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Crystallization characteristics of an amorphous $Nb_{81}Si_{19}$ alloy under high pressure and formation of the A15 phase

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Amorphous Nb–19 at% Si alloy, prepared by rapid quenching from the molten state, was annealed while being subjected to a pressure of 10 GPa. X-ray diffraction investigations on the alloy specimens quenched to ambient conditions have shown that pressure greatly alters the crystallization characteristics and the cubic A15 (Nb_3Si)-phase forms in preference to the tetragonal Nb_3Si-phase at temperatures in the range from 710° C to 800° C. Up to 680° C, the component atoms do not show any tendency towards ordering upon crystallization and the body-centred tetragonal solid solution forms; while, at 830° C, niobium atoms diffuse to form the body-centred cubic Nb precipitates. Superconducting properties have been measured for the single-phase A15 structure with the lattice parameter $a = 0.5155$ nm with the results that the transition temperature, T_C, is 3.4 K and the temperature coefficient of the upper critical field, H_{C2}, is 1.2 MA m^{-1} K^{-1} (15 kOe K^{-1}).

1. Introduction

It was shown earlier [1, 2] that pressure can have an appreciable effect on the crystallization of amorphous alloys: it greatly improves the stability of the amorphous phases with an attendant rise in the crystallization temperature and changes remarkably the sequence of the crystalline phase forming from the amorphous matrix upon annealing. The crystalline phases preferentially forming in the compressed alloys have, in general, structures with a higher packing density and a local atomic configuration nearly identical to that found in the amorphous matrix. These observations suggest that the pressurization technique can be used to suppress or delay the decomposition reaction in the amorphous alloys, which otherwise occurs upon annealing. This can also lead to the formation of new, dense crystalline phases.

Recent progress in rapidly quenching techniques has made it possible to prepare many kinds of alloys in the amorphous state [3]. Among these, particular attention has been focused on the V–IV_b systems, since they can provide excellent superconducting materials. Masumoto *et al.* [4] studied the properties of the amorphous Nb–Si alloys in the composition range encompassing the eutectic composition 17.9 at% Si and found that they are highly ductile superconductors with a transition temperature, T_C, ranging from 4.1 to 4.4 K. They also clarified the crystallization characteristics of the alloys as functions of temperature and annealing time at ambient pressure.

In the Nb–Si system, a crystalline phase forming under equilibrium conditions at the composition $Nb_{75}Si_{25}$ has the tetragonal Ti_3P-type structure, which, however, decomposes into a mixture of the body-centred cubic Nb and a hexagonal Nb_5Si_3-phase at a temperature below 1783° C [5]. Based on an extrapolation of the properties of known A15 superconductors, it has been pre-

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dicted that, if the A15-Nb_3Si were synthesized, it would have a T_C in excess of 25 K [6, 7]. This prediction stimulated a number of researchers who resorted to a variety of methods to produce this compound. Some of them claimed success in the synthesis of the A15 compound and detection of a superconducting transition at relatively high temperatures [8]. Recently, Hasse and Meyer [9] expressed doubt about the high T_C value reported for the A15-Nb_3Si and suggested that the measured transition is that of a different compound, Nb_7Si, having the cubic structure with nearly the same lattice parameter as that of A15-Nb_3Si. On the other hand, Olinger and Newkirk [10] very recently reported that bulk quantities of Nb_3Si were converted by a shock-wave compression into the near-stoichiometric A15 phase having a T_C of 18.6 K and a lattice parameter of 0.5091 nm. It is to be noted that the A15-Nb_3Si hitherto synthesized, including that of Olinger and Newkirk, yielded X-ray diffraction patterns which often included diffraction lines from other co-existing crystalline phases such as Nb, tetragonal Nb_3Si and Nb_5Si_3. It thus seems necessary to obtain A15 phase of good crystallinity and in a single-phase state in order to investigate its superconducting properties.

It has been shown that a crystalline phase having the A15-type structure is found in Nb–Si alloys rapidly quenched from the liquid state [11, 12]. The present authors confirmed this result in a previous report [13], but the quantity of the A15 phase was invariably small and the alloy specimens contained a large amount of amorphous phase. Any attempt to increase the quantity of the A15 phase by annealing was unsuccessful and it readily transformed into the stable tetragonal phase. The fact that the A15-type structure has a higher packing density than the Ti_3P-type structure [14] suggests that the application of high pressure to the splat-cooled amorphous Nb–Si alloy promotes the nucleation of the denser A15-Nb_3Si phase and accelerates its growth over the entire matrix, thus preventing the decomposition of the amorphous phase into a multiphase mixture.

The present work has been undertaken with the primary aim of investigating the crystallization behaviour of the amorphous Nb–Si alloys under high pressure as well as to determine the conditions under which the homogeneous A15 phase is formed. Earlier experiments indicated that the critical cooling rate required for the formation of the amorphous phase increases with increasing Si content and, therefore, attention is focused in the present work on the alloy with the composition of Nb–19 at% Si. As will be shown below, it is possible to find beneficial effects of high pressure on producing the A15 phase. Values of T_C and the upper critical field, H_{C2}, for the A15 phase thus obtained have been measured.

