstrate the expected four-fold dissociation of dislocations in Fe_3Al (D0_3 structure).

Elastic anisotropies, energetic anisotropies of internal surfaces such as APBs and stacking faults, and the often complex core structures of the dislocations themselves lead to still further complications in the geometry and dynamics of dislocations in ordered alloys. One of the most famous of these is the so-called Kear–Wilsdorf lock (Kear and Wilsdorf [64]) shown in fig. 5, caused by a screw superdislocation dissociated into (111) APB and cross-slipped segments on (100) planes.

Consideration of the behavior of dislocations in two-phase alloys, e.g., Ni_3Al particles in a Ni solid solution matrix, brought about more complications. For example, compar-

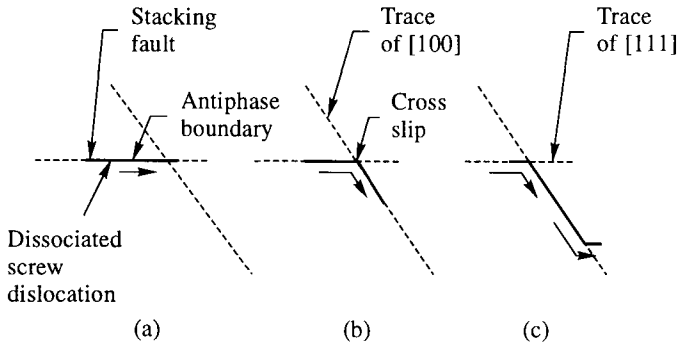


Fig. 5. The Kears-Wilford lock formed by cross-slip pinning (Kear and Wilford [64]).

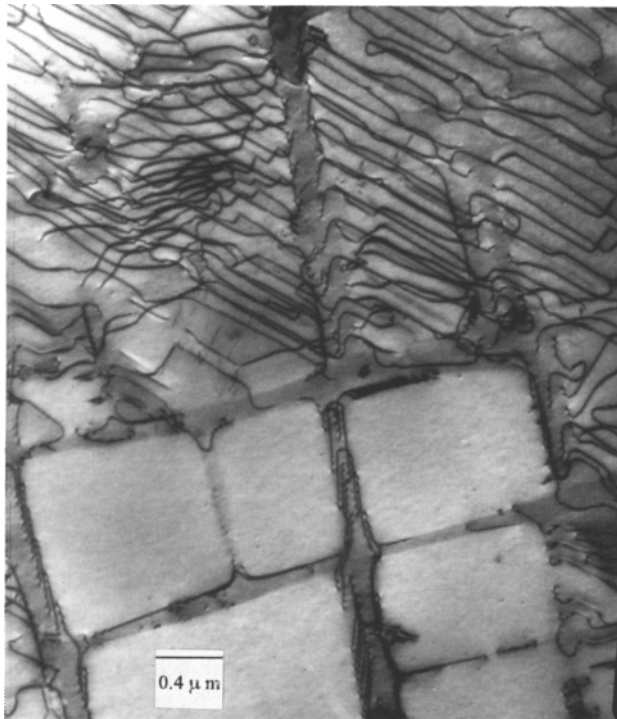


Fig. 6. Dislocation structure developed during primary creep at 850°C of a Ni-base single crystal superalloy, CMSX-3. Dislocations appear in the matrix channels between γ' particles (horizontal channels, upper part and vertical channels, lower part of the figure) (courtesy of T.M. Pollock).

ing the creep behavior at 1000°C of γ , γ' , and a mixture of the two phases, Nathal et al. [65] found for the two-phase alloy a decrease in creep rate of about a factor of 1000 relative to γ' alone. Creep tests of Ni-base superalloy single crystals were coupled with stereo transmission electron microscopy by Pollock and Argon [66]. For their alloy

