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Transformation studies and mechanical properties of melt-quenched amorphous titanium–silicon alloys

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The formation, stability and decomposition characteristics of the amorphous phase in binary titanium–silicon alloys rapidly quenched from the molten state have been investigated. Electron microscopy and diffraction coupled with X-ray diffraction techniques suggested that the amorphous phase could be obtained in alloys containing 15 to 20 at % silicon. The transformation of the amorphous phase to the equilibrium phases took place in two stages. A metastable b c c titanium solid solution, containing silicon in excess of the equilibrium value, formed initially, followed by the precipitation of the Ti_5Si_3 intermetallic compound. Microstructural features at various stages of decomposition have been described and interpreted in terms of the constitution of the alloys. Mechanical properties of the amorphous alloys have also been investigated.

1. Introduction

In recent years, there has been an increased interest in the study of rapidly quenched metals and alloys [1–3]. Amongst the products of rapid quenching, amorphous alloys (or metallic glasses) occupy a prominent place because of the promise of industrial applications owing to their improved corrosion resistance, better mechanical properties, occurrence of superconductivity and superior magnetic properties [4, 5]. However, these amorphous alloys are metastable at ordinary temperatures and so decompose to the equilibrium phases either at elevated temperatures or upon ageing. Hence, for a proper utilization of these materials, their thermal stability is an important criterion. In spite of this, only a few detailed investigations have been undertaken to evaluate the crystallization behaviour of the amorphous alloys (see, for example, [2] Vol. I, p. 198).

The majority of amorphous alloys studied to date contain either a late transition metal and metalloid or an early transition metal and a late transition metal. A novel class of amorphous alloys will be one containing an early transition metal and a metalloid. As an example of this, we have been successful in preparing binary titanium–silicon alloys in the amorphous state. The present paper describes a detailed study of the transformation behaviour of the amorphous phase to the equilibrium ones and the mechanical properties of the amorphous alloys.

On the titanium-rich side, the Ti–Si equilibrium diagram (Fig. 1) [6] features a eutectic reaction at 1603 K and 13.7 at % Si.† In addition to the terminal Ti solid solution, the other product of the eutectic reaction is the congruently melting Ti_5Si_3 intermetallic compound melting at 2393 K. Thus, alloys around the eutectic composition are most prone to the formation of the amorphous phase, because of the low eutectic temperature compared to the melting points of the neighbouring phases.

Polk *et al.* [7] have recently reported that they were able to produce an amorphous phase in binary Ti–20% Si alloy. They measured the crystallization temperature and Vickers hardness value as a part of their investigations on ternary Ti–Ni–Si

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†All compositions are expressed in atomic per cent.

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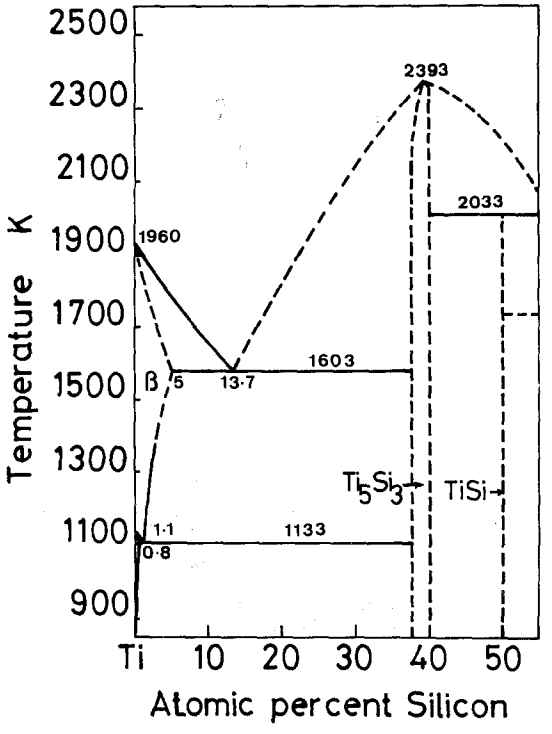

Figure 1 Titanium-rich portion of the Ti–Si equilibrium diagram.

alloys, but did not study the crystallization behaviour.