2. Experimental procedure

Amorphous alloy specimens used in the present work were prepared using the rapid-cooling technique developed in our research group, the details of which were published elsewhere [4]. The specimens are in the form of continuous ribbons 1 to 1.5 mm in width and 0.02 to 0.03 mm in thickness. X-ray examination of the as-quenched specimens showed that most of them were in an amorphous state with two to three observable diffraction haloes.

The high pressure apparatus used was the same as that employed in the previous works [1, 2] and hence is not described here. The amorphous specimens were annealed at temperatures ranging from 600 to 850° C for different periods of time while they were subjected to a pressure of 10 GPa. At the end of the annealing treatment, the a.c. current through the internal heater was shut off and the pressure was then decreased. Crystalline phases, formed during the high-pressure annealing and quenched to ambient conditions, were investigated by X-ray diffraction methods. After annealing, the alloy specimens became brittle and several small flakes could be removed from the high-pressure cell. They were fixed at the tip of a glass fibre with an appropriate adhesive and mounted on a conventional crystal holder. CuKα radiation emitted from the rotating-anode-type generator (Rigaku RU-200) and monochromated by a reflection from the LiF (200) plane was incident on the specimens and the diffraction patterns were recorded on a film installed in a cylindrical camera 70 mm in diameter.

Electron-probe microanalysis (using a Shimazu EMX-SM) was employed to reveal the distribution of the elements in the pressurized specimens. An anodic oxidation technique was also used to observe their microstructure.

Measurements of T_C and the upper critical field, H_{C2}, were made by an a.c. susceptibility method using a Hartshorn bridge, which had a

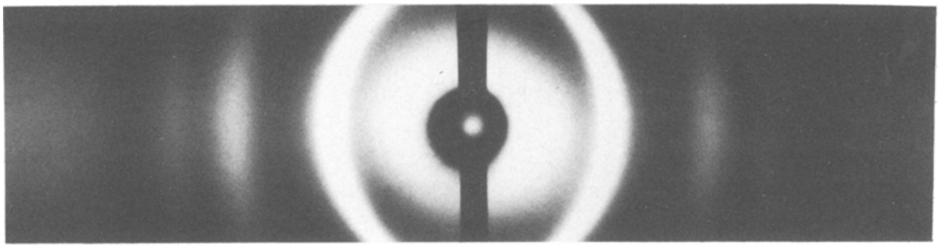

Figure 1 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 630° C for 184 h.

sensitivity sufficient to detect the superconducting transition in a specimen of a weight as small as 1 μg.

3. Experimental results

3.1. Crystallization of the amorphous Nb–19 at% Si alloy at a pressure of 10 GPa

Fig. 1 shows an X-ray diffraction pattern of the Nb–19 at% Si alloy annealed at 10 GPa and 630° C for 184 h. Only diffuse haloes are seen in the pattern. This is in contrast to the observations of Masumoto *et al.* [4] in their annealing experiments at ambient pressure where crystallization was detected after annealing at 600° C for as short a period as 16 h. It is not until the annealing temperature is raised to 680° C that appreciable transformation of the amorphous alloy is detected under high pressure. The increased stability of the amorphous phase with the application of pressure was also observed for Pd–20 at% Si [1] and Fe–17 at% B alloys [2] and was interpreted to be due to the decreased mobility of atoms in the compressed alloys.

Fig. 2 shows an X-ray diffraction pattern of the Nb–19 at% Si alloy annealed at 10 GPa and 680° C for 96 h. Annealing at this temperature results in crystallization of the alloy. The positions and intensities of most of the diffraction lines are those expected from the bcc structure, but a close examination shows that some of them are splitting, indicating a slight tetragonal distortion of the lattice. The lattice parameters determined for this crystalline phase are $a = 0.3385$ nm and $c = 0.3420$ nm with $c/a = 1.01$. The unit-cell volume calculated from these parameters, 0.03919 nm^3, is considerably larger than that of the bcc Nb, of 0.03596 nm^3. The expansion of the lattice indicates that the crystalline phase formed under compression is a solid solution of Nb and Si with the smaller silicon atoms dissolved interstitially. Preferential occupation of the particular octahedral interstitial sites of the bcc Nb lattice by silicon atoms is a possible cause of the observed tetragonal distortion, just as the carbon atoms dissolved in bcc iron distort the lattice tetragonally. It should be noted that a bcc substitutional solid solution forms in Nb–25 at% Si alloy specimens prepared by the high-speed sputtering method [14]. The lattice parameter of that substitutional solid solution is 0.317 nm, which is significantly smaller than the values measured in the present investigation for the compressed alloy. In addition to the diffraction lines from the bct structure, there are weak diffraction lines in Fig. 2.

