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著者	Iwasaki Hiroshi, Wang Wen-Kui
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Structural Transitions of Amorphous Alloys
under High Pressure*

Hiroshi Iwasaki and Wen-Kui Wang**

The Research Institute for Iron, Steel and Other Metals

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Synopsis

An attempt is made in this paper to cover the results of the recent experimental investigations on the effects of high pressure on the crystallization of amorphous Fe-17at.% B, Nb-19at.% Si and Pd-20at.% Si alloys. Pressure is shown to raise appreciably the onset temperature of crystallization and change the structural sequence of crystalline phases forming in the alloys. The phases preferentially forming are the DO_e -type Fe_3B , Al5-type Nb_3Si and bct Si-rich phase. The structural characteristics of these transformations are discussed in the light of the knowledge of atomic structure of the amorphous alloys.

I. Introduction

Amorphous solids can be prepared either by rapidly quenching from the liquid state or condensing from the gaseous state. They remain unchanged unless temperature is raised so that atoms get thermal energy to activate their movement. When the crystallization sets in, it is always accompanied by a decrease in volume and the periodic arrangements of atoms replace the random arrangements. This fact suggests that not only temperature but also pressure can be a factor which controls the initiation of the crystallization of amorphous solids. Pressure-induced crystallization has actually been observed for arsenic¹⁾, germanium²⁾ and other elements. Since the environment around an atom in the amorphous state is not very different from that in the crystalline state, pressure-induced densification of the materials provides nuclei for crystallization and they grow continuously with minor rearrangement of atoms. Although an atomistic mechanism of the

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** On leave from Institute of Physics, Chinese Academy of Sciences, Beijing, China.

crystallization has not yet been clarified, it is certain that it is similar to that upon temperature-induced crystallization.

Recent development in the method of rapidly cooling has made it possible to obtain many kinds of alloys in an amorphous state. The crystallization behaviors of the amorphous alloys were studied in detail by a number of researchers. Since the formation of the amorphous state is invariably found in the eutectic alloys, general characteristics of the crystallization upon heating are the decomposition of a uniform amorphous matrix into crystalline phases having different compositions, as illustrated in Fig. 1. The process of this transformation, however, is not simple, but a stable state consisting of multiphases is reached through a sequence of progressively metastable states³⁾. Masumoto and his collaborators⁴⁾ studied the transformation in the systems consisting of metal and metalloid elements and proposed a time-temperature-transformation diagram which can well express the transformation characteristics observed in them.

What effects can we expect when the amorphous alloys are subjected to high pressure? Since the density of the amorphous state is generally lower than that of the crystalline state, pressure may induce crystallization just as it does in the amorphous elements. On the other hand, the crystallization of the amorphous alloys is a diffusion-controlled process and a decrease in volume by the compression may result in lowering of the mobility of atoms and hence suppression of the transformation. Unlike the case with the elements, no systematic investigation has hitherto been made on the effects of high pressure on the crystallization of the amorphous alloys. The present paper describes a review of our recent experimental investigations of the effects on amorphous Fe-13% P-7% C*, Fe-17% B, Nb-19% Si and Pd-20% Si alloys.

II. Compression of Amorphous Alloys at Ambient Temperature

Bridgman-anvil-type apparatus which can easily produce the pressure of 100 kbar was used in the compression experiments. Several pieces of the amorphous alloys in the form of thin strip are squeezed between a couple of tungsten carbide anvils with boron nitride serving as the pressure transmitting medium and pyrophyllite as the gasket material. X-ray diffraction examination of the alloy samples, which were kept at the pressure for many hours and quenched to the

* All percentages refer to atomic percent throughout the paper.

ambient pressure, has shown that they give no indication of crystallization and only diffuse haloes at the same positions in the diffraction pattern as those in the pattern of the uncompressed samples.