2. Experimental methods

Five different binary Ti–Si alloys with 5, 10, 15, 20 and 25% Si have been prepared from the pure components by arc melting, with a view to studying the composition range of formation of the amorphous phase. These alloys were then quenched using a single roller melt spinning technique where the alloy was levitation melted [8]. About 2 g of alloy was used per run and the roller speed was about 5000 r.p.m.

Crystallization temperatures (T_x) of the amorphous alloys were measured in a differential thermal analyser by heating the foils at a rate of 8.33×10^{-2} K sec^{-1}. The Vickers hardness and fracture strength were measured by a Vickers microhardness tester with a 100 g load and an Instron-type tensile testing machine at a strain rate of 1.7×10^{-4} sec^{-1}. Annealing treatments have been given to the amorphous foils at T_x values of 600, 1800 and 3600 sec to study structural changes. Structural observations have been carried out in a JEM 200B transmission electron microscope operating at 200 kV after electrothinning the foils in a methanol–sulphuric acid mixture cooled to about 220 K [9]. The heat-treated foils have also been subjected to X-ray diffraction studies to corroborate the data obtained by electron diffraction.

3. Results and discussion

The as-quenched foils were very ductile and had a bright lustre. Both X-ray and electron diffraction studies indicated that only the alloys containing 15 and 20% Si are amorphous. The fact that an amorphous phase can be obtained in the Ti–15% Si alloy increases the maximum titanium content for a metallic glass to about 85%, the highest to be achieved so far. The rest of the alloys showed a variety of crystalline phases. Since the present paper deals with only the amorphous phase, attention will be paid to the above two alloys containing 15 and 20% Si.

3.1. Crystallization temperatures

Table I lists the thermal and mechanical properties observed for the amorphous alloys. Fig. 2 shows the differential thermal analysis (DTA) curves. There are clearly two exothermic peaks indicating a two-stage decomposition of the amorphous phase. Surprisingly, the crystallization temperatures of both the alloys are almost the same.

Naka and Masumoto [10] discussed the effect of the type and quantity of the metalloid element as a ternary addition to Fe-based binary amorphous

TABLE I Thermal and mechanical properties of amorphous Ti–Si alloys

Property	Ti–15% Si	Ti–20% Si	
Crystallization temperature, T_{x_1} (K)	702	702	
Crystallization temperature, T_{x_2} (K)	810	817	867*
Hardness, H_v (kg mm^{-2})	510	530	631*
Fracture stress, σ_f (MPa)	1960	1910	
Critical fracture temperature, T_f (K)	670	660	
σ_f/ρ ($\times 10^3$ m)	47.8	47.8	46*
H_v/σ_f	2.6	2.7	

*Results of Polk *et al.* [7].

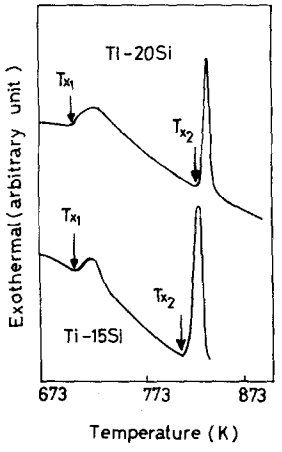

Figure 2 DTA curves for the amorphous Ti–15 and Ti–20% Si alloys.

alloys. They observed that amongst the metalloid elements investigated, B, C, Si and Ge raised the T_x value, while P decreased it. Si was found to have the most significant effect. Although increasing amounts of B increased the T_x in binary Fe–B alloys, no systematic variation of T_x has been noticed for the binary alloys containing Si. In the absence of sufficient data on the variation of T_x with metalloid content for binary alloys, it is difficult to explain why T_x remains practically the same for the Ti–15 and 20% Si alloys.

It is reasonable to assume that T_x (like other physical properties such as electrical resistivity) depends on the degree of randomness (or constitution) of the amorphous phase. Therefore, if one assumes that the amorphous phase in both our alloys has the same "constitution", the T_x will be expected to be the same. However, it is very difficult and time-consuming to determine the exact randomness of two different amorphous alloys. Direct observational techniques such as ultra high-resolution electron microscopy, field-ion microscopy or high-speed computational techniques may be expected to throw some light on this problem.