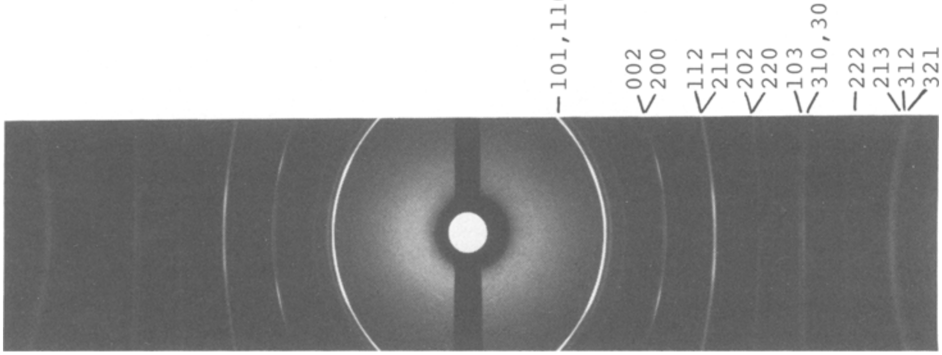

Figure 2 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 680° C for 96 h, showing the formation of body-centred tetragonal solid solution and a trace of A15 phase. Indexing is made for the reflections from the b c t solid solution.

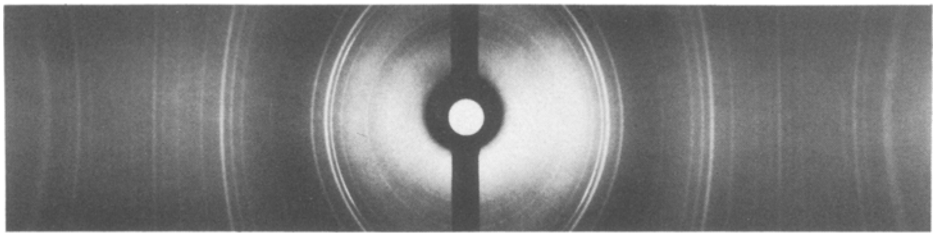

Figure 3 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 700° C for 96 h, showing the formation of A15 phase and a small amount of b c t (quasi-b c c) solid solution.

Comparison of the diffraction pattern with those taken from the alloy annealed at higher temperatures shows that they are from the co-existing A15 phase.

Increase in the annealing temperature has resulted in a reversal of the volume ratio of the two phases, as shown in Fig. 3, which is an X-ray diffraction pattern of the alloy annealed at 10 GPa and 700° C for 96 h, showing many intense diffraction lines. All of these can be indexed in terms of a cubic A15 structure with $a = 0.515$ nm. The co-existing Nb–Si solid solution is now smaller in quantity and the diffraction lines from this phase are indexed in terms of a quasi-b c c structure (very small tetragonal distortion) with $a = 0.337$ nm. This fact suggests that there is a critical temperature below which the A15 phase can not form stably.

Annealing at temperatures ranging from 710 to 800° C has yielded X-ray diffraction patterns showing an abundance of the A15 phase. Fig. 4 shows one of these patterns, which has been taken from the alloy annealed at 10 GPa and 750° C for 57 h. One can see a number of intense, well-defined diffraction lines, indicative of good crystallinity, all of which are favourably indexed in terms of the A15 structure with $a = 0.5155$ nm, as listed in Table I and shown in Fig. 4. No additional lines are present in the pattern. In Table I, I_{obs} is the intensity visually estimated and I_{cal} is the intensity calculated from the structure model,

$$I_{\text{cal}} = M \cdot |F(h\,k\,l)|^2 \cdot Lp, \qquad (1)$$

where m is the multiplicity factor, F is the structure factor and Lp is the Lorentz-polarization factor, in which the A- and B-sites of the A15-A_3B compound are exclusively occupied by niobium atoms and by silicon and excess niobium atoms, respectively. Good agreement has been noted between I_{obs} and I_{cal}. It is particularly to be noted that reflections such as (1 1 0), (2 2 0), (3 1 0), (4 1 1), which are sensitive to the degree of order in the atomic configuration, have observable intensities. Although the mobility of atoms is very restricted in the compressed alloy, there still exists a preference of niobium atoms for occupation of the A-sites on the formation of the crystalline phase.

In order to investigate the microstructure of the annealed alloy specimens, anodic oxidation was carried out in a solution of phosphoric acid, alcohol and water in the volume ratio of 1 : 10 : 50, the anode voltage being fixed at 90 V. Fig. 5 shows a micrograph of the oxidized surface of the alloy fragments. It exhibits a nearly uniform salmon-pink colour, indicating homogeneity of the

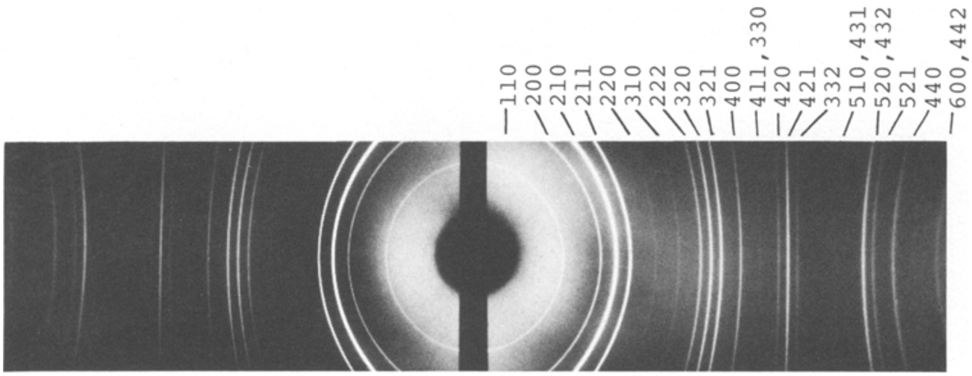

Figure 4 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 750° C for 57 h, showing the formation of a single-phase A15 structure.

