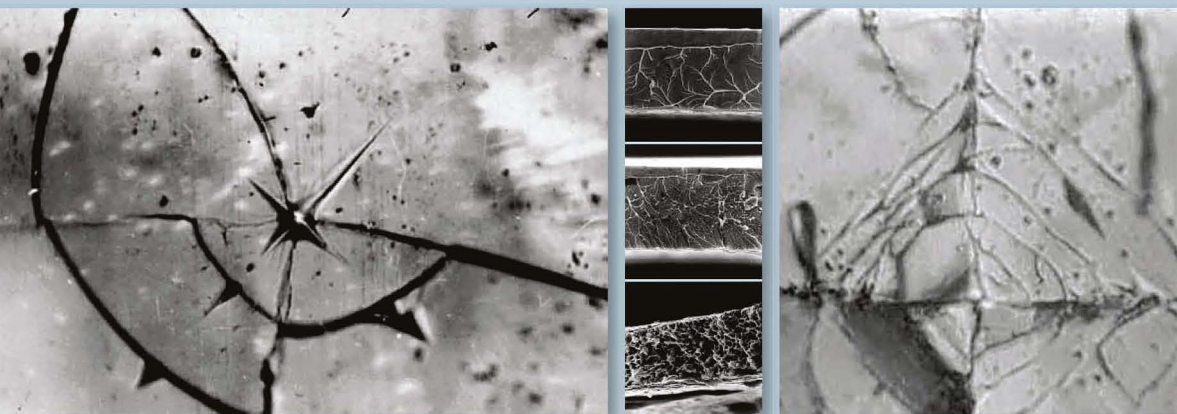




Thermal and Time Stability of Amorphous Alloys

A. M. Glezer, A. I. Potekaev, and A. O. Cheretaeva



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Foreword

The efforts of material scientists have resulted in the development of a large variety of structural states of materials characterised by unique physical–chemical and mechanical properties. However, all these materials, with a small number of exceptions, are far away from the thermodynamic equilibrium state. Therefore, it is not surprising that in the process of long-term or even short-term destabilising effects (temperature, deformation, radiation, etc) the structural–phase states of highly non-equilibrium materials transform in accordance with the general laws of thermodynamics and lose their unique properties. This circumstance greatly restricts or even completely prevents the practical application of highly non-equilibrium materials with unique properties in technology and medicine.

Undoubtedly, these materials with the non-equilibrium structure and unique physical–mechanical properties include metallic alloys produced by melt quenching at a rate exceeding 1 million degrees per second. Under the destabilising effects (especially thermal effects) the structure of these materials undergoes structural and phase transformations which greatly reduce the efficiency and often prevent application in practice. For example, the iron-based amorphous alloys characterised by unique magnetically soft properties combined with high strength, ductility and wear resistance are subject to stringent requirements to prevent changes of the working parameters by more than 10% during 100 years at a service temperature of up to 50°C, during 15–25 years at a temperature of 50–80°C, and for 10 years at temperatures up to 80–150°C. Similar requirements are also imposed on radiation resistance.

In the group of the metallic systems, undergoing structural, phase or structural–phase transformations under thermal and force loading, there are at least two groups which differ both in the nature of formation and behaviour and special features of the structure. In one group, the structural–phase state of the system remains almost unchanged over a wide loading range (these metallic systems are referred to as the materials of quasi-chemical nature). In the other

group, the structural–phase state of the system changes under small thermal and force loading and this is consequently accompanied by stress relaxation (these metallic systems are referred to as the relaxation materials). This group contains a wide range of structural–phase states of the system in the vicinity of the stability loss boundary. These states change ‘quasi-continuously’ under a relatively small change of thermal and force loading. These states are referred to as having low resistance to thermal and force loading. Thus, **the low resistance (or pre-transitional) state of the system is the stage in the vicinity of the structural–phase transformation characterised by anomalies of the structure or properties.** Naturally, the traditionally known structural defects in these specific conditions become already inseparable elements of the structure and interact with each other, and this interaction has a strong effect on the structure and properties of the condensed system. It should be stressed that the density of the structural defects (defects in the traditional sense of the word) is very high and, consequently, they cannot be regarded as isolated and must be studied already as a system of interacting defects in the conditions of the low stability state of the material. This is not a trivial task, especially taking into account the fact that an important role is beginning to be played here not only by the concentration of defects but also their symmetry, the nature of interaction, the depth at which they occur, the type and magnitude of the external effect, and many others. At the background of the state of the condensed system with low resistance to external conditions the role of the interaction of the structural defects becomes very important and sometimes controlling for the structure.