Polk *et al.* [7] reported that they could detect the amorphous phase only in the case when the alloy was arc-quenched using the piston-and-anvil apparatus and that it had a T_x value of 867 K. Our results, on the other hand, indicate that both Ti–15 and 20% Si alloys are amorphous and both of them exhibited *two* crystallization temperatures. It is interesting to note that the value of 867 K reported by Polk *et al.* is higher than even the second T_x value detected by us. This conflicting result leads to the following consequences.

Firstly, the result of Polk *et al.* suggests that crystallization of the amorphous alloy takes place in a single stage, while our results show that it should occur in two stages. This can be clarified by performing detailed electron microscopic and/or X-ray diffraction studies. Our investigations (to be described in subsequent sections) clearly show that crystallization in this system is a two-stage process confirming the result interpreted from our DTA curves. Secondly, one has to account for the difference in the absolute value(s) of the crystallization temperature. The heating rate employed to determine T_x can be expected to have a marked effect on that value. Polk *et al.* used a heating rate of $80\,K\,min^{-1}$ as against $5\,K\,min^{-1}$ employed by us. The hysteresis effects can lead to a higher value at higher heating rates and so the higher value of Polk *et al.* can be justified. However, the difference is 50 K, which is too large to be attributed to a difference in heating rate alone. The difference, at least in part, may be due to the way T_x is determined in both cases. Polk *et al.* determined their T_x as the temperature corresponding to the intersection of the extrapolated base line and the steepest tangent to the exothermic peak. In our investigations, T_x is defined as the point of inflexion where the exothermic peak begins to occur. This also does not fully explain the difference. Thus, it is suggested that the nature of the amorphous phase obtained in both cases is different. In the case of ternary Ti–Ni–Si alloys [11], such a large difference in the T_x value is ascribed to a difference in the nature of the amorphous phase.

3.2. As-quenched structure

Fig. 3 shows a bright-field electron micrograph and the corresponding diffraction pattern for the Ti–20% Si alloy in the as-quenched condition. The lack of contrast in the micrograph and the presence of diffuse haloes in the diffraction pattern clearly show that an amorphous phase was obtained by rapid quenching. Even the Ti–15% Si alloy in the as-quenched state displayed similar features confirming that an amorphous phase can be obtained in binary Ti–Si alloys in the composition range 15 to 20% Si. The other alloys investigated, however, did not show the presence of any amorphous phase.

As mentioned earlier, a eutectic reaction takes

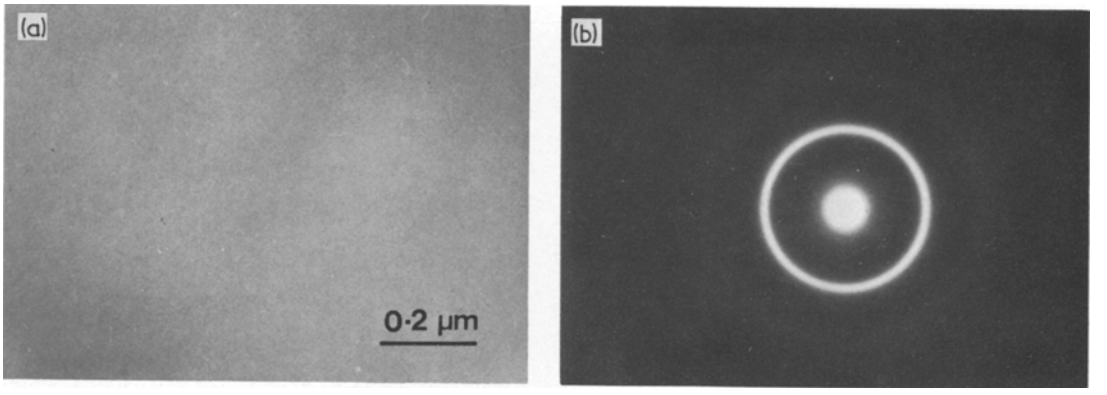

Figure 3 (a) Transmission electron micrograph, and (b) diffraction pattern of the as-quenched Ti–20% Si alloy.