TABLE I X-ray diffraction data for A15 phase formed at 10 GPa and 750° C. Monochromated CuKα radiation, $a = 0.5155$ nm.

$h k l$	d_{obs}(nm)	d_{cal}(nm)	I_{obs}*	I_{cal}(normalized) (arb. units)
110	0.3643	0.3645	M	12
200	0.2575	0.2578	MS	18
210	0.2306	0.2305	VS	100
211	0.2105	0.2105	S	41
220	0.1823	0.1823	VW	1.8
310	0.1630	0.1630	VW	2.6
222	0.1488	0.1488	M	15
320	0.1430	0.1430	MS	24
321	0.1378	0.1378	MS	23
400	0.1289	0.1289	M	13
411,330	0.1215	0.1215	VW	1.6
420	0.1152	0.1153	W	7.2
421	0.1125	0.1125	MS	25
332	0.1099	0.1099	W	6.3
422	–	0.1052	–	0.8
510,431	0.1010	0.1011	VW	2.2
520,432	0.09572	0.09573	MS	29
521	0.09418	0.09412	W	10
440	0.09114	0.09113	M	14
530,433	0.0884	0.08841	VVW	1.5
600,442	0.08590	0.08592	W	6.9
610	0.08474	0.08475	M	11
611,532	0.08363	0.08363	MS	18

*VS, very strong; S, strong; MS, medium strong; W, weak; VW, very weak; VVW, very very weak.

structure. The black line running across the micrograph on the left-hand side is a shadow of the crack edge. Micrographs of the surface imaged using fluorescent NbLα and SiKα radiation in an electron probe microanalyser are shown in Fig. 6a and b. There is no evidence for partial enrichment of one of the components, which is another indication of the homogeneity of the structure.

These observations, together with the results of the X-ray diffraction examination, lead to the conclusion that the alloy annealed at 10 GPa and 750° C for 57 h is, within the limit of the resolution of the analysis, in a single-phase state having the A15-type structure. Hence, this phase must have nearly the same composition as that of the parent amorphous phase. This is an interesting result in that the A15-type structure can be formed at a composition deviating considerably from stoichiometry.

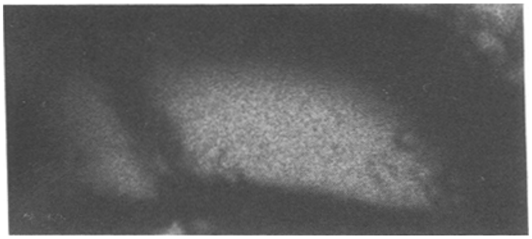

Figure 5 Micrograph of anodic-oxidized surface of $Nb_{81}Si_{19}$ alloy, heat-treated as in Fig. 4 (× 150).

When annealing is carried out at temperatures beyond 800° C, decomposition into phase mixtures is again observed. Fig. 7 shows an X-ray diffraction pattern of the alloy annealed at 10 GPa and 810° C for 42 h, in which a few weak diffraction lines can be seen, in addition to a number of the intense diffraction lines from the A15-phase. The former are identified as those from the bcc Nb phase. At 830° C the quantity of the Nb phase has increased, as shown in Fig. 8, and the A15 phase is now a minor constituent with a slightly increased Si content. This suggests that atoms have gained sufficient thermal energy to form Nb segregates at that temperature, even in the compressed alloy. It is to be noted that at ambient pressure precipitation of Nb can be observed, even after annealing at 700° C [4].

Crystallization characteristics of the Nb–19 at% Si amorphous alloy under a pressure of 10 GPa are summarized in a time–temperature–transformation (T–T–T) diagram, shown in Fig. 9. Within the temperature range investigated, the A15 phase has a wide region of stability and the tetragonal phase, which is often detected in the uncompressed alloy, is not found at all in the pressurized alloy. Formation of the bct Nb–Si solid solution at lower temperatures is due to the insufficient thermal activation of atoms to arrange themeselves in an ordered fashion.

If the logarithm of the reciprocal of the time (in min) for the onset of crystallization is plotted against the reciprocal of temperature (in K), a straight line is obtained, as shown in Fig. 10. The slope of this line gives 211 kJ mol^{-1} as the apparent activation energy for the formation of the A15 phase. Although this value is a little larger than the typical activation energy for diffusion in metals, it suggests that crystallization in the compressed Nb–19 at% Si alloy is still a diffusion-controlled process.

