JOURNAL OF MATERIALS SCIENCE 12 (1977) 975–981

The superconducting properties and structure of Nb_3Ga

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The influence of composition and heat-treatment on the superconducting transition temperature, T_c, of Nb_3Ga has been studied. A complementary structural investigation of the alloys was carried out using X-ray diffraction to determine the degree of long-range order and the proportions of the phases present. It was found that the greater the deviation from stoichiometry, and the more disordered the Nb_3Ga, the lower were the T_c values. The superconducting transition temperature was maximized by producing a non-equilibrium structure of essentially fully ordered, near-stoichiometric Nb_3Ga.

1. Introduction

The intermetallic compound Nb_3Ga has the A15 structure and exists over a range of composition on the Nb-rich side of stoichiometry [1, 2]. The width of the Nb_3Ga phase field is constant (21.0 to 24.5 at.% Ga) up to 1200° C, and then increases towards higher gallium values, e.g. at 1600° C the homogeneity range is from 22.0 to 25.5 at.% Ga [2].

Superconductivity in Nb_3Ga was first observed by Wood *et al.* [3]; the transition temperature, T_c, was found to be 14.5 K. Since then a number of workers have measured transition temperatures but the most extensive investigation of the superconducting properties of Nb_3Ga has been carried out by Webb and co-workers [4–6]. Their measurements of the upper critical field H_{c2} as a function of temperature have shown Nb_3Ga to compare favourably with other high field superconductors such as Nb_3Sn, Nb_3Al and $Nb_3(Al, Ge)$, e.g. H_{c2} for Nb_3Ga was 33.6 Tesla at 4.2 K. They also reported superconducting onsets, measured inductively, as high as 20.3 K with transition widths as low as 0.7 K. In general it has been found that high transition temperatures are obtained when Ga-rich Nb_3Ga is quenched from above the liquidus and is then given a low temperature anneal of typically 24 h at 700° C [4, 5, 7]. The explanation put forward for the effect of heat-treatment on T_c was, unfortunately, based on an erroneous phase diagram and furthermore the degree of long-range order of the Nb_3Ga was not taken into account.

In the stoichiometric compound, A_3B, the A atoms form three mutually orthogonal chains parallel to the edges of the unit cell. It has been suggested [8] that this crystallographic arrangement provides favourable conditions for superconductivity as the squeezing together of the A atom chains implies an anisotropic density of states, and a high electron–phonon interaction. Either of these factors may lead to a high T_c. Although it is not fully understood why particular alloys have high T_cs, it has been shown that the integrity of the A atom chains is important. Matthias *et al.* [9] were able to show that in Nb_3Sn there was a relationship between the superconducting properties of Nb_3Sn and the regularity of the Nb atom chains.

Disruption of the A atom chains may occur by deviations from stoichiometry. The excess A or B atoms in non-stoichiometric alloys are accommodated by the introduction of either vacancies or anti-structure atoms, i.e. A atoms on the B sublattice or vice versa. The disruption of the A atom chains may be increased further than that required by non-stoichiometry by a decrease in the degree of long-range order. This applies to both stoichiometric alloys and non-stoichiometric alloys and the mechanisms for disorder are similar to those mentioned for accommodating non-stoichiometry, namely, the interchange of A and B atoms to pro-

duce anti-structure atoms (interchange disorder [10, 11]) or the creation of vacancies on the A or B sublattice (vacancy disorder [12, 13]).

This paper reports the results of an investigation into the effect of heat-treatment and composition on the superconducting transition temperature of Nb_3Ga. The transition temperature is correlated with the degree of non-stoichiometry and the degree of long-range order, as measured by X-ray diffraction.

2. Experimental procedure

2.1. Materials

The preparation of the alloys will only be briefly described as a detailed account has been previously published [2]. Two-phase alloys with compositions close to the Nb-rich and Ga-rich phase boundaries of Nb_3Ga were prepared by arc melting presintered Nb–Ga powder compacts. The percentage of Nb_3Ga in the two-phase samples was approximately 90%. The casts were homogenized at 1600° C for 24 h in an argon stream. Samples were then wrapped in molybdenum foil to help to prevent contamination, sealed in silica capsules under an argon atmosphere, and heat-treated for appropriate times in order to attain equilibrium at temperatures in the range 700 to 1600° C. All heat-treatments were terminated by quenching into cold water.