place in Ti-rich Ti–Si alloys at 13.7% Si. Previous investigations [12, 13] had clearly shown that alloys around the eutectic composition are most prone to the formation of the amorphous phase. Thus, one would have expected the alloys with 10 and 15% Si to be amorphous in the as-quenched condition. But, our present results suggest that alloys with only 15 and 20% Si can be made amorphous. Further experiments on alloys with small silicon increments in the range 10 to 15% Si will clearly demonstrate whether the eutectic composition will be included in the glass-forming range. However, the dense random packing of hard spheres to model the amorphous phase suggests that it is easiest to obtain an amorphous phase in alloys containing about 20% of the metalloid element [14]. In the light of the above, our present results suggest that the above two criteria may be necessary but not sufficient for the formation of the amorphous phases. A similar conclusion has also been arrived at by compiling the information on the composition ranges for the formation of metallic glasses [15]. As such it appears that the eutectic composition – while it can act as a useful guide to selecting an alloy for forming the glass – is not a sufficient criterion for predicting the formation of amorphous phases.

3.3. Decomposition structures

The amorphous alloys heat treated at temperatures corresponding to T_{x1} and T_{x2} for different times have been examined in the electron microscope. Even though the general decomposition behaviour is the same for both the amorphous alloys, the kinetics are different.

Fig. 4 shows the bright-field micrograph and diffraction pattern for the Ti–15% Si alloy annealed for 1800 sec at 673 K. It may be noted that this temperature is about 30 K lower than the first crystallization temperature. Except for a slight sharpening of the diffraction rings and precipitation of a few very tiny particles seen in the micrograph, there is not much difference between Figs. 3 and 4. Thus, even if there is some structural relaxation in the amorphous phase, it cannot be evaluated using transmission electron

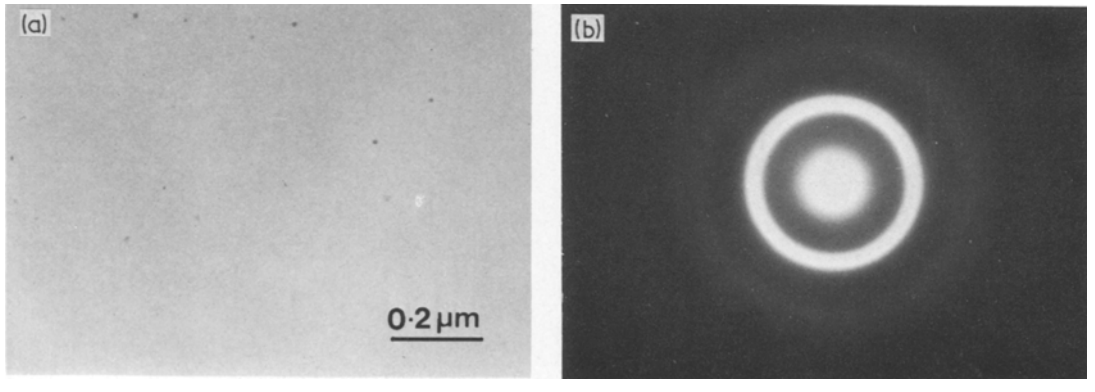

Figure 4 (a) Bright-field micrograph, and (b) diffraction pattern of the Ti–15% Si alloy annealed at 673 K for 1800 sec.