The A15 phase thus formed is most stable if maintained at the ambient conditions. Furthermore, no structural change has been observed, even when it is heated up to 600° C. This high stability of the A15 phase enables the repeated measurement of the superconducting properties, as will be described below.

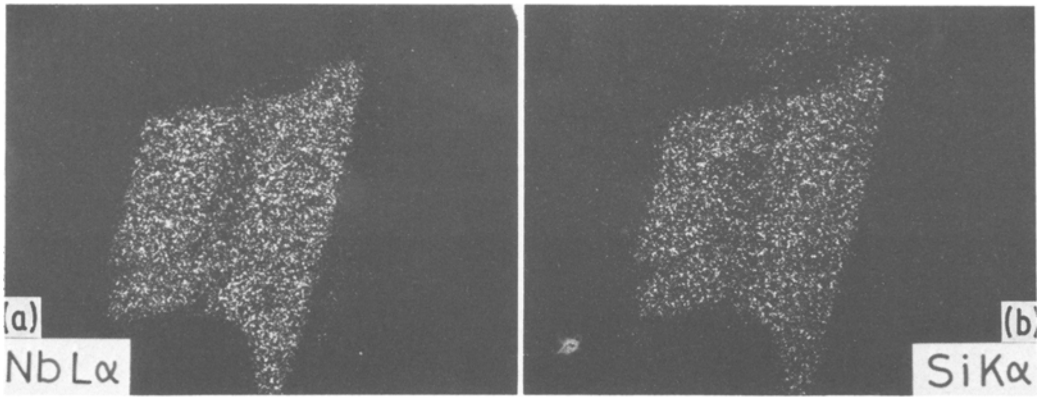

Figure 6 Fluorescent X-ray image of $Nb_{81}Si_{19}$ alloy heat-treated as in Fig. 4. (a) NbLα radiation and (b) SiKα radiation (×1400).

3.2. Superconducting transition temperature and upper critical field of the A15 phase formed under a pressure of 10 GPa

Fig. 11 shows the a.c. susceptibility of the A15 phase synthesized by annealing the amorphous Nb–19 at% Si alloy at 10 GPa and 800° C for 63 h, plotted against temperature. On lowering the temperature the real part of the susceptibility, χ', begins to decrease abruptly at 3.4 K, indicating the onset of the superconducting transition, while the imaginary part of the susceptibility, χ'', reaches a maximum at 3.25 K. The width of the maximum, found to be 0.2 K, is a measure of the width of the transition. In comparison with the measurements reported by previous researchers on synthesized A15 phases, the transition observed in our specimen is relatively sharp, but T_C is unexpectedly low. Although X-ray diffraction examination has shown that there exists an atomic ordering in the A15 phase prepared in the present work, the degree of order is not necessarily perfect and this may be the primary cause for the observed low T_C value. An attempt to raise the T_C value by annealing the specimens at ambient pressure has been unsuccessful, suggesting that it is difficult to increase the degree of order in the metastable phase. The T_C value of our specimens follows the relation between T_C and lattice parameter proposed by Haase and Meyer [9]. On the other hand, if our T_C value and those measured by Stewart *et al.* [15] and by Olinger and Newkirk [10] are plotted against composition, T_C goes through a minimum of about 3 K at 16 to 17 at% Si. It is surprising that the T_C value of the present A15 phase is slightly lower than that of the as-prepared amorphous phase (T_C = 3.7 K).

The superconducting transition of the A15 phase has been measured under the constant magnetic field, and the upper critical field, H_{C2}, thus determined is plotted against temperature, as shown in Fig. 12. The slope of the straight line is 1.2 MA m^{-1} K^{-1} (15 kOe K^{-1}), which is in an agreement with a value measured by Dew-Hughes [16] for shock-recovered Nb_3Si specimens but definitely smaller than that measured for the typical A15 superconductor. It is significantly larger than that measured for the Nb–Si amorphous phase.

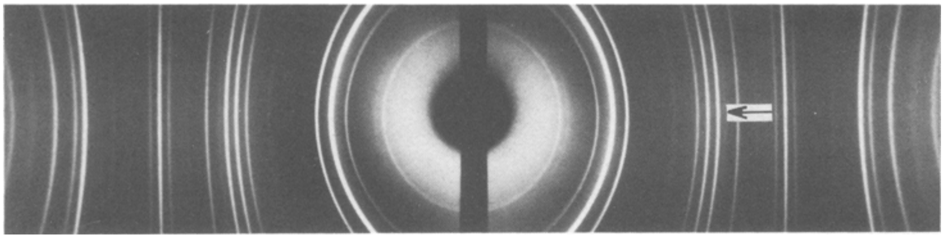

Figure 7 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 810° C for 42 h, showing the formation of A15 phase and a trace of b c c Nb. Arrow indicates the reflections from b c c Nb.