In order to see the structure of the amorphous alloys under high pressure, in situ X-ray diffraction examination by means of a diamond anvil-type apparatus was carried out. Figure 2(a) shows an X-ray diffraction pattern of Fe-13% P-7% C alloy subjected to the very low pressure. Owing to the limitation on the X-ray diffraction geometry inherent to this type of apparatus, the observable range of the diffraction pattern is not wide and only a main halo is seen along with the Laue spots from the diamond crystals. When the pressure is increased to about 200 kbar, the diffraction pattern shown in Fig. 2(b) is obtained, which is much similar to that in Fig. 2(a) except for a shift in the position of the main halo. The change in the 2θ -value suggests a decrease in an average interatomic distance by 4 %. An analysis of the intensity profile of the halo was not made, but it can be said that the amorphous alloy retains its structure almost unchanged even under the severest compression. Similar observation has been made for other amorphous alloys.

The high stability of the amorphous structure against the compression makes a striking contrast to the behavior of the amorphous elements. The structure model recently proposed for the amorphous alloys consisting of metal and metalloid elements tells that there exists short-range order in atomic configuration which is similar to that found in the crystalline state. The results of the present compression experiments show that it can not provide stable nuclei for continuous crystallization as long as the alloys are kept at the ambient temperature.

III. Crystallization of an Amorphous Fe-17% B Alloy at the Pressure of 100 kbar

The application of pressure to the "cool" amorphous alloys does not induce transformation and it is necessary to give the atoms thermal energy high enough to rearrange themselves to conform to the state under compression. An amorphous Fe-17% B alloy was compressed and simultaneously heated in the sample cell of the Bridgman anvils. Thin tantalum foils placed in contact with the sample cell served as the internal heater, through which A.C. current was conducted. After being kept at the increased pressure and temperature for definite periods of time, firstly temperature and subsequently pressure were decreased rapidly. X-ray diffraction examination was made on the alloy

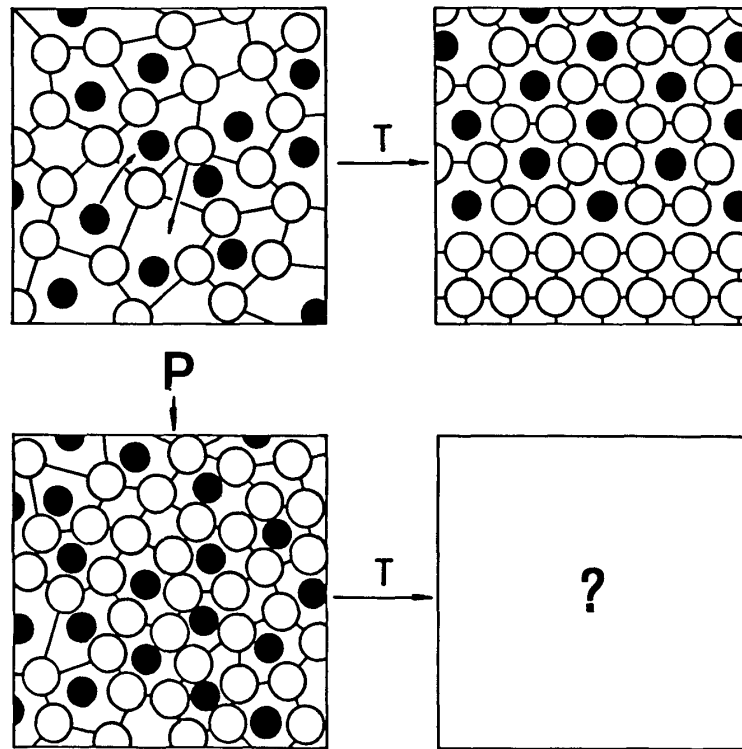


Fig. 1. Schematic representation of the atomic arrangement in an amorphous alloy and its change upon heating and compression.

