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Effect of high pressure on the crystallization of an amorphous $Pd_{80}Si_{20}$ alloy

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Amorphous $Pd_{80}Si_{20}$ alloy was annealed at temperatures ranging from 200 to 400° C while being subjected to a pressure of 100 kbar. Structural changes taking place in the alloy during the annealing were investigated by X-ray diffraction after each pressurization experiment. Pressure has been shown not to enhance, but to retard the crystallization of the amorphous alloy on annealing. Crystalline phases which form under high pressure have, in contrast to those forming under atmospheric pressure, simpler structures; i.e. the phase appearing initially has a face-centred cubic structure and the other, appearing subsequently and having a higher silicon content, has a body-centered tetragonal structure.

1. Introduction

Crystallization of amorphous alloys prepared by a splat-quenching technique from the liquid state has been studied in a number of systems. On annealing, most of the amorphous alloys change to a stable state through a sequence of progressively metastable states. The thermal instability and crystallization characteristics of the amorphous $Pd_{80}Si_{20}$ alloy were studied in detail by one of the present authors (TM) and a time–temperature–transformation (T–T–T) diagram was established [1, 2], as shown in Fig. 1. In this alloy the crystallization proceeds first by the appearance of small crystallites having a face-centred cubic (fcc) structure dispersed within the amorphous matrix on annealing at temperatures above 250° C. This metastable state is designated as MS-I. On further annealing another metastable state, designated as MS-II and having a complex superstructure, forms throughout the entire matrix. Prolonged annealing finally produces the stable phases, consisting of a metallic palladium and an intermetallic compound, Pd_3Si. Below 250° C, annealing gradually changes the amorphous structure into a crystalline phase having an fcc structure, which is considered as a supersaturated metastable solid solution. This state, designated as SS, remains stable over a long period of annealing.

An amorphous state has in general a lower density than a crystalline state. The crystallization rate of amorphous alloys is hence expected to be enhanced if they are subjected to high pressure. On the other hand, a decrease in volume available for atoms results in a lowering of their mobility and hence some of the transformations which might take place will be suppressed. It is thus of

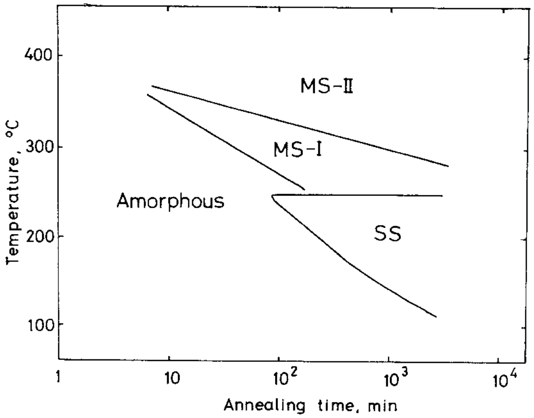

Figure 1 Time–temperature–transformation diagram of amorphous $Pd_{80}Si_{20}$ alloy on annealing.

interest to investigate how pressure affects the crystallization characteristics of amorphous alloys.

The pressure effects on oxide glasses have been extensively studied and many anomalous and interesting results have been obtained [3]. However, only a few studies have been made on metallic glasses. Emmens *et al.* [4] reported briefly the results of an investigation of the effect of pressure on $Pd_{75}Ag_5Si_{20}$ alloy. By means of electrical resistance measurement on the alloy heated continuously, the "crystallization temperature" was shown to be shifted towards higher temperatures. However, no description was made of the crystallization characteristics of the alloy. Masumoto and Kimura [5] studied the effect of uniaxial stress, of the order of 40 kg mm^{-2}, on the $Pd_{80}Si_{20}$ alloy and found that the transformation is accelerated on annealing at temperatures below 250° C. Since uniaxial stress is different in nature from pressure, it is uncertain whether the same effect can be expected when pressure is applied.

In the present work the effect of high pressure, of the order of 100 kbar, or 10^3 kg mm^{-2}, on the crystallization of amorphous $Pd_{80}Si_{20}$ alloy has been studied with a special emphasis on the structural characteristics, and some remarkable effects have been found in the crystallization behaviour.

2. Experimental

The amorphous alloy samples were prepared by rapidly cooling from the liquid state using a centrifugal mill device [6]. The alloy was in a form of thin strip, 0.04 mm in thickness and 0.5 mm in width.