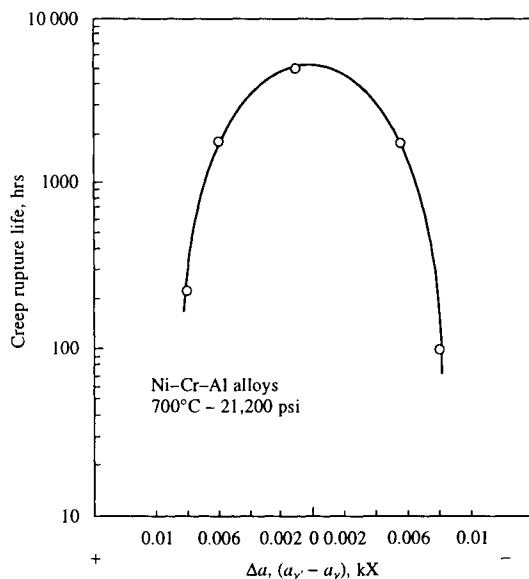


Fig. 7. Effect of lattice mismatch (Δa) on creep-rupture life of Ni-Cr-Al alloys (after Mirkin and Kancheev [67]).

with a γ' volume fraction $\sim 67\%$ and particle size $\sim 0.5 \mu\text{m}$ (typical of present day superalloy microstructures), they found that for creep at 850°C or less the γ' was essentially dislocation-free and undeformable. As a result, dislocations are forced to move through the relatively narrow channels between γ' particles, ultimately forming complex 3D networks and thereby constituting the principal cause for the high creep resistance. The dislocation structure developed during early stages of primary creep at 850°C and 552 MPa is shown in fig. 6. No dislocations appear within the cuboidal γ' particles that extend through the foil thickness. The dislocations visible occur in matrix channels between γ' precipitate particles: vertical channels (lower part of the figure) and horizontal channels (upper part of the figure) that are contained within the thickness of the foil.

To be effective in practice, where superalloys are stressed for long times at high temperatures, the microstructure must be stable. The coherent interface between γ and γ' contributes basically to a low interfacial energy, which is further minimized by appropriate alloying. The practical result of this is seen in the work of Mirkin and Kancheev [67] illustrated in fig. 7. Still further contribution to microstructural stability can be obtained by addition of elements such as Re, which dissolves almost exclusively in γ rather than in γ' (Giamei and Anton [68]). One interpretation of this benefit is that any growing γ' particles must drive Re away from the γ/γ' interface, and thus Re diffusion becomes the limiting step. However, solutes not only partition between γ and γ' but may also segregate to grain boundaries, APBs, or interfaces between phases and contribute to strengthening and microstructural stability through various mechanisms. Furthermore the relative degree of partitioning and segregation may vary with solute concentration and temperature, so a general picture of the contribution of alloying to microstructural stability and strengthening does not readily emerge.

Modern views of the dislocation behavior of superalloys may be found in Sims et al. [9], Anton [47], and Pollock and Argon [66]; Ardell [69] reviews dislocation/particle interactions in precipitation and dispersion strengthened systems at room temperature and low volume fraction of the dispersed phase.

Another historical development that must be remarked on is the use of the computer to perform various simulation “experiments”. These may be used either to generate possible structures or to make quantitative or semi-quantitative estimates of dislocation behavior given known or assumed values for various key parameters. Such studies began as early as that of Foreman and Makin [63] and continue to this day. A summary of early work with this approach is given by Puls [71]. The method may be expected to be even more fruitful in the future with better interatomic potential models and as better estimates or experimental measures of key modelling parameters come to hand, e.g., elastic constants, vacancy formation energy, stacking fault and antiphase boundary energies, etc.

We conclude this section with a brief citation of some other key reviews. Duesbery and Richardson [72] discuss dislocation core structures in all crystalline materials. Veyssi re and Douin [73] review dislocations in intermetallic compounds with particular emphasis on core structures and core-related mechanical properties. Sun [25] discusses how defects in intermetallics (including dislocations) differ from those in ordinary metals and disordered solid solutions and the implications these differences have for mechanical behavior at both room and elevated temperatures. Yoo et al. [74] provide a convenient summary of currently unsolved problems. It must finally be noted that there are several aspects of the relevance of dislocations to the formation and behavior of superalloys that are not considered by the other papers in this volume; among these are: low temperature toughness and fracture, solid solution hardening, dislocation interaction with solute atoms and point defects, microstructural stability, grain boundaries and crystal growth. These topics, which are summarized in detail in two reference works (Sims and Hagel [1] and Sims et al. [75]), therefore, receive only incidental mention in this Introduction.