In addition, a series of specimens was produced in order to study the superconducting properties and the development of long-range order as a function of annealing time. The specimens were cut from an arc-cast Ga-rich specimen and annealed for times in the range 12 to 505 h at 700° C.

2.2. X-ray diffraction

X-ray diffraction was used to measure the lattice parameters and long-range order parameters of the A15 phase in the alloys. A Philips Diffractometer with Cu$K\alpha$ radiation and a graphite monochromator was used. The lattice parameters were obtained from the peaks lying within the 2θ angular range 100° to 135°, namely 520, 521, 440, 600, 610 and 611 peaks. A counting technique was used to measure the relative intensity of the 320 and the 321 peaks. The ratio of these two peak intensities was used to find the degree of long-range order of each sample. Similarly the proportion of Nb_5Ga_3 in the samples was obtained by measuring the relative intensity of the 211 peak of Nb_3Ga and the 112 peak of Nb_5Ga_3, which has an oxygen stabilized Mn_5Si_3 type structure. These data were used in conjunction with the calculated structure factors to determine the percentage of Nb_5Ga_3 present.

2.3. Transition temperature measurements

The superconducting measurements were carried out at AERE Harwell. Continuous transition curves were plotted by measuring the change in inductance of a coil when the permeability of the material it contains suddenly changes as its temperature goes through its superconducting transition temperature against the output of a gold–iron/constantin thermocouple [14]. The specimens for the T_c measurements were small pieces, typically 0.1 to 0.2 g from the annealed samples. These were placed in one coil, and a piece of niobium wire, as an internal standard placed in the other to ensure good accuracy in the measurements. The coils were connected as the arms of an a.c. bridge. The superconducting transition temperature was taken as the temperature at which the onset of superconductivity occurred.

3. Results and discussion

3.1. Order–disorder in Nb_3Ga

It is impossible to unambiguously distinguish between interchange or vacancy order–disorder mechanisms from X-ray intensity measurements. However, it has been previously shown from lattice parameter data that non-stoichiometry in Nb-rich alloys takes place by the introduction of niobium antistructure atoms, i.e. niobium atoms on the gallium sublattice [2]. Consequently, it is not unreasonable to assume that disorder occurs by the interchange mechanism.

The normal Bragg–Williams long-range order parameters for the A(Nb) and B(Ga) sites are given by:

$$S_A = \frac{r_A - X_A}{1 - X_A}$$

$$S_B = \frac{r_B - X_B}{1 - X_B}$$

where r_A is the fraction of A atom sites occupied by A atoms, r_B is the fraction of B atom sites occupied by B atoms, and X_A and X_B are the atomic fractions of A and B. For stoichiometric alloys the Bragg–Williams long-range order parameter is satisfactory, and $S_A = S_B$ if the interchange mechanism is operative. For non-stoichiometric alloys $S_A \neq S_B$ and the parameters are a measure

of disordering due to both non-stoichiometry and the break-down of long-range order.

A more convenient measure of long-range order in non-stoichiometric alloys has been proposed by van Reuth and Waterstrat for interchange disorder in A15 compounds [15]. They redefined the state of full order to that corresponding to the maximum amount of ordering possible considering the degree of non-stoichiometry. In a binary non-stoichiometric alloy this simply means that the sublattice which can never be completely filled by one type of atom, is assigned a long-range order parameter of 1 when the position is filled to the maximum extent permitted by the degree of non-stoichiometry. In this situation the other sublattice must be completely filled with the other atomic species and its order parameter would, therefore, also correspond to unity. Thus by redefining the long-range order parameter in this manner, a single parameter suffices to describe the extent of long-range order on both sublattices as it varies from random occupancy to complete ordering.