The high pressure apparatus used is of the Bridgman-anvil type. The anvil has a truncated face of 20 mm in diameter, and a disc-shaped gasket, made of pyrophyllite, is squeezed between a couple of the anvil faces. A hole 5 mm in diameter is drilled in the centre of the pyrophyllite disc, into which the alloy sample and heater are loaded. The details of the sample and heater assembly were published elsewhere [7]. Several pieces of the alloy strip cut in a length of 3 mm were embedded in boron nitride powder in the hole. An alumel–chromel thermocouple was used to measure the temperature of the sample being subjected to pressure.

High pressure was generated by pressing the anvils by means of hydraulic rams. The pressure at the sample position was determined by using standard calibration procedures utilizing known phase transitions of bismuth (25.5 and 77 kbar) and tin (100 kbar). With this type of apparatus the pressure generated was not purely hydrostatic. Our experience [7] showed that the effect of shear is minimized when materials such as boron nitride are used as a pressure-transmitting medium.

In the present experiment, the pressure was first raised to a predetermined value and the temperature was gradually raised to the desired value. The temperature was then held constant for some hours and finally quenched. The annealing temperature was in the range from 200 to 400° C. After the temperature had dropped to ambient, the pressure was slowly released and the sample was removed for analysis.

All quenched samples were characterized by using the X-ray diffraction camera technique, using filtered CuKα radiation. Since the crystalline phases formed in the $Pd_{80}Si_{20}$ alloy under high pressure were small-grained, it was difficult to determine accurate values of their lattice parameters from reflections with higher indices. Instead, an internal standard method, using high-purity silicon powder coated on the sample surface as a calibration material, was adopted in the present analysis of the crystal structure.

3. Results

3.1. Compression of the amorphous alloy at room temperature

Using the high pressure apparatus described in the previous section, the amorphous alloy was first subjected to compression at room temperature. The maximum pressure 100 kbar was applied. After maintaining the pressure for 2900 min, X-ray diffraction examination was carried out for the alloy samples removed from the gasket. The X-ray diffraction pattern showed only diffuse haloes, suggesting that no appreciable crystallization took place and the alloy was still in the amorphous state.

3.2. High-pressure annealing in the SS region

The alloy was annealed at 200° C for different periods of time while being subjected to the pressure of 100 kbar. Fig. 2a shows the X-ray diffraction pattern of the alloy annealed for 2000 min. To clarify the effect of pressure the diffraction pattern of the alloy annealed at 1 bar and 200° C for approximately the same period is shown in Fig. 2b. One can see that no appreciable

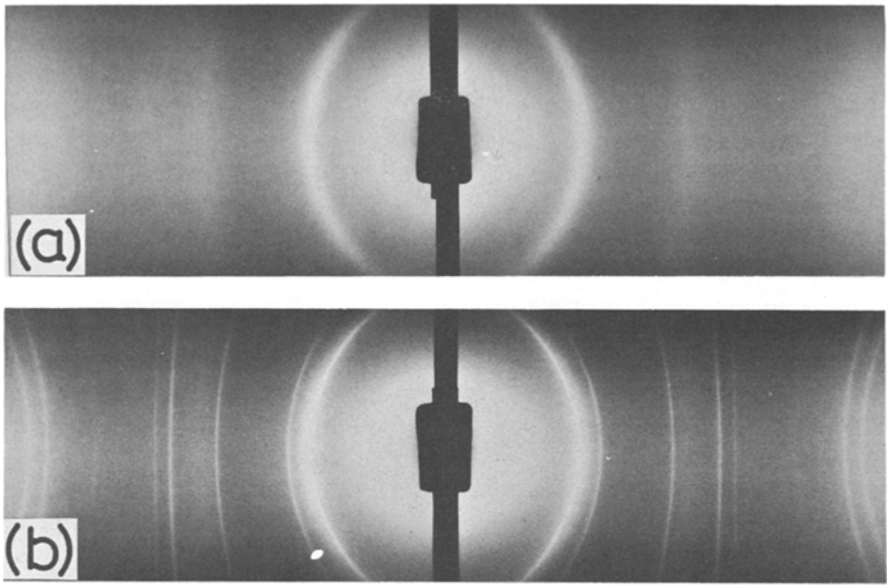

Figure 2 X-ray diffraction pattern of $Pd_{80}Si_{20}$ alloy annealed (a) at 100 kbar and 200° C for 2000 min, and (b) at 1 bar and 200° C for 1600 min. Filtered CuKα radiation.

crystallization has proceeded in the pressurized alloy even at elevated temperature, while the transformation into an f c c crystalline phase, the SS state, has already occurred in the alloy annealed normally. The degree of crystallization in this alloy, however, is not high, as is inferred from the weakness and broadening of reflection lines, and diffuse haloes arising from the remaining amorphous phase are observed superimposed on the reflection lines. High-pressure annealing at 200° C for a longer period, 11 000 min, did not induce any crystallization.