4. Some significant problems and observations

4.1. On dislocations in intermetallics

Anomalous temperature dependence of flow stress. This phenomenon was first reported by Westbrook [76] from hot hardness measurements on Ni_3Al where it was found, as seen in fig. 8, that the hardness increased with increasing temperature in contrast to the behavior of all other intermetallic compounds he studied.⁴ He also found that the effect was both intrinsic to the material and temperature-path history independent. This surprising result was soon confirmed (Flinn [79], Davies and Stoloff [80]), and

⁴It is recognized that more modest increases in strength with increasing temperature for intermetallics were previously reported for CuZn (Barrett [77]) and for Cu_3Au (Ardley [78]). These results, however, are readily interpreted as due to change in domain size and/or degree of long range order. Ni_3Al does not have a stable domain structure nor does its ordering degree decrease significantly with increasing temperature; hence its strength increase is truly anomalous.

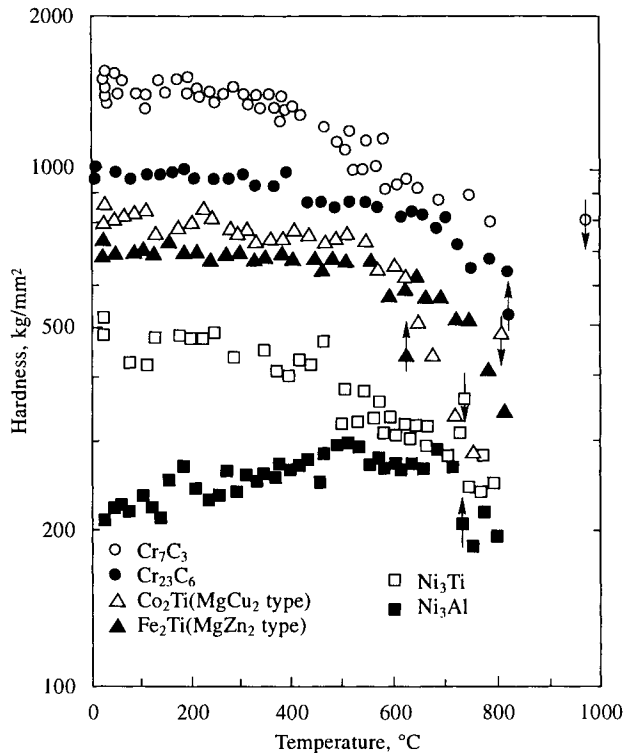


Fig. 8. Hardness as a function of temperature for several phases common in superalloys. The vertical arrows indicate a $T_h = 0.5$ (after Westbrook [76]).

many other aspects of the phenomenon documented by Thornton et al. [81]. These are summarized by Vitek et al. in this volume to include:

- 1) the yield and/or flow stress increases with increasing temperature;
- 2) flow stress is temperature-path history independent;
- 3) failure to obey Schmid's law;
- 4) different strengths obtain in tension and compression;
- 5) flow stress is virtually strain rate independent in the anomalous region;
- 6) slip occurs predominantly on $\{111\}\langle 101 \rangle$ system below peak temperature and on $\{001\}\langle 101 \rangle$ above it;
- 7) predominantly long $\langle 101 \rangle$ screw dislocations are seen in the anomalous region;
- 8) no anomaly occurs in the microstrain range, 10^{-6} – 10^{-5} ;
- 9) the temperature dependence of the (low) work hardening rate is unusual in the anomalous region.

Scores of papers over the nearly forty years past have shown that the phenomenon occurs in many other intermetallic structures, yet not all $L1_2$ structures exhibit it. Much effort has been expended over this period to develop a model that would satisfactorily include all of the above listed features. The five papers that comprise the bulk of this

volume present our current level of understanding, which in many respects appears to be very good. In essence, all the proposed models envision the thermally activated locking of superdislocations by cross-slip from the primary plane onto another plane, leading to an APB partly or completely out of the primary plane. They differ in the way they account for secondary characteristics of the phenomenon. Before the problem can be regarded as solved, however, we must have a generic mechanism which can both apply to structures other than $L1_2$ and account for the absence of anomalous flow stress behavior in certain $L1_2$ compounds. (See especially the chapter by Caillard and Couret.)