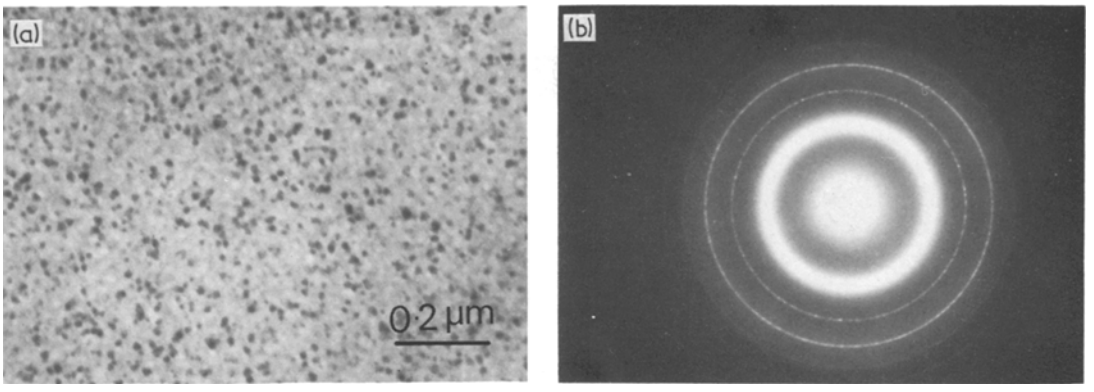

Figure 5 (a) Electron micrograph showing the typical morphology of the MS I phase in the Ti–20% Si alloy annealed for 600 sec at 703 K. (b) Diffraction pattern of (a).

microscopy. Perhaps electrical resistivity or physical dimensions of the ribbon may be able to yield better information.

When the amorphous ribbons were heat treated at a temperature corresponding to T_{x1}, the amorphous phase decomposed to a metastable b c c solid solution (MS I). This MS I phase, present in the form of extremely fine particles (about 15 nm diameter), is distributed uniformly throughout the matrix (Fig. 5a). The electron diffraction pattern from this phase showed very sharp rings (Fig. 5b). The lattice parameter of this b c c phase calculated from several diffraction patterns works out to approximately 0.32 nm.

The solid solubility of Si in β-Ti at the eutectic temperature has been reported to be 5% and that in α-Ti at the eutectic temperature to be 0.8%. The solid solubility of Si in α-Ti at room temperature is almost negligible. The lattice parameter of 0.32 nm calculated for the β-Ti solid solution is smaller than that for pure β-Ti ($a = 0.3306$ nm) indicating that the MS I phase does indeed contain some silicon. In the absence of data for the variation of lattice parameter of Ti solid solutions as a function of silicon content, it is difficult to estimate the actual silicon content in the metastable solid solution. But, it appears that the metastable solid solution contains silicon in excess of the equilibrium limit as evidenced by the precipitation of a second phase on subsequent ageing.

Annealing treatments for 1800 and 3600 sec at T_{x1} for the Ti–20% Si alloy showed only a slight coarsening of the MS I phase (the average size of the particle is about 30 nm when annealed for 3600 sec). However, in the Ti–15% Si alloy, another phase appeared when annealing was carried out even for 1800 sec. We shall refer to this phase as MS II. This phase has a morphology shown in Fig. 6 and was found to co-exist with the MS I phase. Because of the large size (up to 0.4 μm) of this phase, it has been possible to obtain single-crystal diffraction patterns and analyse them for its structure. Sometimes, this phase was also manifest in a fine-grain structure giving rise to ring patterns. A typical micrograph and diffraction pattern are shown in Fig. 7. From both the ring and single-crystal diffraction patterns, it could be shown that MS II corresponds to the intermetallic compound Ti_5Si_3, possessing a hexagonal symmetry. Sometimes, a lamellar structure was also observed as a decomposition product (Fig. 8) in the Ti–15% Si alloy, probably due to the eutectoid decomposition of the β phase.

Heat treatments given to the samples at T_{x2} gave results similar to the above. Except for a difference in the kinetics of the process, both the alloys yielded similar microstructures and diffraction patterns. From these results it is clear that

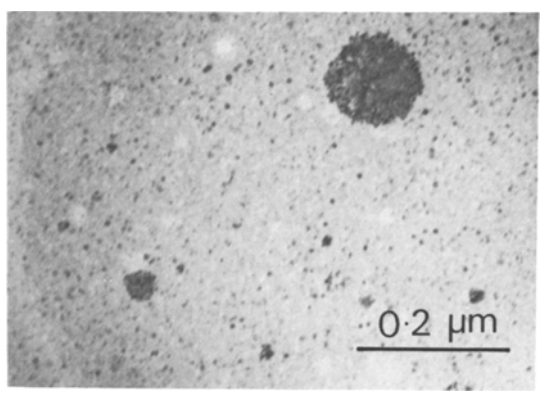

Figure 6 Electron micrograph showing the morphology of the MS II phase in the Ti–15% Si alloy annealed for 1800 sec at 703 K.

