JOURNAL OF MATERIALS SCIENCE 12 (1977) 1759–1763

V_3Si formation by the bronze process

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Previous studies of the reaction between V and Cu(Si) solid solutions have reported that the V_3Si layers formed are much thinner than the accompanying V_5Si_3 layers. We have found that, although V_5Si_3 layers are formed for matrix compositions at least as low as 1 at. % Si, the proportion of V_3Si produced increases as the Si concentration in the matrix decreases. Furthermore, if the total proportion of Si to V in the composite is kept sufficiently low, the V_5Si_3 formed is eventually converted to V_3Si. Results are discussed in terms of a proposed partial Cu–V–Si phase diagram.

1. Introduction

There has been considerable interest in means of producing practical superconducting materials based on A-15 compounds of high critical temperature, which include Nb_3Sn, V_3Ga, V_3Si, Nb_3Ge, Nb_3Al, and Nb_3Ga. Current commercial processes for the production of muitifilamentary Nb_3Sn or V_3Ga are based on the reactions between Nb or V filaments and matrices of Cu(Sn) or Cu(Ga) solid solutions, the so-called "bronze" process. [1, 2]. Although direct reactions between Nb and Sn or between V and Ga at temperatures below about 900° C preferentially produce more Sn-rich or Ga-rich compounds, reactions with the copper solid solutions produce only Nb_3Sn or V_3Ga. Apparently the chemical activity of Sn or Ga in solid solution in Cu is insufficient to produce the more Sn-rich or Ga-rich compounds.

Attempts have also been made to produce V_3Si by the bronze process, i.e. by reaction between V and Cu–Si alloys. [3–5]. However, for Si contents ranging from 5 to 30 at. %, the primary reaction layer has been found instead to be V_5Si_3. A much thinner layer of V_3Si is found between the V and V_5Si_3, but long times at high temperatures are necessary for appreciable V_3Si growth, and this yields low critical-current densities. It was decided to study whether a further reduction of Si concentration would suppress V_5Si_3 and make V_3Si formation more favourable.

2. Experimental

The conductor initially studied (conductor *A*) was a composite wire about 0.25 mm in diameter, and consisted of a matrix of Cu–9.0 at. % Si containing 19 filaments of V about 20 μm in diameter. It had been prepared by extrusion and wire drawing from an original billet 2.86 cm in diameter. Another conductor of identical geometry was later prepared with a matrix of Cu–3.5 at. % Si (conductor *B*).

A portion of conductor *A* that had been only partially drawn was inserted in a copper tube and then co-drawn to produce a final composite (conductor *C*) with a 0.25 mm core equivalent to conductor *A*, surrounded by a copper sheath of 0.43 mm diameter. If we were to assume the Si in the core of conductor *C* to become uniformly distributed throughout both the core and sheath, the matrix Si concentration in conductor *C* would fall slightly below 3 at. %.

Short sections of monofilamentary conductors with matrix compositions of Cu–2.0 at. Si and Cu–1.0 at. % Si were also prepared by casting 2.54 cm copper alloy ingots around 0.64 cm diameter V rod and subsequently extruding these ingots to about 0.64 cm in diameter.

For some experiments, portions of conductors *A* and *B* were rolled to produce tapes 0.064 mm thick. Such deformation greatly flattens the V filaments, increasing the interface area available for chemical reaction and decreasing the times necessary for completion of the reaction.

Short lengths of the various conductors were sealed in evacuated quartz tubes and annealed for various times at temperatures from 700 to 900° C. Transverse sections were viewed by light microscopy. Several etches were used during the study, but an etch of 10 parts HF, 10 parts HNO_3, and 3 parts glycerine produced the best contrast between the reaction layers. Critical temperatures were measured resistively, using currents of about 30 mA.

3. Results

For conductor *A* (initial matrix composition 9 at.% Si), the thickness of the V_5Si_3 layer was always much greater than that of the V_3Si layer (e.g., Fig. 1a), as reported by earlier workers [3–5]. Although the thickness of both layers initially increased with time, as the reaction approached completion (as in tape annealed 11 days at 800° C), all the V and V_3Si was eventually converted into V_5Si_3.

Conductor *C* consisted essentially of conductor *A* surrounded by a copper sheath. Annealing at 800° C and above resulted in rapid outward diffusion of Si into the copper sheath, lowering the matrix Si concentration. As a result, conductor *C* showed a thinner V_5Si_3 layer and thicker V_3Si layer than conductor *A* after the same reaction time (Fig. 1b). However, the copper sheath did not change the overall V/Si ratio in the conductor, and the total Si content therefore remained sufficient to convert all the V and V_3Si to V_5Si_3 at long reaction times.

In contrast, the composition chosen for conductor *B* was sufficient to convert most of the V to V_3Si, but insufficient to convert it to V_5Si_3. Initially, both reaction layers were formed, although the V_3Si layer was generally thicker than the V_5Si_3 layer (Fig. 1c). For late stages of reaction in the tape formed from this conductor, when the Si content of the matrix has fallen well below 1 at.%, the V_5Si_3 layer eventually disappeared and only a V_3Si layer remained (Fig. 1d).