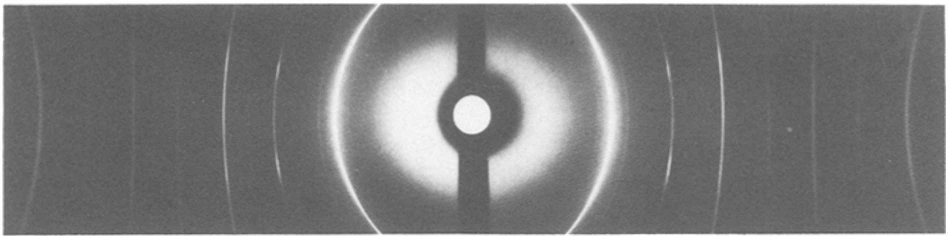

Figure 8 X-ray diffraction pattern of amorphous $Nb_{81}Si_{19}$ alloy annealed at 10 GPa and 830° C for 3 h, showing the formation of b c c Nb and a trace of A15 phase.

4. Discussion

4.1. Preferential formation of the A15 phase in the amorphous Nb–19 at% Si alloy subjected to high pressure

The results of the present high-pressure experiments clearly show that pressure favours the formation of the A15 structure in the amorphous Nb–19 at% Si alloy, in conformity with the expectation described in Section 1. It is now possible to discuss the preferential formation of the A15 phase in the light of the atomic-scale structure of the amorphous alloy. Cargill [17] studied the structure of amorphous Nb–Ge alloys by means of X-ray diffraction and extended X-ray absorption fine structure spectroscopy (EXAFS) and showed that each germanium atom has on the average 6.3 niobium atoms at a distance of 0.266 nm and each niobium atom has 10.7 niobium atoms at the distance of 0.299 nm. The total pair correlation function derived from the observed intensity curve can not be explained in terms of a simple dense-random-packing model but rather in terms of a quasi-molecular-building block model; thereby the molecular unit consists of a germanium atom surrounded by six strongly-bonded niobium atoms at the distance of 0.266 nm in the form of an expanded octahedron. This arrangement is sketched in Fig. 13a. Chemical similarity between germanium and silicon allows the credible supposition of the presence of identical structural units in amorphous Nb–Si alloys. It is these units which are found in the A15-type structure, as shown in Fig. 13b, as well as in the Ti_3P-type structure, (although in this structure they are distorted). Therefore, it is highly likely that these units can act as nuclei for crystallization of the amorphous alloy. The crystalline phase thus formed can have the A15- or Ti_3P-type structure, but in the uncompressed alloy the stability of the latter is higher and the cubic A15 phase, even if formed, ceases to grow continuously and the stable tetragonal phase becomes the dominant phase. This is confirmed in our previous work [13] and also by Hammond and Hazra [18]. On the other hand, the stability of the A15-type structure increases with application of pressure owing to its higher packing density. According to the estimation of Waterstrat *et al* [14], the ideal A15-Nb_3Si will have an average atomic volume of 0.01668 nm^3 while that of the tetragonal Nb_3Si

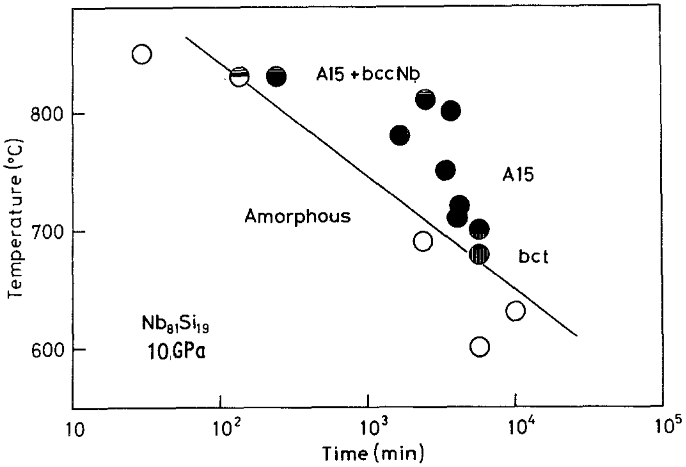

Figure 9 Time–temperature–transformation diagram of amorphous $Nb_{81}Si_{19}$ alloy on annealing at 10 GPa.

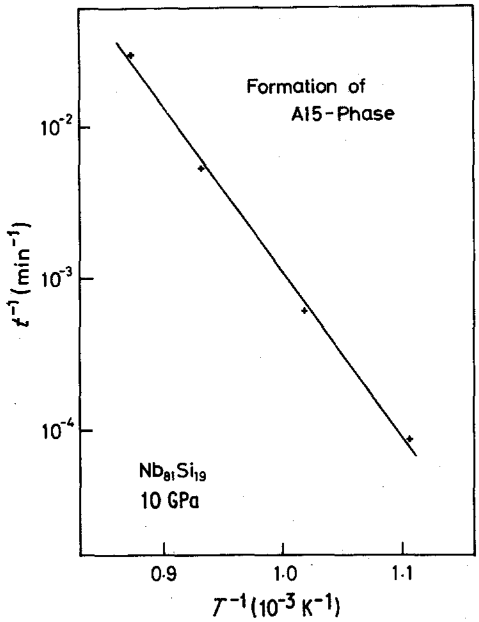

Figure 10 Reciprocal of the time required for the formation of the A15 phase from amorphous matrix plotted against the reciprocal of the annealing temperature at 10 GPa.

is 0.01695 nm^3. In the alloy with non-stoichiometric composition, crystallization proceeds by occasionally adding to the nuclei the expanded octahedron consisting solely of niobium atoms until the entire compressed matrix is covered with the A15-type structure. The present experiments, however, can not determine whether the A15 phase is really a stable phase in the Nb–Si system at 10 GPa or not. Only an *in situ* high-pressure structural study using the tetragonal Nb_3Si as the starting material will answer the question.