3.3. High-pressure annealing in the MS-I region

High-pressure annealing was carried out at a still higher temperature, 300° C, for 600 min. Fig 3a shows the diffraction pattern of the alloy thus

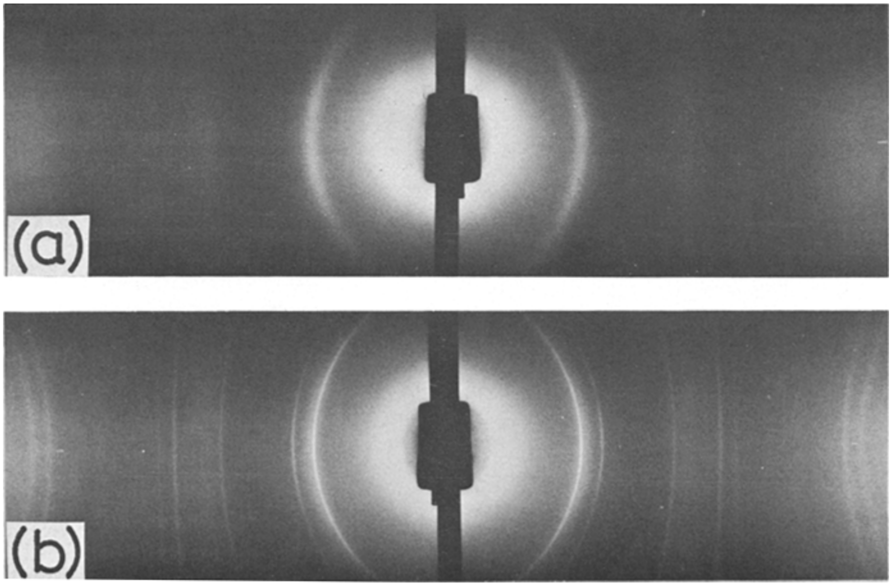

Figure 3 X-ray diffraction pattern of $Pd_{80}Si_{20}$ alloy annealed (a) at 100 kbar and 300° C for 600 min, and (b) at 1 bar and 300° C for 600 min.

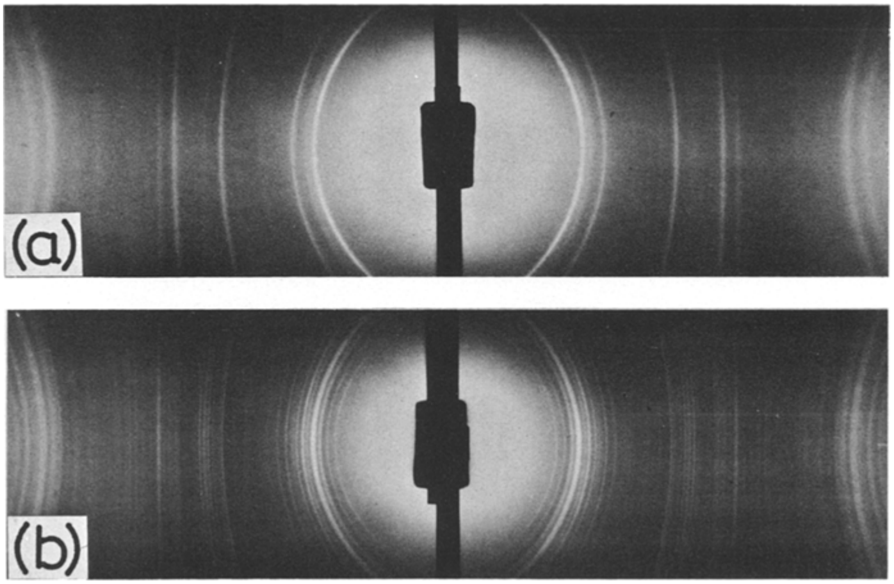

Figure 4 X-ray diffraction pattern of $Pd_{80}Si_{20}$ alloy annealed (a) at 100 kbar and 400° C for 600 min, and (b) at 1 bar and 400° C for 600 min.

heat-treated. No indication of crystallization has been obtained by this annealing. On the other hand, the alloy annealed at 1 bar and the same temperature for the same period has given the pattern shown in Fig. 3b, indicating a coexistence of fcc crystals and a small amount of the amorphous matrix. The lattice parameter of the fcc crystals is nearly the same as that of metallic palladium and the diffraction pattern is merely that of the MS-I state.