The geometry of the monofilamentary conductors was such that the reaction could proceed without a significant drop in the matrix concentration of Si. It was found for both 1 and 2 at.% Si, at both 800 and 900° C, that although the reaction produced predominantly V_3Si, a thin V_5Si_3 layer still appeared between the Cu(Si) matrix and the V_3Si (Fig. 1e).

Microprobe measurements, primarily on conductor *C*, indicated that very little Cu was incorporated in either the V_5Si_3 or the V_3Si, in agreement with eariler workers [4]. Layer thicknesses were insufficient for precise determination of the stoichiometry of the reaction layers.

In conductor *A*, where the dominant reaction layer was V_5Si_3, voids were often seen in the matrix adjoining the filament, as reported earlier [3]. In conductor *B*, however, where the predominant reaction layer was V_3Si, voids appeared at the V–V_3Si interface, suggesting that Si may be the faster diffuser in V_5Si_3, but V may be the faster diffuser in V_3Si.

Where the thickness of the V_3Si reaction layer exceeded about 1 μm, the critical temperatures found in conductors, *A*, *B*, and *C* aged at 700 to 900° C were 16.4 to 16.7 K midpoint, with a transition width (90% to 10% transition) of 0.2 to 0.4 K. Transitions for thinner layers were lower and broader. These critical temperatures are consistent with earlier studies [3, 5].

4. Discussion

The results of diffusion reactions, such as the one studied here, are conveniently discussed in terms of the appropriate ternary phase diagram. We make the assumption that local equilibrium is approximately attained across the various interphase boundaries in the diffusion couples, and that compositions across such boundaries are approximately related by two-phase tielines in the equilibrium phase diagram.

The production of Nb_3Sn by direct reaction between Nb and Cu(Sn) thereby indicates the existence of a two-phase field in the Cu–Nb–Sn diagram with tielines linking the Nb_3Sn and Cu(Sn) phase fields. A recent determination of the Cu–Nb–Sn diagram [6] indeed shows such a two-phase field. (Two other Cu–Nb–Sn diagrams recently suggested [7, 8] are probably incorrect.) The production of V_3Ga by reaction between V and Cu(Ga) similarly indicates a two-phase field between the V_3Ga and Cu(Ga) phases, but no Cu–V–Ga phase diagram has yet been published.

The production of V_5Si_3 on the matrix side of the diffusion couples studied here indicates a two-phase field in the Cu–V–Si diagram linking the V_5Si_3 and Cu(Si) phase fields, extending down to Si concentrations at least as low as 1 at.% (Fig. 1e). However, the eventual disappearance of the V_5Si_3 in favour of V_3Si in tapes of conductor *B*