The Bragg-Williams parameters are related to the single long-range order parameter S' by:

$$S_A = K_A S' \quad \text{and} \quad S_B = K_B S'$$

where K_A and K_B are constants which depend on the degree of non-stoichiometry. In this study, as only deviations on the niobium side of stoichiometry were found, $K_A = 1$. The phase field of Nb_3Ga was assumed to be of constant width, from 21.0 to 24.5 at.% Ga; the boundary compositions are termed Nb-rich and Ga-rich respectively. The corresponding values for K_B were calculated to be 0.80 and 0.97 for the Nb-rich and Ga-rich alloys respectively.

The long-range order parameters for Nb-rich and Ga-rich Nb_3Ga as a function of annealing temperature are presented in Figs. 1 and 2. Because of the errors involved in measuring intensities, there is an uncertainty in the values for S' of approximately 5%.

For both degrees of non-stoichiometry there are similarities in the variation of the long-range order parameter with temperature. The main feature is that S' has a value of unity up to and including 900° C and then decreases rapidly with increasing temperature reaching 0.75 to 0.8 at 1300° C. The apparent increase in S' to approximately 0.85 at 1600° C is considered to be a consequence of assuming the limits of the Nb_3Ga phase field are constant at 21.0 and 24.5 at.% Ga. Previous work has shown that at 1600° C the phase boundaries are nearer to 22.0 and 25.5 at.% Ga [2]. If this is taken into account the long-range order parameter at 1600° C is reduced and hence it is concluded that S' is constant, within experimental error, over the temperature range 1300 to 1600° C.

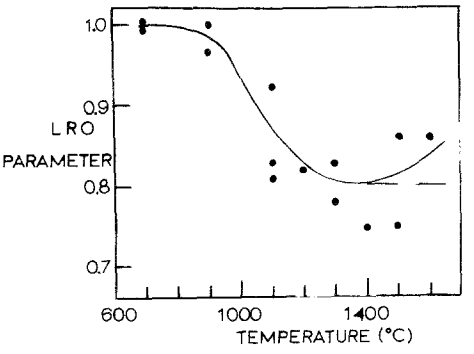

Figure 1 The long-range order parameter as a function of annealing temperature for Nb-rich Nb_3Ga.

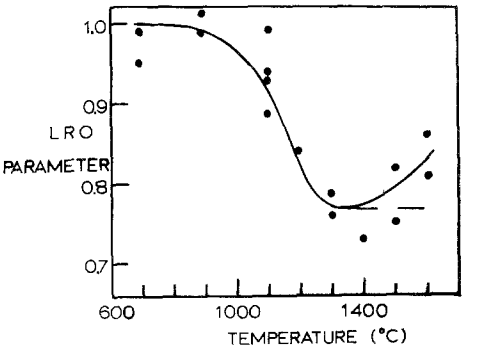

Figure 2 The long-range order parameter as a function of annealing temperature for Ga-rich Nb_3Ga.

The observation that annealing below 900° C is necessary to maximize S' is in agreement with the general observation that a low temperature anneal maximizes the degree of long-range order in A15 compounds, e.g. V_3Au [16] and Nb_3Al [11]. In fact the behaviour of Nb_3Ga is very similar to that observed by Fluckiger *et al.* [16] in V_3Au. They found that the long-range order parameter of Au-rich samples was constant at approximately 0.84 for annealing temperature above 1000° C, but increased rapidly at lower temperatures reaching a maximum of 0.94 at 600° C.

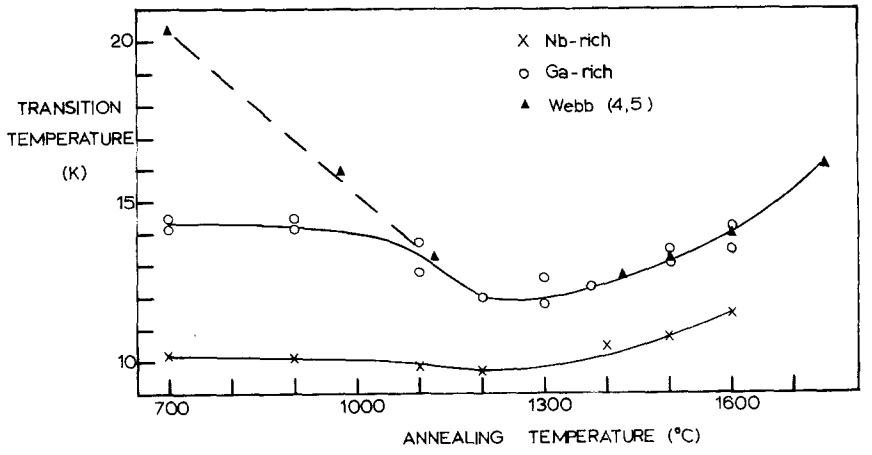

Figure 3 The effect of annealing temperature on the superconducting transition temperature of Nb-rich and Ga-rich Nb_3Ga.