The condensed systems, undergoing phase and structural transformations, are interesting especially due to the fact that their structure in the range of the transitions has the special features characteristic of the transitional processes. It is well-known that the structural–phase transformations are one of the phenomena that are most difficult to describe.

Unfortunately, the books and articles published in recent years pay only little attention to the problem of the thermal and time stability of the structure and properties of amorphous alloys [1–7]. Reviews, concerned with similar problems in nanomaterials, appeared only recently [8–13]. The authors believe that this book is the first attempt for examining this important problem in both the fundamental and applied aspect. As the stability criterion the authors

decided to examine the behaviour of the ductility of amorphous alloys because this property is a highly sensitive characteristic of the structural changes which can take place in the amorphous state under the destabilising effects [9]. In the first chapter, the reader can become acquainted with the fundamental characteristics of amorphous alloys which are most important for understanding the structural and physical processes associated with ductility changes. The second chapter is concerned with the main relationships of structural relaxation – the processes leading to the extensive evolution of the structure and properties in the area of the amorphous state under destabilising effects. The third chapter deals with the ΔT -effect discovered by the authors. This effect is associated with the change of the structure and properties during rapid cooling of the amorphous alloys to cryogenic temperatures. Undoubtedly, the fourth chapter is most important because it contains generalised information about the phenomenon of the ductile–brittle transition (temper brittleness) which forms the basis of the approach proposed by the authors to the analysis of the thermal–time stability of the amorphous alloys. The fifth chapter deals with the development of the methods for predicting the stability of the properties, physically justified by examining the phenomenon of the ductile–brittle transition. Finally, [chapter 6](#) presents information on the attempts for the purposeful effect exerted on the structure in order to suppress or prevent the ductile–brittle transition and, consequently, increase the thermal and time stability of the amorphous state.

The authors note that this book does not deal with all the questions. Many aspects remain unclear and disputable. The authors will conclude that their task has been completed if this book will attract the attention of the scientific community to the very interesting and urgent problem of the thermal and time stability of highly non-equilibrium materials with unique properties.

In particular, this book is concerned with the fundamental and, most importantly, physical aspects of the formation, behaviour and special features of the structure and properties of the amorphous state of the condensed systems of advanced materials with low resistance to external influences.

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The main characteristics of amorphous alloys

1.1. Structure

The special features and uniqueness of the physical properties of the amorphous alloys are determined completely by the features of their structural state. From the start of extensive investigations (the middle of the 70s), special attention has been paid to the problems of investigating the structure of amorphous alloys. A number of important results have been obtained using advanced experimental structural methods. Considerable successes have been achieved in the area of computer simulation. However, the problem of the structural state of the amorphous alloys is far from final solution.

Already the first X-ray investigations of the amorphous alloys demonstrated that they do not contain translational symmetry and that their structure is similar to the structure of the liquid. Evidently, the term ‘amorphous state’, like the term ‘crystalline state’, assumes the existence of a wide spectrum of different structures, formed in dependence on the production method, chemical composition and subsequent treatment.

It should be noted that the individual models of the structure of the amorphous alloys differ in the construction algorithms (the models based on the random dense packing of the atoms, cluster and polycluster models, the models based on distorted spaces, disclination and dislocation–disclination models), the selection of the atomic interaction potential and the methods of minimisation of energy [1–3]. The models of amorphous substances are constructed using methods of simulation of the atomic systems, like the molecular dynamics method, the statistical relaxation method, the Monte Carlo

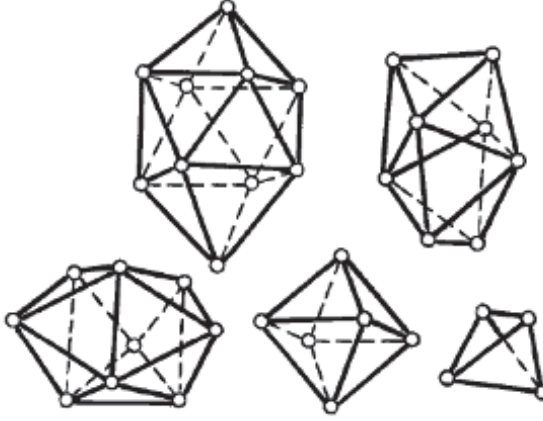


Fig. 1.1. Possible types of Benal's polyhedrons.

method, the methods used for constructing the models on the basis of the available diffraction data on the structure, etc. [2].