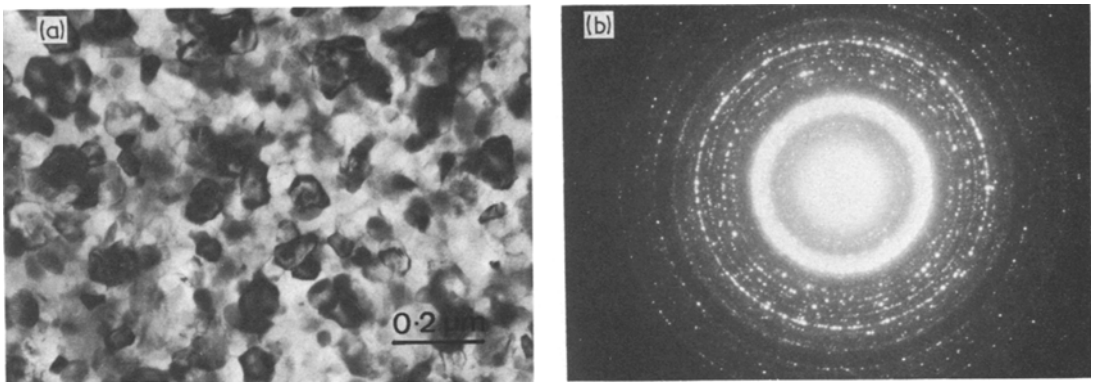

Figure 7 (a) Granular morphology of the MS II phase, and (b) its diffraction pattern.

both β-Ti solid solution and the intermetallic compound Ti_5Si_3 are present in samples heat treated at T_{x2}. However, at longer times of annealing, the proportion of the Ti_5Si_3 phase is very much more.

With a view to confirming the formation of the equilibrium phases from the amorphous phase, the alloy ribbons were given heat treatment for 1 day at 973 K. Well-developed grain structures giving very clear single-crystal diffraction patterns could be obtained from these foils. Fig. 9 shows two bright-field micrographs corresponding to this condition. It is interesting to note the many fringes associated with the precipitate particles in Fig. 9b. Two typical diffraction patterns of the Ti_5Si_3 phase are shown in Fig. 10.

The MS II phase in both the alloys seems to be closely related to the equilibrium intermetallic compound Ti_5Si_3, if not actually the equilibrium Ti_5Si_3. This phase under equilibrium conditions has a hexagonal structure with $a = 0.7429$ nm and $c = 0.5139$ nm [16]. Because of the complex nature of this phase, it is difficult to accurately determine the lattice parameters from electron diffraction patterns. X-ray diffraction patterns recorded from samples annealed for 1 day at 973 K gave the following lattice parameters

$$\alpha\text{-Ti: } a = 0.2946\,\text{nm}, c = 0.4667\,\text{nm},$$
$$c/a = 1.584$$
$$Ti_5Si_3\text{: } a = 0.7409\,\text{nm}, c = 0.5182\,\text{nm},$$
$$c/a = 0.699.$$

These values are essentially the same as those reported for the equilibrium phases. Thus, it can be concluded that the amorphous phase has returned to complete equilibrium by this annealing treatment. At intermediate stages of annealing, such as at T_{x1} for longer times or at T_{x2}, also the lattice parameters of the Ti_5Si_3 phase are quite close to the values reported above. Thus, we can conclude that the decomposition sequence may be represented as

$$\text{amorphous} \rightarrow \text{amorphous}' + \text{MS I} \rightarrow \text{MS I} + Ti_5Si_3 \rightarrow \alpha\text{-Ti} + Ti_5Si_3.$$

This sequence is the same as reported for the classic Pd–Si [17] and other metal–metalloid systems. We have also recently observed [18] such a decomposition sequence in a metal–metal amorphous system.