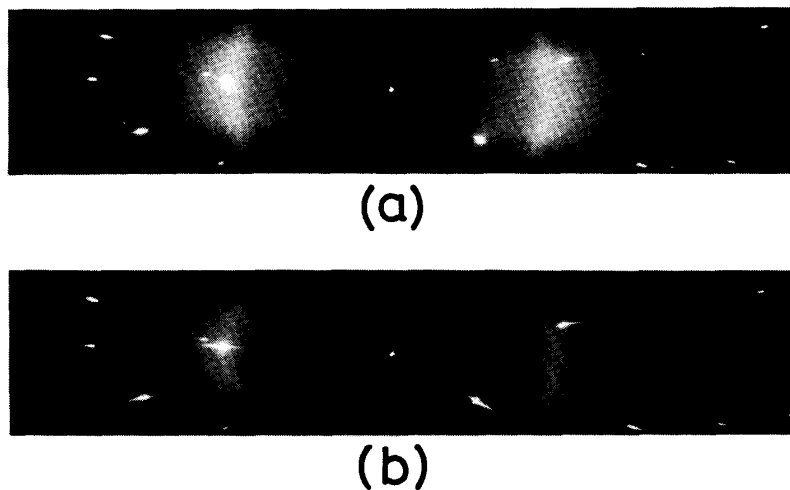


Fig. 2. X-ray diffraction pattern of amorphous Fe-13% P-7% C alloy in the diamond-anvil cell and subjected to (a) 1 kbar and (b) 200 kbar. Filtered $\text{MoK}\alpha$ radiation.

samples removed out of the gasket using a conventional diffraction equipment. Annealing at 100 kbar and temperatures below 400°C does not give rise to any appreciable change in the diffraction pattern of the alloy. It is not until the temperature is raised to 500°C that the diffraction lines indicative of the crystallization are detected. Or, annealing at 460°C for long period of time gives the same result. This is in contrast to the behaviors of the amorphous alloy at the ambient pressure and annealing at the temperature as low as 350°C brings the alloy to become crystalline state.

Figure 3 shows an X-ray diffraction pattern of Fe-17% B alloy annealed at 100 kbar and 460°C for 21 hours. All of the diffraction lines are identified as the tetragonal DO_e -type Fe_3B . The lattice parameters are $a=8.64 \text{ \AA}$ and $c=4.28 \text{ \AA}$. Fe_3B is a metastable phase and forms in the amorphous alloy on annealing at the ambient pressure after the bcc Fe has been precipitated. High-pressure annealing experiments have been done at different temperatures for different periods of time. The crystallization characteristics of the Fe-17% B alloy can be summarized as follows: pressure appreciably decelerates the crystallization reaction and raises the crystallization temperature at an approximate rate of 1 deg/kbar. Sequence of the structures forming from the matrix is changed from amorphous - bcc Fe - bcc Fe + Fe_3B to amorphous - Fe_3B - Fe_3B + bcc Fe. Besides, the lattice parameter of bcc Fe forming at 100 kbar is a little larger than that of bcc Fe forming at 1 bar, indicating an increase in an amount of boron dissolved in the bcc lattice. The preferential formation of Fe_3B under high pressure will be discussed in a later section.

IV. Crystallization of an Amorphous Nb-19% Si Alloy at the Pressure of 100 kbar

When the amorphous Nb-19% Si alloy is subjected to the pressure of 100 kbar, the crystallization has been detected at 700°C, higher by 100 deg than the temperature found at the ambient pressure. The crystalline phase first forming is cubic Al_5-Nb_3Si , which is the same as what is observed at the lower pressure. Whereas the cubic phase in uncompressed alloy is immediately transformed into the stable, tetragonal Nb_3Si and bcc Nb is precipitated from the remaining amorphous matrix on continued annealing, the Al_5-Nb_3Si in the compressed alloy is stable. It must be stressed that the quantity of this phase is large.