At the present time, the proposed series of the structural models of the amorphous alloys [1, 2] can in principle be divided into two large groups [1]: the first group of the models is based on the quasi-liquid description of the structure using the continuous network of the randomly distributed atoms; the second group of the models is based on the quasi-crystalline description of the structure using clusters or crystals, containing a high density of defects of different types.

The atomic structure of the amorphous alloys can be determined by experiments using diffraction investigation methods. The scattering of the X-rays, neutrons and electrons on the amorphous substance makes it possible to determine the general structural factor of the multi-component system $I(k)$ (Fig. 1.1), which corresponds to the sum of the partial structural factors $I_{ij}(k)$ [4]:

$$I(k) = \sum_i \sum_j W_{ij}(k) I_{ij}(k), \quad (1)$$

where

$$W_{ij}(k) = \frac{c_i c_j f_i(k) f_j(k)}{\langle f(k) \rangle^2}, \quad (2)$$

c_i and f_i are the atomic concentration and the scattering amplitude of the element i , respectively; $k = (4\pi/\lambda)\sin\theta$ is the length of the diffraction vector; $\langle f \rangle = \sum c_i f_i(k)$.

The distribution of the atoms in the amorphous alloy can be determined only by means of the atomic radial distribution function (RDF), and the division of the scattering intensity into the structural factor and the interference function, as was the case in the crystals, is not possible in this case.

The local environment can be analysed by the EXAFS method (examination of the fine structure of the X-ray absorption spectra), using synchrotron radiation [5]. The local fluctuations of the atomic density or concentration are usually analysed by the low-angle scattering method which is sensitive to the variation of the electronic density on the scale of the order of 2 nm.

Because the position of the atoms in the amorphous alloys cannot be determined unambiguously by the diffraction methods, the verification of the structural models is usually carried out by the independent measurement of a number of physical properties (density, heat capacity) and also by investigating the structure by spectroscopic (NMR, NGR) and microscopic (high-resolution electron microscopy, atomic force microscopy) methods.

Most detailed experiments have been carried out into the group of amorphous alloys of the transition metal (TM)–metalloid (M) type whose composition is close to $\text{TM}_{80}\text{M}_{20}$. For the multi-component systems, which include in fact the most frequently investigated amorphous alloys, the total set of the structural characteristics requires the determination of the partial paired correlation functions. They can be determined most accurately by EXAFS spectroscopy [6].

Although the ensemble of the randomly oriented microcrystals does not have the translational symmetry at large distances, it has been shown [7] that their radial distribution function (RDF) cannot be described by the microcrystalline model, even if the crystals are very small or deformed. In principle, the fact that the microcrystalline model cannot be used reflects the fundamental differences in the nature of the short-range order of the amorphous and crystalline phases. At the same time, there is a number experimental studies in which it is shown that the amorphous state of the majority of amorphous alloys, produced by melt quenching, is of the microcrystalline origin. All these experiments have been carried out by transmission electron microscopy in the regime of formation of the phase contrast. In this case, under specific conditions it is possible to visualise the individual crystallographic planes and even individual atoms.

To describe the structure of the single-component amorphous systems, initial investigations were carried out using the Bernal model [8] which was originally proposed for the description of the structure of simple liquids. The model is based on the random dense packing of rigid spheres ((RDPRS). An important role in the identification of the structure in the framework of the quasi-liquid description is played by the computer simulation methods [1, 2, 9]. However, the methods of successive attachment and collective rearrangement, used in the simulation, did not make it possible to obtain the structure of the randomly close-packed rigid spheres of the same density as that in the experiments. In addition to this, another important problem was the problem of the boundary conditions of the simulated ensemble. In [10] it is proposed to investigate the relaxation of the structure based on the Bernal model assuming the effect of the paired atomic Lennard–Jones potentials which reproduce the radial distribution function for the soft and not for rigid spheres. The model of the random close-packed soft spheres (RCPSS) leads to the considerable improvement of the correspondence of theory and experiment both from the viewpoint of the nature of splitting of the second peak of the radial distribution function and the viewpoint of the density of the amorphous state obtained in the model. The structure in the description by the RDPRS and RCPSS models can be characterised using the Bernal or Voronoi polyhedrons (Figs. 1.1 and 1.2). The Bernal polyhedrons can be used to determine the shape of cavities or potential areas of penetration in the amorphous matrix and contain the atomics spheres at each tip.