3.2. Superconducting transition temperatures

The effect of annealing on the superconducting transition temperature T_c of Nb-rich and Ga-rich Nb_3Ga is shown in Fig. 3, together with the results of Webb *et al.* [4, 5] for Ga-rich samples. The T_c values for the Nb-rich are lower than for the Ga-rich although both show a similar dependence on the annealing temperature, i.e. T_c falls with decreasing temperature in the range 1600 to 1300° C but then increases with a further decrease in temperature down to 700° C.

The Nb-rich and Ga-rich specimens are both on the niobium side of stoichiometry, hence the Nb-rich specimens are the most non-stoichiometric. The lower T_c values for these specimens is a direct consequence of the larger number of niobium anti-structure atoms. By occupying the gallium sublattice the niobium anti-structure atoms disrupt the integrity of the niobium sublattice chains and so degrade T_c. The fall in T_c as the annealing temperature is reduced from 1600 to 1300° C is also associated with the degree of non-stoichiometry as, according to the previously determined phase diagram, Nb_3Ga is more Nb-rich at 1300° C. These results, together with other data on A15 compounds (e.g. V_3Ga [17]) suggest that the highest T_c should correspond to the stoichiometric composition and that any deviation from stoichiometry leads to a degradation of T_c.

The increase in T_c on annealing below 1300° C can be correlated with the increase in long-range order of the material, and a slight decrease in a_0 from 5.177 to 5.176 Å for Ga-rich and 5.184 to 5.183 Å for Nb-rich. In Fig. 4 there are shown plots of S' against T_c for Nb-rich and Ga-rich material annealed below 1300° C. The increase in T_c with increasing degree of long-range order is linear in both cases. The degree of order has only a very small effect on T_c for Nb-rich specimens because of the much more disruptive influence of the large number of niobium anti-structure atoms already present due to non-stoichiometry. Sahm and Pruss [18] observed a similar increase in T_c on annealing Al-rich Nb_3Al. The transition temperature of Nb_3Al annealed at 1100° C was 16.7 K but this was increased to 18.5 K by reducing the annealing temperature to 750° C.

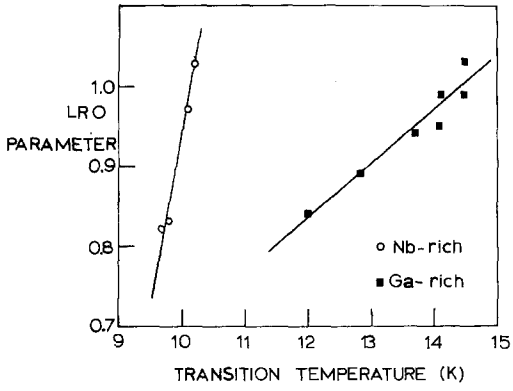

Figure 4 Graph showing a linear relationship between T_c and the degree of long-range attained on annealing at temperatures below 1300° C.

The variation of transition temperature of the Ga-rich material with annealing temperature is in good agreement with that of Webb *et al.* [4, 5] above 1100° C. The discrepancy below 1100° C

lies in the nature of the thermal history of their specimens. Their short time, low temperature anneal subsequent to quenching from above the liquidus does not produce the low temperature equilibrium state of Nb_3Ga. Instead the degree of long-range order is maximized for Nb_3Ga of the high temperature composition, which corresponds approximately to the stoichiometric composition. Thus these specimens would be expected to have high superconducting transition temperatures. This point is discussed further in Section 3.3.