4.2. Superconducting properties of A15-Nb_3Si

A range of T_C values has hitherto been reported by various researchers for the A15-Nb_3Si phase. The high T_C value of around 17 K is measured for specimens containing a multitude of phases including the A15 phase, while a low T_C value of around 6 K is reported for specimens which contain this phase as a major constituent. For instance, Nb_3Si alloys explosively compressed by Pan *et al.* [8] exhibit the transition at 19 K but their X-ray diffraction pattern includes the A15 diffraction lines superimposed on the intense diffraction lines from the co-existing phases, while the liquid-quenched Nb_3Si alloys exhibit the transition at 5.4 K and their X-ray diffraction pattern clearly shows the A15 diffraction lines together with a weak halo from the amorphous matrix [12]. The results of the present work can of course be classified into the latter group, but our alloy specimens contain the A15 phase in a single-phase state. An effort should be made in future to reveal the origin of the high T_C value observed in the specimens of the former group, because the existence of the Nb_7Si phase has not yet been confirmed. Besides, there still remains a problem of synthesizing the stoichiometric A15-Nb_3Si and revealing its superconducting properties. The work of Olinger and Newkirk [10] appears to be a step towards solving the problem. It may be noted that a peak associated with the superconducting transition has been observed in a specific-heat curve of their specimens [19]. Similar work, using amorphous specimens, is currently in progress in our group.

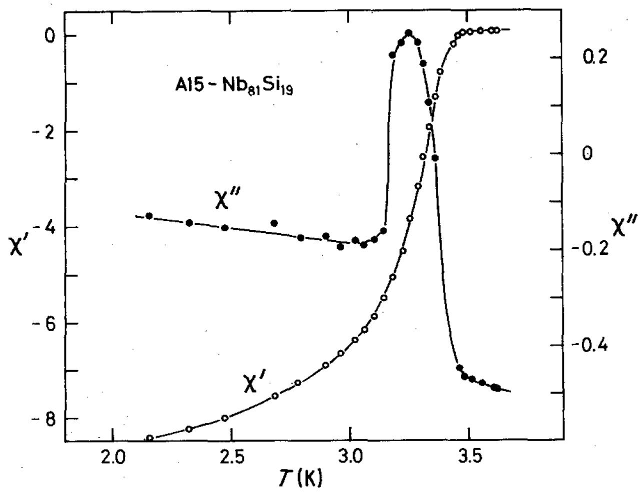

Figure 11 A.c. susceptibility of the A15 phase formed in the $Nb_{81}Si_{19}$ alloy plotted as a function of temperature showing superconducting transition. χ' and χ'' represent the real and imaginary parts of the suceptibility.

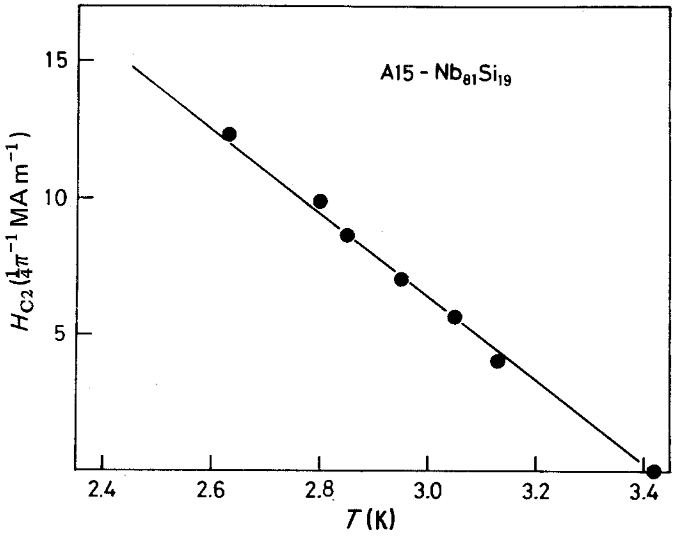

Figure 12 Upper critical field of the A15 phase formed in the $Nb_{81}Si_{19}$ alloy plotted as a function of temperature.