Annealing under pressure at 250° C for 5800 min also has not succeeded in producing crystalline phase in the alloy.

Examination of the diffraction patterns of the pressurized alloys showed, however, that the intensity of the haloes increased and their position shifted slightly toward higher angles. The facts suggest that ordering and densification have occurred in the alloys to some extent, although they have not led to an appreciable crystallization.

3.4. High-pressure annealing in the MS-II region

The T–T–T diagram shows that on annealing the MS-II state follows the MS-I state and the transformation is promoted by raising the temperature. The diffraction pattern of the alloy annealed at 1 bar and 400° C for 600 min is shown in Fig. 4b. The appearance of a number of reflection lines is characteristic of the MS-II state. When the alloy was annealed at the same temperature for the same period under pressure, the diffraction pattern shown in Fig. 4a was obtained. Crystallization has set in, but the structure is a simple fcc one with lattice parameter $a = 3.897 \pm 0.008$ Å, nearly the same as that of metallic palladium. Annealing at 100 kbar and 340° C for a longer period, 4300 min, also gave a diffraction pattern which indicated the formation of the crystalline phase with the fcc structure. The same structure was obtained on high pressure annealing at 280° C for a still longer period, 5000 min, but with a slightly larger lattice parameter, $a = 3.920 \pm 0.008$ Å, suggesting that the structure contained some silicon. In all the pressurized alloy samples described in this subsection crystallization is not complete, as shown by the presence of weak diffuse haloes superimposed on the reflection lines in the diffraction pattern.

Annealing at 390° C under pressure for 4200 min gave the diffraction pattern shown in Fig. 5. This pattern can be interpreted as consisting of the two phases, one with the fcc structure and the other with a body-centered tetragonal (bct) structure. Table I gives a list of the intensities and interplanar spacings, d, of the observed reflections. The d-values calculated from the fcc structure with $a = 3.897$ Å and the bct structure with $a = 3.143$ Å and $c = 2.989$ Å are also shown in the table. Agreement between the observed and calculated d-values is fairly good. The lattice

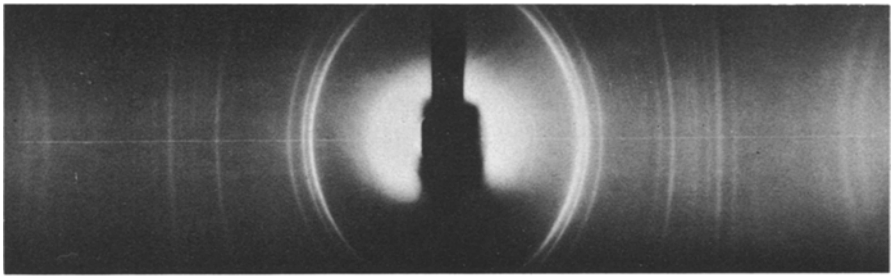

Figure 5 X-ray diffraction pattern of $Pd_{80}Si_{20}$ alloy annealed at 100 kbar and 390° C for 4200 min.

parameter of the fcc structure suggests that the phase with this structure is palladium metal, either pure or containing a small amount of dissolved silicon. Judging from the size of the unit cell of the bct structure, the possible number of atoms in the cell is two. Since the bct crystals formed after the fcc phase (almost pure palladium) had precipitated from the amorphous matrix, it is not unreasonable to assume that the silicon content in the bct phase is larger than that of the fcc phase, although it presumably does not exceed 25 at.%. In the Pd–Si system several intermetallic compounds are known to form but none of them has the simple bct structure. The bct phase thus found is a new crystalline phase forming only under high pressure.