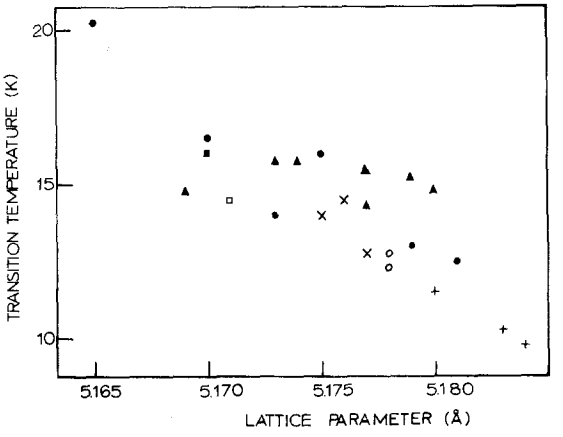

Figure 5 Superconducting transition temperature against lattice parameter for Nb_3Ga of varying compositions and thermal histories.
Ga-rich: • Webb and co-workers [4, 5]
▪ Otto [20]
▫ Wood *et al.* [3]
Vapour deposited: ○ Webb and co-workers [4, 5]
▲ Johnson and Douglass [19]
This study: × Ga-rich
\+ Nb-rich

T_c data obtained in this study and by other workers [3, 4, 5, 19, 20] are plotted against the lattice parameter of Nb_3Ga in Fig. 5. The general trend is that the smaller the lattice parameter (i.e. the higher the degree of long-range order and/or the lower the niobium content) of Nb_3Ga the higher the transition temperature. Similar relations between T_c and lattice parameter have been observed in other A15 compounds where B is a non-transition element, e.g. Nb_3Sn, Nb_3Al and V_3Ga [21].

From Fig. 5 it can be seen that, on the whole, the transition temperatures measured in this study are slightly lower than those reported previously. This may, in part, be due to the lack of equilibrium in the specimens of some of the previous workers. On the other hand, it is known that the oxygen content of the present alloys is relatively high [2] and it is probable that this has a detrimental effect on T_c.

3.3. The development of long-range order with time

The variation of S', T_c and a_0 of Ga-rich Nb_3Ga, and the percentage of Nb_5Ga_3 present, with annealing time at 700° C for an arc cast 26.5 at.% Ga alloy is given in Fig. 6. The composition of the Nb_3Ga was assumed to be 25.0 at.% Ga in the calculation of the long-range order parameter.

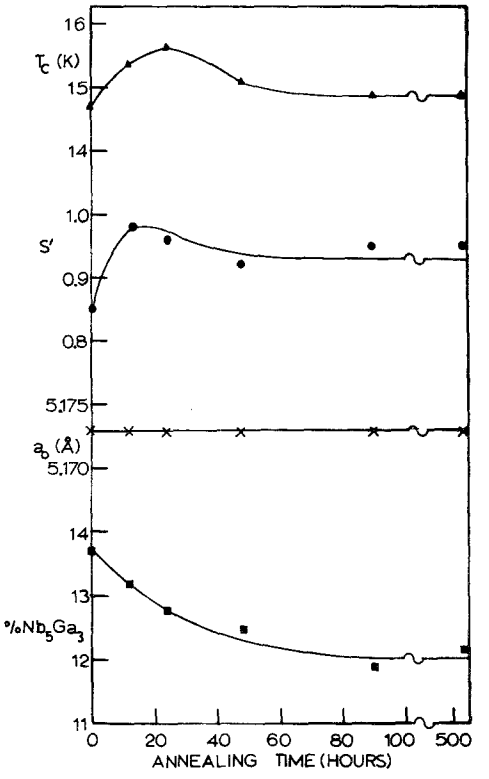

Figure 6 The effect of annealing time at 700° C on the superconducting transition temperature, long-range order parameter and lattice parameter of Nb_3Ga, and the proportion of Nb_5Ga_3 present, in a Nb–26.5 at.% Ga alloy.

Fig. 6 shows that T_c and S' both reach a maximum after about 24 h and then gradually decrease at longer annealing times. The incremental change in T_c to the maximum is 1.0 K; this is a smaller change than might have been expected from previous work on Nb_3Ga and other A15 compounds and is probably associated with the high oxygen content of the alloys used in this investigation.