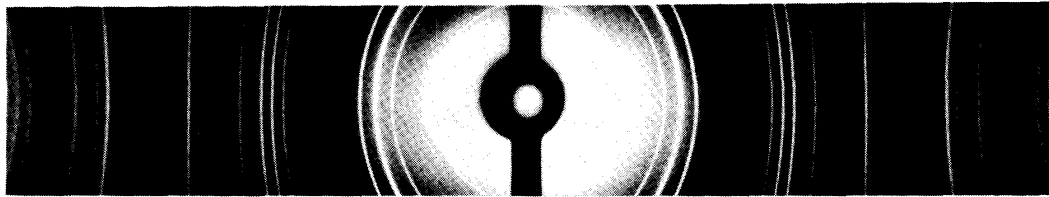
Figure 4(a) shows an X-ray diffraction pattern of Nb-19% Si alloy annealed at 100 kbar and 700°C for 96 hours. The diffraction lines



Fig. 3. X-ray diffraction pattern of Fe-17% B alloy annealed at 100 kbar and 460°C for 21 hours and quenched to the ambient conditions, showing the formation of the DO_e -type Fe_3B . Filtered $FeK\alpha$ radiation.



(a)



(b)

Fig. 4. X-ray diffraction pattern of Nb-19% Si alloy annealed at (a) 100 kbar and 700°C for 96 hours and (b) 100 kbar and 750°C for 57 hours. In (a), the diffraction lines are from both $Al5-Nb_3Si$ and bcc-Nb and in (b) they are from $Al5-Nb_3Si$ only. Filtered $CuK\alpha$ radiation.

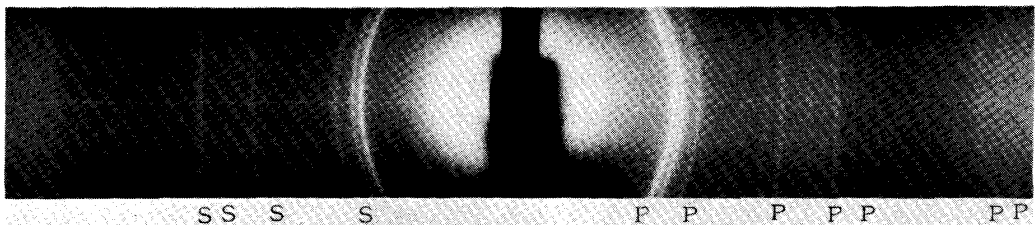


Fig. 5. X-ray diffraction pattern of Pd-20% Si alloy annealed at 100 kbar and 490°C for 70 hours, showing the formation of bct Si-rich phase and fcc Pd. Filtered $CuK\alpha$ radiation.

with stronger intensities are those from the Al5 structure with $a = 5.15 \text{ \AA}$. There are other diffraction lines which are from a small amount of the coexisting bcc phase with $a = 3.37 \text{ \AA}$. This value is considerably larger than that of pure Nb, indicating that the bcc phase is a solid solution of Nb and Si.

High pressure annealing at the temperatures ranging from 710°C to 800°C alters the crystallization behavior and the alloy now contains a single-phased Al5 structure. An X-ray diffraction pattern taken from this state of the alloy is shown in Fig. 4(b). The pattern exhibits sharp diffraction lines characteristic of the good crystallinity. The reflections which are sensitive to the degree of atomic order are seen clearly. This Al5 phase does not decompose even if annealed at the ambient pressure.

The high pressure effects on the Nb-19% Si alloy can be summarized as follows: pressure appreciably shifts the onset temperature of the crystallization, suppresses the decomposition of the amorphous matrix into multi-phases and converts the alloy into the cubic Al5 phase with increased stability.

V. Crystallization of an Amorphous Pd-20% Si Alloy at the Pressure of 100 kbar

High pressure effects similar to those found in the Fe-B and Nb-Si alloys have been observed for the amorphous Pd-20% Si alloy. Crystallization temperature is appreciably raised. High pressure annealing at 280°C produces the fcc structure with $a = 3.920 \text{ \AA}$, which is Pd dissolving some amount of Si. At 390°C the amorphous alloy decomposes into a mixture of the pure Pd and Si-rich phase, as shown in Fig. 5. The latter has a simple body-centered tetragonal structure with two atoms in the unit cell of $a = 3.143 \text{ \AA}$ and $c = 2.898 \text{ \AA}$. This is a new structure found on the high pressure annealing. The MS-II phase having a complex ordered structure and forming in the amorphous matrix at the ambient pressure⁵⁾ does not form in the compressed alloy annealed at the temperatures below 400°C .