TABLE I Diffraction data for the crystalline phases formed on annealing at 100 kbar and 390° C for 4200 min in $Pd_{80}Si_{20}$ alloy

I_{obs}	d_{obs}(Å)	fcc*		bct*	
		hkl	d_{cal}(Å)	*hkl*	d_{cal}(Å)
S	2.246	111	2.250		
VW	2.20			110	2.222
M	2.132			101	2.131
M	1.948	200	1.949		
VVW	1.6			200†	1.572
W	1.45			002†	1.449
M	1.377	220	1.378		
W	1.27			211	1.265
W	1.22			112	1.214
M	1.176	311	1.175		
W	1.13	222	1.125		
–	–			220†	1.111
VW	1.07			202†	1.065

*fcc $a = 3.897$ Å, bct $a = 3.143$ Å and $c = 2.898$ Å

† There exists some degree of preferred orientation in the thin strip of the alloy samples such that the shorter *c*-axis of the tetragonal crystallites preferentially lies in the direction perpendicular to the strip surface, resulting in more opportunities for the (0 0 2) and (2 0 2) planes to reflect X-rays than the (2 0 0) and (2 2 0) planes.

3.5. General characteristics of crystallization in the pressurized alloy

The experimental results described in the foregoing sections clearly suggest that pressure does not enhance but retards the crystallization of the $Pd_{80}Si_{20}$ alloy over the whole temperature range examined. Below 250° C it has not been possible to obtain the crystalline phase even after prolonged annealing (of the order of a week). At higher temperatures, transformation begins gradually with the appearance of the fcc phase, the silicon content of which decreases with increasing annealing temperature. At 390° C further annealing produces a second phase with the simple bct structure in place of the formation of a complex superstructure corresponding to the MS-II state.

4. Discussion

Some elements are known to be obtained in an amorphous state. When pressure is applied to these elements, the amorphous state is transformed into a crystalline state even at ambient temperature; for instance, amorphous arsenic crystallizes at 18 kbar [8] and amorphous germanium at 100 kbar [9]. Although an atomistic mechanism of these transformations has not yet been clarified, it is certain that 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. In two-component systems such as the Pd–Si system, however, the situation seems to be somewhat different. The present work shows that a simple pressurization cannot induce any appreciable crystallization in the alloy. It is only when the temperature is raised in addition to the application of pressure that crystalline phases form in the amorphous matrix. The overall retardation of the crystallization observed can be accounted for if the transformations which take place in the $Pd_{80}Si_{20}$ alloy, i.e. the formation of the MS-I and SS states, are more or less diffusion-controlled processes. In other words, rearrangement of atoms over a distance much greater than the nearest neighbour distance is necessary to convert the amorphous state into the crystalline state. The activation volume for diffusion of most solids is a positive quantity, so that the decrease in volume available for atoms due to the compression suppresses the atomic diffusion and hence the transformation. The experimental results by Emmens *et al.* [4] for $Pd_{75}Ag_5Si_{20}$ alloy are consistent with those of the present work. As for non-metallic glasses, pressure has been shown in many cases to enhance the crystallization and hence to lower the crystallization temperature [3]. This may be partly due to the different nature of the chemical bonding from that in the metallic glasses, and partly due to the markedly larger difference in the density between the glassy and crystalline states. The acceleration of the transformation observed for the $Pd_{80}Si_{20}$ alloy by Masumoto and Kimura [5] with the application of a uniaxial stress does not contradict the interpretation mentioned above, since uniaxial tension or compression, unlike hydrostatic compression, is known to produce appreciable shear components within the material which provide a driving force for atoms to move.

The two crystalline phases forming under pressure in the $Pd_{80}Si_{20}$ alloy are both simple in their structure. The fcc structure is one of the ideally close-packed atomic arrangements and therefore it is natural that the palladium-rich phase also has this type of the structure under pressure. On the other hand, the phase containing more silicon has the bct structure, in which the two kinds of atoms occupy the lattice sites statistically randomly. It is not unusual, however, that the materials containing atoms which have a tendency to form tetrahedral bonds do not always crystallize in the close-packed structure under pressure. In this connection it is worthwhile to note that a high pressure form of tin is a simple bct structure with $c/a = 0.911$ [10], which is close to the value 0.922 of the high pressure phase of the $Pd_{80}Si_{20}$ alloy.

5. Conclusion

Pressurization of the amorphous $Pd_{80}Si_{20}$ alloy has been shown to result not in an acceleration but in a retardation of the crystallization transformation, and hence it can be said that the amorphous state is more stable on annealing under the uniformly compressed condition than under normal conditions. In addition, pressure has been shown to make the structures of the crystalline phases that appear on high temperature annealing simpler.

Acknowledgement

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