Effects of stoichiometric deviation on flow stress. It was observed very early (Kurnakov and Zhemchuzhnyi [82]) that deviations from ideal stoichiometry resulted in an increase in the strength properties of intermetallics. Later, when measurements could be extended to high homologous temperatures (T_h) at least for model compounds, as seen in fig. 9

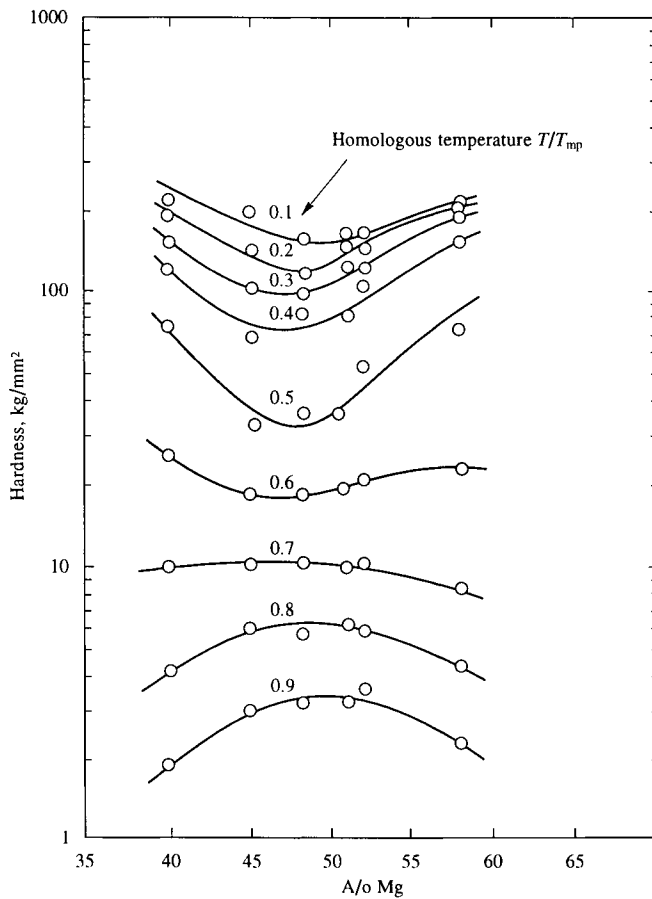


Fig. 9. Influence of defect concentration (deviation from stoichiometry) and homologous temperature on the hot hardness of single phase AgMg alloys (after Westbrook [83]).

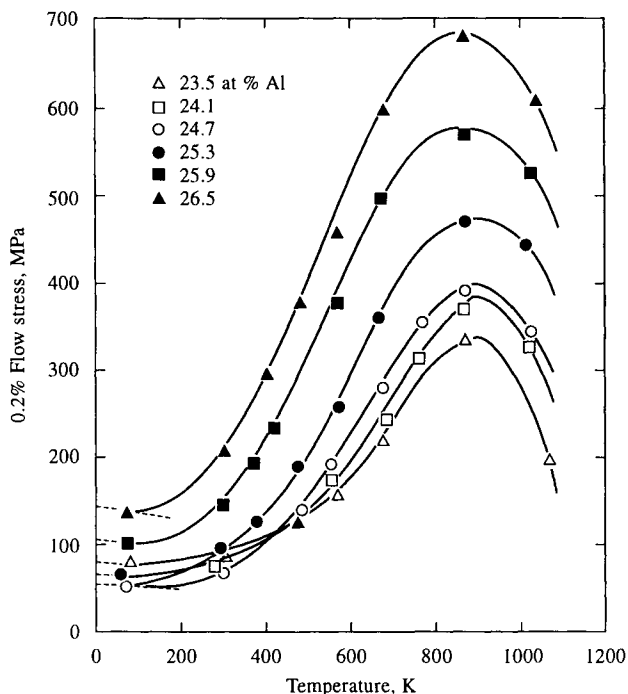


Fig. 10. Effect of Al concentration on yield strength of Ni_3Al as a function of temperature (after Noguchi et al. [84]).

from hot hardness studies on B2 AgMg by Westbrook [83], it was found that the reverse situation obtained. Thus, the same defects that impeded slip at low T_h enhanced diffusion and lowered diffusion-controlled deformation resistance at high T_h .⁵ The defect structure of off-stoichiometric AgMg is very simple: substitution of the excess species on atom sites of the other component for both sides of stoichiometry. Marked effects of stoichiometric deviation are also to be found in Ni_3Al as seen from the results of Noguchi et al. [84] in fig. 10. In this case the strength *decreases* rather than increases with departure from stoichiometry on the Ni-rich side. Whether this result occurs because of interaction of the anomalous yield phenomenon with the point defects or because of a more complex defect structure, the possibilities for which have been studied by Fleischer [85], is not yet clear. In any case, in superalloys the composition of the Ni_3Al particles in equilibrium with the nickel solid solution matrix is always Ni-rich, although its exact composition may vary with the bulk composition of the alloy as well as with temperature.