VI. Characteristics of the Structural Transitions in Amorphous Alloys under High Pressure

This section describes an interpretation of the high pressure effects on the crystallization of the amorphous alloys.

The fact that not only compression but also heating are required to induce structural changes in the amorphous alloys suggests that the

crystallization is still a diffusion-controlled process even in the compressed alloys. Pressure, however, can have a significant influence on the structure of the crystalline phases forming in the amorphous matrix. Under the constrained mobility, the best way for the atoms to yield the compression is to rearrange themselves making particular local atomic configurations to be the nuclei for the crystallization. If the local configuration is identical or nearly identical to that found in the crystalline phase with higher packing density, pressure can promote the growth of the nuclei. Thermal activation assists the rearrangement in this process and depletion of the particular component of atoms may take place in the remaining amorphous matrix. If the composition of that crystalline phase is not very different from that of the matrix or it has an allowance for the non-stoichiometry, the crystallization proceeds continuously without diffusion of atoms over long distance.

Polk⁶⁾ showed that the structure of the amorphous alloys consisting of metal and metalloid elements can well be described as a dense-random packing (DRP) of metal atoms with metalloid atoms occupying the interstitial holes in the network of DRP. Gaskell⁷⁾ suggested that the holes most appropriate are the center of the trigonal prism capped with three half-octahedra and a metalloid atom has nine metal atoms as its nearest neighbors. It is this trigonal prism that is found in the crystal structure of Fe_3B . As shown in Fig. 6, every boron atom is surrounded by nine iron atoms. That circumstance leads to the preferential formation of Fe_3B in the transformation of the Fe-17% B alloy.

Although structure analysis has not yet been performed for the amorphous Nb-Si alloys, the results obtained for the isoelectronic Nb-Ge alloys⁸⁾ strongly suggests that every silicon atom is located in the center of the expanded octahedron which is found in the Al5-type structure. Besides, simple geometrical consideration shows that the cubic Al5-type structure is denser than the stable tetragonal structure. Therefore, the preferential formation of Al5-Nb₃Si in the compressed amorphous alloy is explained on the basis of the same structural principle.

The situation in the case of the amorphous Pd-20% Si alloy is somewhat different. According to Gaskell⁷⁾, the local atomic configuration in this alloy has a resemblance to that in the DO_{11} -type Pd_3Si . But the pressure of 100 kbar can not promote the formation of this compound. Instead, the bct structure containing much Si is formed. It may be noted that this is isostructural to the high-pressure modification of Sn, the element belonging to the same group in the Peri-

odic Table as Si.

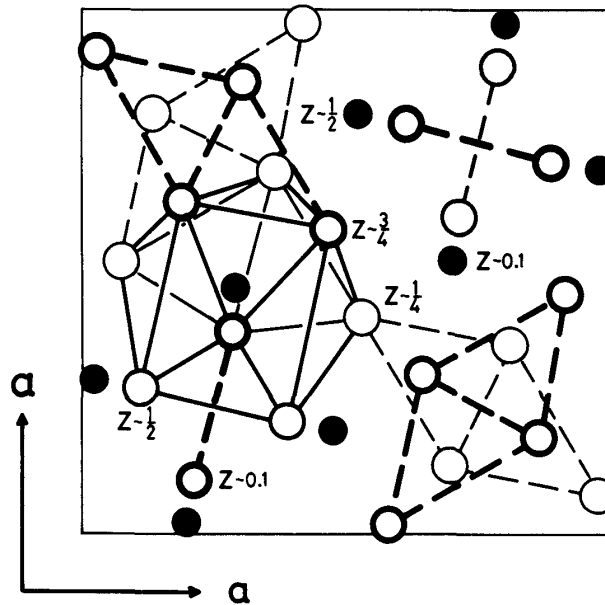


Fig. 6. Structure of the DO_e -type Fe_3B projected onto the (001) plane. Every boron atom (small full circles) occupies the center of the trigonal prism capped with three half-octahedra consisting of iron atoms (large open circles).

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