Based on the results obtained through X-ray diffraction and electron microscopy studies on specimens annealed for different times, we can differentiate the decomposition behaviour of the two alloys with the help of Table II.

It may be noted from the above table that the

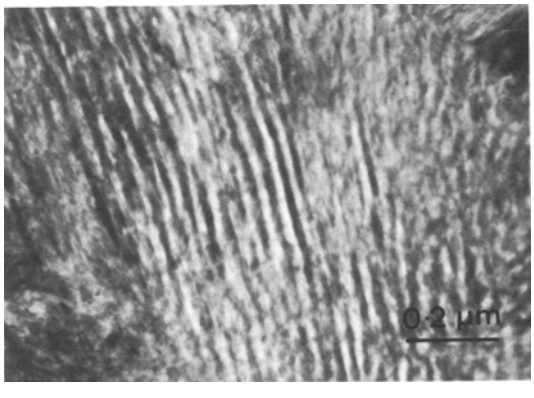

Figure 8 Lamellar microstructure observed in the Ti–15% Si alloy annealed for 1800 sec at 818 K.

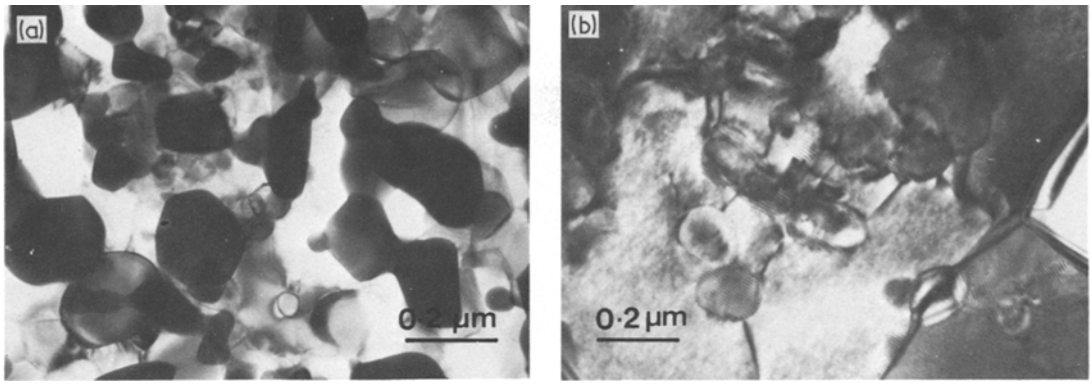

Figure 9 Bright-field micrographs of alloys annealed for 1 day at 973 K. (a) Ti–15% Si, (b) Ti–20% Si.

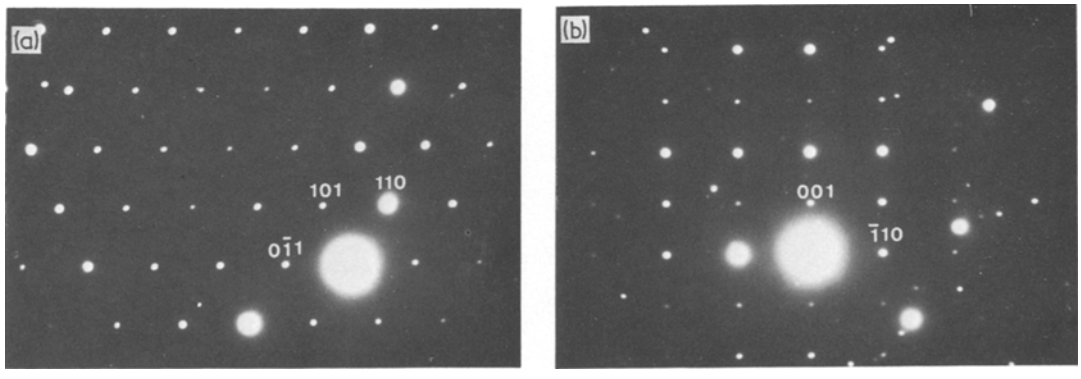

Figure 10 Two typical single-crystal diffraction patterns of the Ti_5Si_3 phase. (a) [$\bar{1}$ 1 1], (b) [1 1 0] orientations.

