Phase Relations and A15-Phase Diffusion Layer Formation in the System Ag-Nb-Ga

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Nb₃Ga layers can be synthesized by diffusion from Ag-Ga alloys at 1100°C. This is consistent with the hypothesis that the orientation of two-phase tielines in a ternary system, such as Ag–Nb–Ga, play an important role in determining whether superconducting layer formation will occur. Although the superconducting transition onset was 12.3 K, the Nb₃Ga layer growth rates in this system are too slow for practical application. Chemical modification of the phase diagram however does appear to be a feasible approach for promoting the diffusion synthesis of A15 phase layers for multifilamentary conductors.

SOLID state synthesis is a key step in the fabrication of high Tc multifilamentary superconductors. Our recent studies of the Cu-Nb-Ge and Cu-Nb-Sn systems suggest that phase diagram geometry plays an important role in determining whether superconducting β phase (A15 structure) layers can be made by the bronze diffusion technique. Briefly, we found that the β phase formed in bronze-Nb diffusion couples so long as the tieline sequence bronze-β-Nb was stable in the respective ternary system. If, however, no two-phase tielines connected the bronze and β phases, the diffusion path followed an alternate route through other phase fields in the system, and the β phase did not appear in the diffusion couple. We suggested that chemical modification or replacement of the bronze with another element could favorably modify the phase relations to promote the existence of the required tielines. The approach, in fact, does work: β-Nb₃Ga layers form by diffusion when Ag is substituted for Cu in the Cu-Nb-Ga system. The phase relations and diffusion layer formation in the Ag-Nb-Ga system at 1100°C are described below.

EXPERIMENTAL PROCEDURE

We determined the condensed phase assemblages in the Ag-Nb-Ga system via silica tube quenching experiments of the type described in detail previously. Heat treatment times ranged from 700 to 900 h at 1100°C. Ag (ASARCO, 99.999 pct), Ga (Alusuisse, 99.999 pct), and Nb (Kawecki Berylco, 99.85 pct) were the starting materials for all runs.

The cylindrical diffusion geometry used in our previous experiments was again adopted for the 1100°C experiments. Two terminal compositions for the "bronze" phase were investigated—Ag-12 pct Ga and Ag-1.5 pct Ga. The master alloys were levitation melted, cast in pin molds, then homogenized for 300 h at 700°C. The alloy inserted into a 0.4 cm hole in a Nb cannister, formed the ternary diffusion couple. A limited number of lower temperature experiments were conducted on Nb-bronze composite wires fabricated by drawing Nb cylinders in which the Ag-Ga alloys had been imbedded.

Phase identifications were made by standard metallographic, electron microprobe, and Debye-Scherrer X-ray diffraction (Ni filtered, CuKα radiation) analyses. The diffusion layer thicknesses were measured with a micrometer eyepiece on polished longitudinal sections through the diffusion couples.

RESULTS AND DISCUSSION

The 1100°C phase relations deduced from our experiments are depicted in Fig. 1. Considerable controversy exists over the number and composition of the phases in Nb-Ga system. We adopted the recent results of Ashby and Rawlings and Fleschotte and Spitz for the Nb₃Ga phase boundaries. Our diagram was drawn to give the best fit to the X-ray, metallographic, and microprobe analysis of the runs studied. According to the microprobe analyses the composition of the 5/3 phase ranges from 36 to 39

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pct Ga, in fair agreement with Ref. 4. We detected no Ag in either the \(\beta\) or Nb\(_3\)Ga\(_3\) (5/3) phases thus ternary extensions of these fields are not shown. The presence of the \(\beta\) phase was deduced primarily from Debye-Scherrer X-ray patterns which could be indexed on the basis of a cubic cell (Cr\(_3\)Si-type). X-ray patterns for the 5/3 phase were best indexed according to the hexagonal modification of Nb\(_5\)Ge\(_3\) (Mn\(_3\)Si\(_3\) type) suggested by Asby and Rawlings. Devitrification of the silica tubes used for the quenching experiments prevented the collection of reliable data from samples containing more than about 60 pct Ga. The Ga-rich portion of the diagram, therefore, remains incomplete.