The maximizing of the transition temperature of V_3Au [16] and Nb_3Al [11] by low tempera-

ture anneals has been discussed in terms of two opposing processes, namely ordering and the precipitation of a second phase. As shown in the previous section, ordering acts to raise T_c, whereas the precipitation of a second phase with the corresponding increase in degree of non-stoichiometry of the A15 phase acts to decrease T_c.

In the present case of Nb_3Ga, it is clear that the increase in T_c at short annealing times is, in part, attributable to the increase in the degree of long-range order. However, there is also a significant initial reduction in the proportion of Nb_5Ga_3 with time. The arc-cast material consists of cored Nb_3Ga in an eutectic matrix and it is the solution of gallium into the primary Nb_3Ga crystals to facilitate the removal of the coring that leads to the decrease in the amount of Nb_5Ga_3 present. The primary Nb_3Ga crystals become homogeneous and approach the stoichiometric composition; this process would, therefore, also favour high T_c values. These local rearrangements (i.e. ordering and removal of coring) which occur at short times may well be aided by an excess vacancy concentration produced by the rapid cooling from the liquid state.

After 24 h there is little change in the percentage Nb_5Ga_3 present and the transition temperature gradually falls closely following the time dependence of S'. Undoubtedly slight adjustments in the composition of the Nb_3Ga takes place in this time period but unfortunately these are difficult to monitor. As can be seen from Fig. 6, lattice parameter measurements are not sensitive enough to changes in composition to detect these relatively small compositional adjustment (a change in gallium content of 1 at.% alters the lattice parameter by only 0.002 Å, which is of the order of the experimental error in the X-ray determination).

Kohr *et al.* [11] have examined the effect of annealing at 750° C on the superconducting properties and structure of a two-phase (Nb_3Al, Nb_2Al) niobium–aluminium alloy. Their results were similar to those observed for niobium–gallium in that a maximum T_c occurred after a short annealing time of 48 h, which corresponded to a maximum in the degree of long-range order and a minimum in the proportion of the second phase. At longer annealing times (100 h) the proportion of Nb_2Al increased and T_c fell. Equilibrium would have eventually been reached in the present investigation if the anneal had been continued for longer than 505 h so that sufficient diffusion could have taken place for gross structural changes. Equilibrium would have been attained by the precipitation of Nb_5Ga_3 and by the reduction of the Ga-content of the Nb_3Ga to 24.5 at.%. As the equilibrium Nb_3Ga at 700° C is non-stoichiometric T_c will fall. Thus, it is clear from the present results, and those of Kohr *et al.*, that for a low temperature anneal to be beneficial the temperature must be such that ordering and local homogenization occurs more rapidly than precipitation of a second phase and attainment of the equilibrium microstructure.

4. Conclusions

(1) High annealing temperatures (> 1300° C) produce partial order ($S' \sim 0.8$) in both Ga-rich and Nb-rich Nb_3Ga. However, full order is obtained if the anneal is carried out at 900° C or below.

(2) The superconducting transition temperature T_c is less for Nb-rich than for Ga-rich Nb_3Ga, due to the greater degree of non-stoichiometry of the former.

(3) For a given degree of non-stoichiometry the transition temperature increases with increasing degree of long-range order. The dependence of T_c on S' is less marked for the Nb-rich Nb_3Ga because of the large number of niobium anti-structure atoms already present due to non-stoichiometry.

(4) T_c is maximized by annealing for a short time (24 h) at a low temperature (700° C).

This critical low temperature anneal does not produce the equilibrium structure but maximizes the degree of long-range order in near-stoichiometric Nb_3Ga.

Acknowledgements

The authors are very grateful to Dr J. Lee (AERE Harwell) for providing the facilities for transition temperature measurements and to his staff, Mr R. Bett, Mr A. Jeffreys and Dr J. P. Charlesworth for their assistance. The provision of research facilities by Professor J. G. Ball is acknowledged together with the financial support of the Science Research Council and the Metallurgy and Materials Science Department of Imperial College.

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Received 5 August and accepted 31 August 1976.