decomposition sequence in both alloys is very similar. However, it is interesting to note that the MS I phase is quite stable in both cases and that the Ti_5Si_3 phase starts appearing at a very early stage (1800 sec at 703 K) in the Ti–15% Si alloy. In contrast, Ti_5Si_3 does not appear till the Ti–20% Si alloy has been heat treated for 600 sec at 818 K. This behaviour indicates that the activation energy for the precipitation of Ti_5Si_3 phase is lower in the Ti–15% Si alloy. This observation of precipitation of the second phase at an early stage in a dilute alloy in comparison to the concentrated alloy of the metal–metalloid system seems to be at variance with the previous observations [19]. The earlier results suggested that the MS II phase starts precipitating at an early stage in the alloy containing a higher amount of the metalloid. The present result may be explained on the basis that the T_{x2} temperature for the Ti–15% Si alloy is lower than for the Ti–20% Si alloy, thus hastening

TABLE II Constitution of Ti–Si binary alloys as a function of heat treatment

Treatment	Ti–15% Si	Ti–20% Si	Remarks
As-quenched	Amorphous	Amorphous	
Annealed at 673 K for 1800 sec	Amorphous' (Am')	Am'	
Annealed at 703 K for 600 sec	Am' + MS I	Am' + MS I	Very fine grains
Annealed at 703 K for 1800 sec	Am' + MS I + Ti_5Si_3	Am' + MS I	
Annealed at 703 K for 3600 sec	Am' + MS I + Ti_5Si_3	MS I	Slight coarsening of the grains
Annealed at 818 K for 600 sec	MS I + Ti_5Si_3	MS I + Ti_5Si_3	
Annealed at 818 K for 1800 sec	MS I + Ti_5Si_3	α-Ti + Ti_5Si_3	Fine grains and lamellar structure
Annealed at 818 K for 3600 sec	α-Ti + Ti_5Si_3	α-Ti + Ti_5Si_3	Slight coarsening of the grains
Annealed at 973 K for 1 day	α-Ti + Ti_5Si_3	α-Ti + Ti_5Si_3	

the process of decomposition when both the foils were annealed at the same temperature, i.e. 818 K.

3.4. Mechanical properties

Finally, we would like to discuss the mechanical properties of the amorphous alloys. The hardness, H_v, fracture strength, σ_f and critical fracture temperature, T_f, are also presented in Table I. T_f is defined as that temperature at which foils annealed for 3600 sec fracture when bent between two faces of a vice.

Similar to the crystallization temperature, the hardness value reported by Polk *et al.* [7] is also higher than the value obtained by us. However, it should be noted that the T_f of about 670 K is considerably higher than for other amorphous systems (see, for example, [2]). Another interesting aspect is that the amorphous alloy continues to be ductile to a temperature quite close to the first crystallization temperature. This result may also substantiate the tentative electron microscopic observation (mentioned in the previous sections) that the structural relaxation is perhaps quite minimal in the Ti–Si amorphous alloys even after low-temperature annealing. In conformity with other titanium-based amorphous alloys [20, 21], σ_f/ρ is about 47.8×10^3 m and H_v/σ_f about 2.7 implying that these alloys also exhibit a plastic–rigid behaviour [22].

4. Conclusions

The present investigation has shown that it is possible to produce an amorphous phase in binary Ti–Si alloys containing 15 to 20% Si. This has been confirmed by both X-ray and electron diffraction and electron microscopy techniques. It was observed that the crystallization of the amorphous phase takes place in two stages. Temperatures corresponding to these stages are practically the same in the two alloys investigated. The first stage of crystallization involves the precipitation of a metastable b c c β-Ti solid solution. The lattice parameter of this phase indicates that some amount of silicon is contained in excess of the equilibrium content in β-Ti. The second stage of decomposition is the precipitation of the equilibrium Ti_5Si_3 phase. Annealing for 1 day at 973 K resulted in the formation of the equilibrium phases.

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