The most significant aspects of the diagram are the tielines connecting the \(\beta\) and L phases and the wide extent of the 5/3 + L phase field. The presence of the \(\beta + L\) field signifies that it should be possible to synthesize \(\beta\) phase by diffusion; the extensive intrusion of the 5/3 + L field suggests that—except for the most Ga-deficient liquids—the diffusion couples should contain Nb\(_5\)Ga\(_3\) as well as \(\beta\).

The results portended by the Ag-Nb-Ga phase diagram were borne out of the diffusion experiments at 1100°C. For diffusion times up to almost 1800 h, the Nb/Ag-12 pct Ga diffusion couples always contained two layers sandwiched between the quenched Ag-Ga liquid phase and the Nb jacket. Fig. 2. X-ray patterns of the material comprising the layers indicated that both the \(\beta\) and 5/3 phases were present. Microprobe analysis on one couple gave the composition of the dark layer adjacent to the Ag-Ga phase as 64 pct Nb-36 pct Ga (+1 pct), a value close to the Nb-rich phase boundary for the 5/3 phase. The light layer was difficult to analyze precisely because it was relatively thin; a composition of 83 pct Nb-17 pct Ga (+3 pct) was determined. For this sample the superconducting transition onset measured inductively was 12.3 K and the transition width was 1.6 K. The \(\Tc\) value for stochiometric Nb\(_5\)Ga\(_3\) is as high as 20.7 K, so that the above figure of 12.3 K is certainly consistent with an off-stoichiometric composition. The fairly wide 1.6 K transition width might also be expected for a diffusion layer with a composition gradient across it.

When the composition of the Ag-Ga phase was reduced to 1.5 pct Ga, the diffusion couples contained only one layer. Even after 600 h at 1100°C, however, the layer remained relatively nonuniform and less than 2 \(\mu\)m in thickness. For this reason we were unable to obtain microprobe or X-ray data sufficiently reliable for phase identification. The disappearance of the second layer from the diffusion couples is consistent with the phase relations of the system, Fig. 1, which suggest that for low Ga contents, tielines should follow the sequence Ag(Ga)-\(\beta\)-Nb. In this case only one diffusion layer, \(\beta\)-Nb\(_5\)Ga\(_3\), would be expected.

If layer growth is diffusion controlled, then the thickness of the layers in the diffusion couple should increase in proportion to \(t^{1/2}\) at any given temperature \(t\) (the reaction time). Our data for the \(\beta\) and 5/3 layers formed from the Ag-12 pct Ga couples, Fig. 3, fit the parabolic thickening law within experimental error (the scatter in thickness data for the 5/3 phase is larger than for the \(\beta\) phase because the rough Ag(Ga)-5/3 interface is difficult to locate precisely, \(\text{v}iz.,\) Fig. 2). What is notable about the data in Fig. 3 is the rather small layer thicknesses exhibited by both the \(\beta\) and 5/3 phases even after prolonged diffusion times. For example, after 170 h at 1100°C, the Nb\(_5\)Ge\(_3\) phase would be about 3.5 \(\mu\)m thick. In contrast, a Nb\(_5\)Ge\(_3\) layer 60 \(\mu\)m thick formed at 1100°C from a Cu-11.8 pct Ge bronze in the same length of time.\(^1\) \(\beta\)-Nb\(_3\)Sn layers 3 to 5 \(\mu\)m in thickness readily grow at 700°C.\(^1\) Comparable time periods at 1100°C would produce Nb\(_5\)Ga\(_3\) layers less than 2 \(\mu\)m thick in the Ag-12 pct Ga/Nb couples. After 700 h at about 710°C we could detect no layer formation in our Ag-12 pct Ga/Nb wire composites. Thus, even though Nb\(_5\)Ga\(_3\) can be synthesized by diffusion from Ag-Ga solutions, layer growth appears too slow to be amenable to practical application.