⁵Note that both species need to diffuse for dislocation climb to occur. A given type of defect arising from stoichiometric deviation will not necessarily affect the two diffusion rates equally, although both should increase with increasing defect concentration.

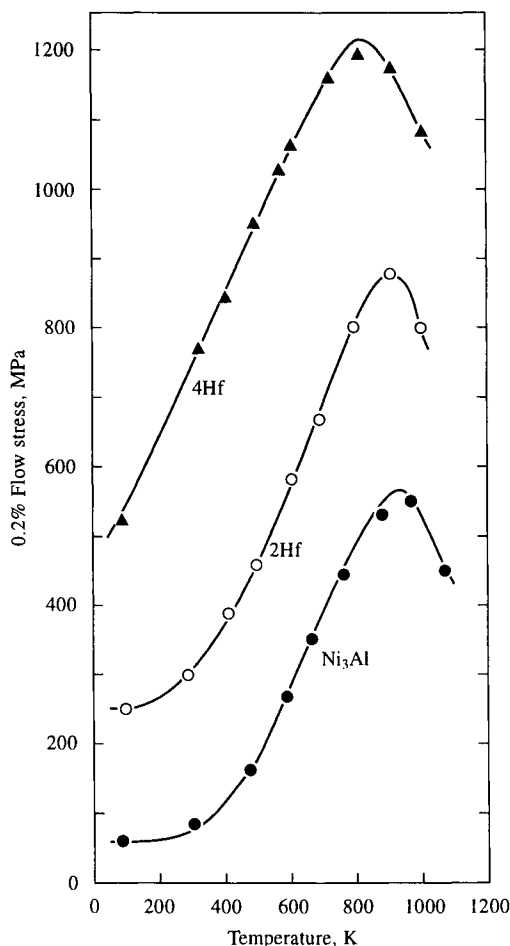


Fig. 11. Effect of a large misfit solute (Hf) on the yield strength–temperature characteristics of Ni_3Al (after Mishima et al. [86, 87]).

Anomalous solid solution hardening at high temperature. Mishima et al. [86, 87] have shown that at room temperature the solution hardening that is observed in Ni_3Al is consistent with the model that this is caused by atom size and modulus interactions with moving dislocations, just as in Ni or other metallic matrices. However, this model would predict a decrease in solid solution hardening at elevated temperatures in contrast to a persistence or even an increase that have been observed in intermetallic compounds. This anomaly obtains for both large misfit solutes such as Hf in Ni_3Al (see fig. 11)⁶ or small misfit solutes such as Fe in CoAl (see fig. 12). Whether complications of the nature of defects introduced by alloying or changes in the character of dislocations

⁶Note that while the magnitude of the solid solution hardening increases at high temperatures, the relative increase is lessened.

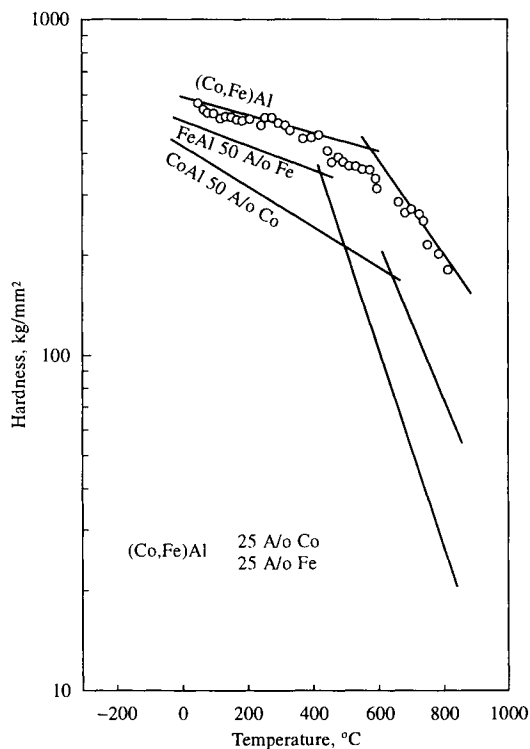


Fig. 12. Effect of a small misfit solute (Fe) on the hot hardness of CoAl (Westbrook, unpublished).