The first attempts to solve the simulation problem of the two-component amorphous alloys were made in [11] where was assumed that an alloy of the metal–metalloid type can be simulated using the RCPRS. The ‘skeleton’ is represented by the metal atoms, and the metalloid atoms occupy the largest cavities. As expected, the number of large-volume cavities in the RCPRS model is not sufficient for distributing 20 at.% of the atoms–metalloids. Nevertheless, the

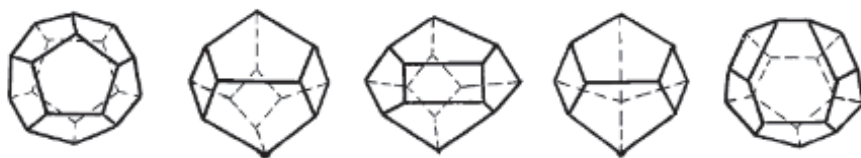


Fig. 1.2. Possible types of Voronoi polyhedrons.

assumption made in [11] resulted in the important qualitative aspect of understanding the structure of amorphous alloys: the coordination cell of the atom of the metalloid consists only of the atoms of the metal and is identical with that observed in the crystalline phases, formed in alloys with a high concentration of the metalloid atoms. For example, in the Ni_3P crystalline compound each phosphorus atom is surrounded by nine nickel atoms, forming a trigonal prism. The identical coordination was observed by experiments in the amorphous alloys of the same composition [12].

Subsequent attempts to construct the models of the structure of the binary amorphous alloys can be divided into two main directions:

1. Computer construction within the framework of the model of the RCPRS of the structure which would then be subjected to relaxation using the appropriate potentials of the paired atomic interactions V_{AA} , V_{BB} and V_{AB} . The final structure should describe accurately the main special features of the general radial distribution function [13]. Although the algorithm of construction of this model for the case of the metal–metalloid alloys assumes the minimisation of the number of the nearest neighbours of the metalloid–metalloid type, the resultant number of these bonds greatly differs from zero.

2. The construction of ‘stereochemical’ models, proposed by Gaskell [14]. The clusters, consisting of the atom-metalloid and of the metal atoms surrounding it, also form together the coordination cell (for example, in the form of a trigonal prism) (Fig. 1.3). The binary alloys of different composition are regarded as a simple mixture of close-packed areas of the pure metal and areas with the structure of the dense packing of the trigonal prisms in the vicinity

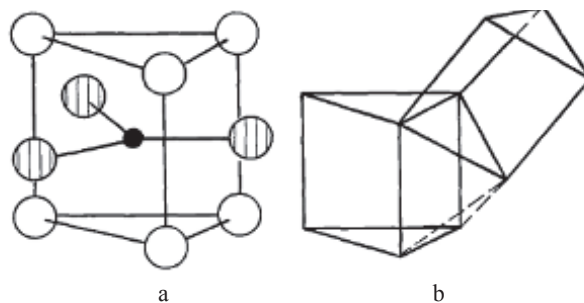


Fig. 1.3. Trigonal–prismatic element (a) used in the initial configuration of the model by attachment of other such elements (b). The smallest black circle is the atom of the metalloid, open circles are the metal atoms [44]; crosshatched circles are the atoms of the metal situated in the second coordination sphere.

of the atoms–metalloids [15]. The stereochemical model has been studied in the greatest detail in [7, 16] where attention was given gradually to the mechanism and dynamics of the variation of the structure in transition from the liquid to solid amorphous state. Analysis of the suitability of the stereochemical model shows that the model describes accurately the structure of the amorphous alloys of the TM–M type at high concentrations of the metalloid [17]. In all stereochemical models, the knowingly non-periodic packing of the atoms indicates the absence of the periodic potential of the lattice so that the existence in the structure of the effects of the type of vacancies and dislocations is associated with problems, but the concept of inter-cluster boundaries is introduced.

Although the existence of a very strong chemical short-range order in the amorphous alloys of the metal–metalloid has been convincingly confirmed, it is quite difficult to determine its quantitative characteristics. The problem of the topological order in the amorphous alloys is far more complicated than the problem of the compositional (chemical) ordering, because the selection of the ordering parameter is not entirely accurate.