4.3. High-pressure annealing of amorphous alloys as a novel method of synthesizing new crystalline phases

During the past several decades, various attempts have been made to synthesize new materials using high-pressure techniques. Success in synthesizing diamonds is a well-known example. For the two-component systems, however, there are difficulties which are not encountered in one-component systems. In order to prepare an A_3B compound, a mixture of the component materials A and B is usually compressed in the ratio of 3:1 and, simultaneously, the temperature is raised. This method of synthesis was actually used by Lèger and Hall [20] with the intention of obtaining A15-Nb_3Si. However, even if the temperature was raised as high as 2000° C, the reaction was always incomplete and unreacted niobium remaind, in addition to the reacted materials and, in this particular case, the A15-type structure could not be detected in the reacted materials. The incomplete reaction was probably due to the limited rate of atomic diffusion and it would take a prohibitively long time to complete the reaction. Another way of obtaining the compound is to induce the transformation in the starting materials which has the same composition as that of the compound. Waterstrat *et al.* [14] annealed the tetragonal Nb_3Si under pressure with the aim of converting it into the A15-Nb_3Si, but this attempt was unsuccessful. The stable crystalline phase is in general located at the deep minimum in the energy space and there always exists a potential barrier across which the transformation must proceed.

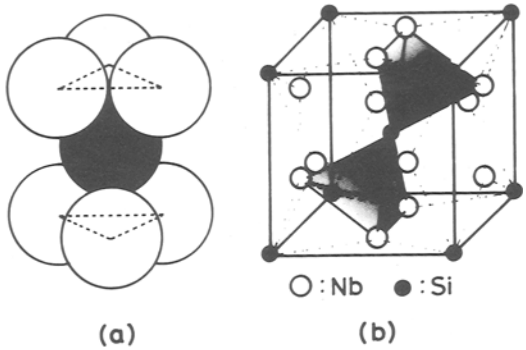

Figure 13 (a) M_6X structural unit frequently found in amorphous V_a–IV_b alloys. Open circles represent group V_a atoms and solid circles represent group IV_b atoms (after [17]). (b) The structure of A15-Nb_3Si and the M_6X structural unit found in the amorphous state.

On the other hand, if one uses the amorphous binary alloys as the starting materials, the two kinds of atom are already mixed on an atomic scale and the heterogeneity in the reacted materials is negligibly small, provided that the composition of the amorphous alloy does not deviate much from that of the compound. Moreover, the amorphous state is metastable and easily transforms into the crystalline state upon heating. Pressure works as a guide to produce denser crystalline phases.

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References

1. H. IWASAKI and T. MASUMOTO, *J. Mater. Sci.* **13** (1978) 2171.
2. W. K. WANG, H. IWASAKI and K. FUKAMICHI, *ibid.* **15** (1980) 2701.
3. C. SURYANARAYANA, "Rapidly Quenched Metals – A Bibliography 1973-1979" (IFI Plenum, New York, 1980).
4. T. MASUMOTO, A. INOUE, S. SAKAI, H. KIMURA and A. HOSHI, *Trans. JIM* **21** (1980) 115.
5. "Metals Handbook" Vol. 8, 8th Ed (American Society for Metals, Metals Park, Ohio, 1973) p. 283.
6. L. GOLD, *Phys. Stat. So.* **4** (1964) 261.
7. D. DEW-HUGHES, *Cryogenics* **15** (1975) 435.
8. V. M. PAN, V. P. ALEKSEEVSKII, A. G. POPOV, Yu. I. BELETSKII, L. M. YUPKO and V. V. YAROSH, *JETP Lett.* **21** (1975) 228.
9. E. L. HASSE and O. MEYER, *IEEE Trans. Mag.* **17** (1981) 541.
10. B. OLINGER and L. R. NEWKIRK, *Sol. Stat. Commun.* **37** (1981) 613.
11. R. M. WATERSTRAT, F. HAENSSLER and J. MÜLLER, *J. Appl. Phys.* **50** (1979) 4763.
12. K. TOGANO, H. KAWAMURA and K. TACHIKAWA, *Phys. Lett.* **76A** (1980) 83.
13. C. SURYANARAYANA, W. K. WANG, H. IWASAKI and T. MASUMOTO, *Sol. Stat. Commun.* **34** (1980) 861.
14. R. M. WATERSTRAT, F. HAENSSLER, J. MÜLLER, S. D. DAHLGREN and J. C. WILLIS, *J. Appl. Phys.* **49** (1978) 1143.
15. G. R. STEWART, L. R. NEWKIRK and F. A. VALENCIA, *Phys. Rev.* **B20** (1979) 3647.
16. D. DEW-HUGHES, *IEEE Trans. Mag.* **15** (1979) 490.
17. G. S. CARGILL III, in "Liquid and Amorphous Metals", edited by E. Lüsher and H. Coufal (Sijthoff and Noordhoff, Alphen aan den Rijn, 1980) p. 161.
18. R. H. HAMMOND and S. HAZRA, in Proceedings of the Low Temperature Conference, Boulder, Colorado, 1972, edited by K. D. Timmerhause, W. J. O'Sullivan and E. F. Hammel (Plenum Press, New York, 1974) p. 465.
19. G. R. STEWART, B. OLINGER and L. R. NEWKIRK, *Sol. Stat. Commun.* **39** (1981) 5.
20. J. M. LÈGER and H. T. HALL, *J. Less-Common Met.* **32** (1973) 181.

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