at high temperatures is responsible cannot presently be determined, as discussed by Fleischer [85]. Analogous effects are also seen in the creep resistance of ternary vs. binary stoichiometric B2 aluminides, as shown by Sauthoff [88] in fig. 13. The correlation with the effective diffusion coefficient suggests that this factor must also be taken into account, at least for long-time tests at elevated temperatures. This high temperature solid solution hardening anomaly is both something that must be understood and could well be exploited in practical materials.

Strength of ternary compounds. Many binary compounds have ternary counterparts, not simply solid solutions extending from the binary but true ternary compounds, usually possessing further degrees of order based on the same crystal structure motif as the binary. The few cases that have been examined – ternary sigma phase, $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ vs. FeCr and CoCr (Westbrook [76, 83]), $(\text{Co}, \text{Ni})_3\text{V}$ vs. Ni_3V or Co_3V (Köster and Sperner [89]), Ni_2TiAl vs. Ni_3Al (Strutt and Polvani [90]), and $\text{Nb}(\text{Ni}, \text{Al})_2$ vs. NiAl (Sauthoff [91–93]) – all show strength increases relative to the binary of as much as a factor of 3 or 4, especially at high temperatures. In the example shown in fig. 14, the ternary compound is a C14 Laves phase (hence better represented as $\text{Nb}(\text{Ni}, \text{Al})_2$) and is contrasted with binary B2 NiAl and DO_{22} Al_3Nb . Not only is this strength benefit desirable in and of itself, but diffusion rates in ternary compounds may be expected to be even lower than in

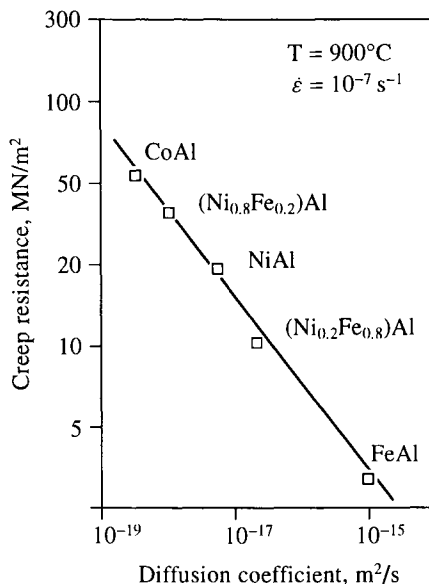


Fig. 13. Effect of solid solution hardening of Fe in NiAl and Ni in FeAl on compressive creep resistance at 900°C and correlation with the diffusion coefficient (after Sauthoff [88]).

their binary counterparts, thus improving strength in temperature regimes where diffusion control exists as well as contributing to microstructural stability.

Ductilization or embrittlement phenomena in intermetallics. Several different classes of these effects have been reviewed by Stoloff [43, 94] and Westbrook [10]: ductilization by macroalloying, ductilization by microalloying, ductilization by grain refinement, ductilization by increase in mobile dislocation density, and embrittlement by stoichiometric excess of the active metal component. Not every effect appears in every system, and dislocation-based models in this area are too poorly developed to permit useful exploitation of those effects beneficial in intermetallics or superalloys. They are not discussed in the other chapters in this volume.

4.2. On dislocations in superalloys

Peak strengthening in two-phase alloys. While good success has been obtained in modelling the strength of under-aged and over-aged alloys at low temperatures and with low to moderate volume fractions of the ordered phase (Ardell [69]), the same model does not account well for the behavior of alloys aged to peak strength, especially where the intermetallic phase is very strong relative to the matrix.

Strengthening by multi-modal particle size distributions. Empirical optimization of strength of practical superalloys by multi-stage heat treatments frequently results in bi- or