In accordance with the concept proposed by Egami [18], in addition to the topological order it is also important to consider the short-range order of the distortions, associated with the existence in the amorphous matrix of the local geometrical distortions which are in fact structural defects. Together with the topological short-range order, the short-range order of the distortions is regarded as a geometrical short-range order. The topological order in the amorphous alloys is exclusively polytetrahedral. This order is not comparable with the short-range order spatially de-concentrated in the three measurements and existing in the crystals. Nevertheless, it has been shown [19] that in the distorted three-dimensional space (i.e., on the surface of the four-dimensional polytype) the similar perfect polytetrahedral packing becomes possible. To show this structure in the three-dimensional space, it is necessary to introduce defects. These defects are represented, for example, by a number of disclination lines [20]. It has been shown that the ordered series of the dislocation lines describes the Frank–Casper polytetrahedral phase, and the disordered series – the structure of the amorphous state. The problem examined here is very close to the problem of the description of the structure of quasi-crystals experimentally detected in the Al–Mn alloys produced by melt quenching [21]. In fact, the

submicroscopic quasicrystals can be used as structural elements when describing the amorphous state.

As already mentioned, the introduction of the disclination considerations is extremely useful when describing the main special features of the structure of the amorphous alloys. In a general case, the defects (linear sources of internal stresses) are referred to as the Volterra dislocations who examined for the first time the methods of producing and describing the stress state for a doubly-connected solid within the framework of the continual theory of elasticity. There are six types of such defects [22].

The concept of the defective lattices assumes the possibility of reaching the amorphous state if the density of the effects is higher than some critical value. It is well-known that to verify the characteristic of any model it is necessary to compare the model with a large number of experimentally obtained data for the structure and, primarily, with the radial distribution functions (RDF) (or paired correlation functions PCF), and also the packing density coefficient ξ . For this purpose, computer simulation of amorphous clusters was carried out in [23] and the PCF and ξ are the functions of the disclination density (or the average distance $\bar{L}$ between them). The initial structures formed by introducing point wedge-shaped disclinations with the Frank vector $\bar{\Omega} = \pm(\pi/3)\bar{i}_3$ to the planar triangular lattice (the positive and negative wedge-shaped disclinations corresponded to 5- and 7-term environments of the central atom).

The disclination theory shows [22, 24] that the dislocations cause Cartan torsion in the crystal without changing its metrics. Therefore, the crystal is investigated in the Euclidean space, and the dislocations are the linear defects of the structure. If the crystal contains disclinations, the latter greatly change its metrics, i.e., the crystal should be regarded as a crystal in the space characterised by the Rieman–Christoffel curvature as a function of the tensor of the disclination density, with the disclinations regarded as the linear defects of its structure. A detailed construction of the models of the structure of the amorphous alloys from the polytypes in the distorted space is used quite widely, mostly for calculating the electronic properties. For example, in [25] it was shown that the dense-packed structures can be produced by imaging the polytype figures from the distorted space to the Euclidean space. Naturally, this imaging is obtained by adding a network of disclination lines transforming the space curvature to zero.

1.2. Structural defects

To understand the role of the defect in a specific process, it is necessary to consider the state of the structure free from defects. Comparison of the state with defects and without them can be carried out in the terms of the topological properties or stress fields. The majority of the defects, typical of crystals, lose their specific features in the amorphous state. Nevertheless, the results of large numbers of experiments carried out to investigate the structure-sensitive properties of the amorphous alloys show that the structural defects can also exist in the amorphous alloys. The deviations in the structure of the amorphous bodies from the low-energy equilibrium state can be described on the basis of the increase of the density of these defects. Taking these considerations into account, the defects cannot be represented by some small disordered region in the amorphous matrix, although small disordered regions in the crystal can be regarded as clusters of elementary defects.

Several attempts have been made to provide a generalised definition of the structural defects in the amorphous solids [26]. On the one hand, a model of the ideal amorphous structure was constructed and defects were then introduced into the model on the basis of the purely geometrical considerations by analogy with what is done in the crystal [27]. This was followed by measuring the resultant displacement which was usually very large. A similar definition of the defects, using the considerations of local deformation, proved to be acceptable only for covalent amorphous solids [27].

Some investigators divide defects in the amorphous alloys into internal and external. The internal defects are typical of the material even after extensive relaxation, and the external defects annihilate during relaxation changes in the structure. Since it is difficult to obtain by experiments only detailed information on different types of defects and their distribution, this is achieved using widely the computer simulation methods which provide data on the defects and their evolution during different external effects [28]. In addition to this, it is evident that these calculations can also help in understanding the amorphous state.

The defects in the amorphous alloys can be divided into point, microscopic elongated and macroscopic. The main point defects, existing in the amorphous matrix, are [27]: broken bonds; irregular bonds; pairs with changed valency; the atoms with a small stress field