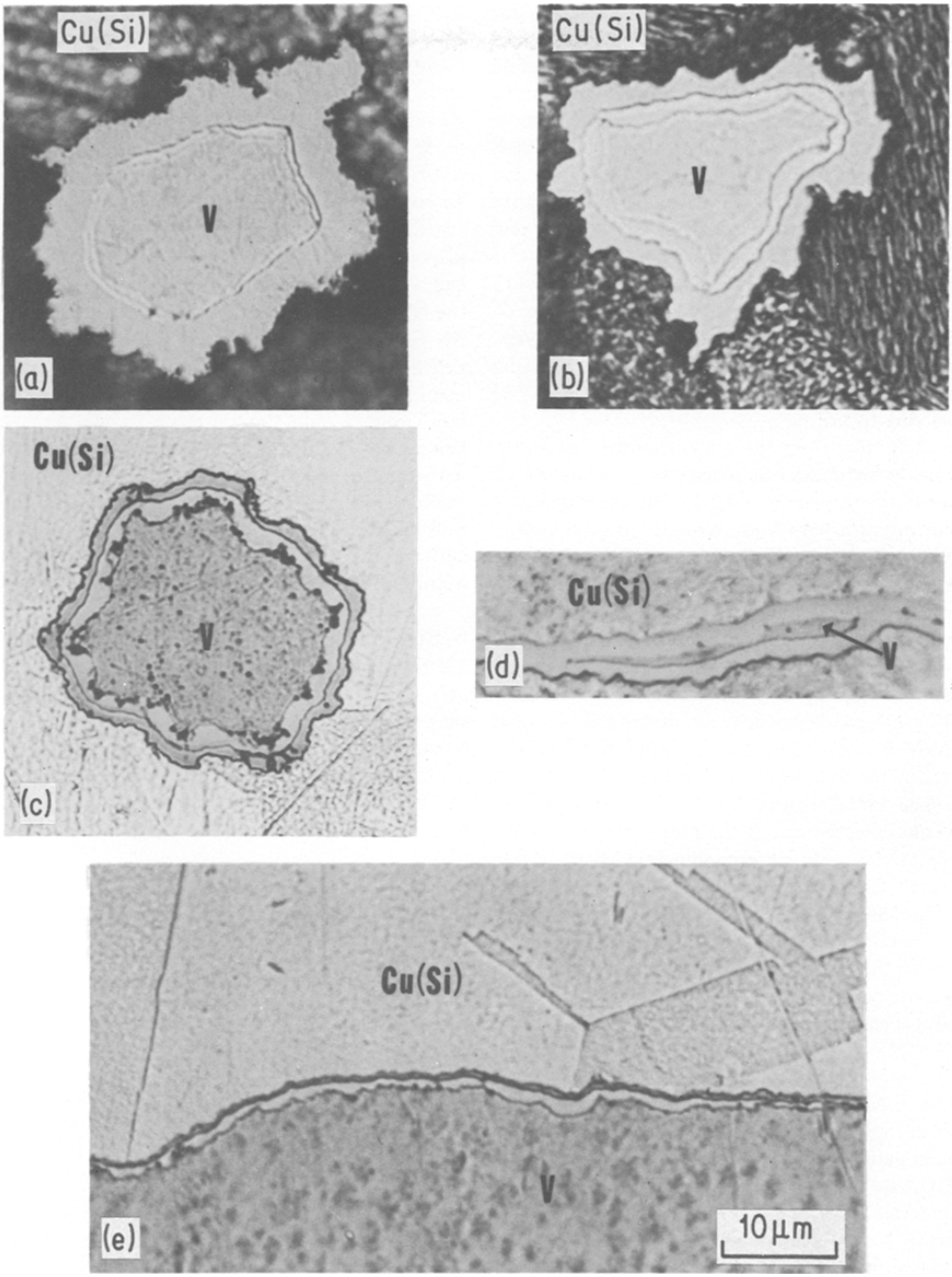

Figure 1 Reaction layers between V filamens and various Cu(Si) matrices after 21 h at 900° C. (a) Conductor *A* (9 at. % si); a very thin V_3Si layer within a thick V_5Si_3 layer. (b) Conductor *C*; copper cladding has lowered the average matrix Si concentration, and has resulted in an increase in the V_3Si layer thickness and a decrease in the V_5Si_3 layer thickness. (c) Conductor *B* (3.5 at. % Si); V_3Si layer is thicker than the V_5Si_3 layer. (d) Tape from conductor *B*; reaction is nearing completion (V nearly consumed) and reaction layer is now nearly all V_3Si. (e) Monofilamentary conductor with matrix of Cu–1 at. %. Si; reaction layer is mostly V_3Si, but a thin V_5Si_3 layer remains adjacent to the Cu(Si).

(Fig. 1d) indicates that a two-phase field also exists between V_3Si and Cu(Si) solid solutions of sufficiently low Si concentrations. A schematic representation of these inferred phase relations in the Cu-rich corner of the Cu–V–Si system is shown in Fig. 2. The points A, B, and C represent the overall compositions of conductors A, B, and C. Points A' and B' represent the initial matrix compositions of conductors A and B. Point C' represents the matrix composition of conductor C if the Si were distributed uniformly through both core and sheath. Although points A', B', and C' determine the nature of the initial reaction layers, points A, B, and C determine the equilibrium phase distributions which are approached at long reaction times.

It is clear from the present results that an extremely low matrix Si concentration would be required to completely avoid the formation of V_5Si_3 and produce only V_3Si. Kinetics in such a composite would be very slow and only a small volume fraction of V_3Si could be produced. A much more practical approach towards producing a multifilamentary V_3Si conductor appears to be that represented by conductor B. Although the initial matrix composition (B') produces V_5Si_3, the overall V/Si proportion in the composite is such that the V_5Si_3 eventually disappears in favour of V_3Si, as can be seen from the location of point B. A higher initial matrix composition (such as A') would be acceptable if the proportion of V in the composite were correspondingly higher, i.e., an overall composition such as point D.

In addition to possible technological promise, the development of a multifilamentary conductor containing V_3Si but not V_5Si_3 (e.g. tape from conductor B) will be useful in studying grain size–critical current relationships in V_3Si. Such data are desirable for comparison with similar data for Nb_3Sn [9] and V_3Ga [10] and for comparison with theories of grain-boundary pinning based on anisotropy of superconducting parameters, since basic data for this anisotropy exist for V_3Si [11]. Alternate means of producing V_3Si conductors include reactions between V and SiO_2 [12–14], between V and silicone [15], and between V and thin surface coatings of Si [16, 17]. Direct reaction between V and Si where the Si supply or activity is not limited preferentially produce VSi_2 [13, 14].

It is also of interest to consider whether the present results have any implications concerning the possible production of multifilamentary Nb_3Ge, Nb_3Al, or Nb_3Ga by the bronze process. Previous studies have reported instead the preferential production of more Ge-rich, Al-rich, and Ga-Ga-rich compounds [3, 18, 19]. If the appropriate phase diagrams were similar to Cu–V–Si, composition control might instead produce the desired A-15 compounds. However, a recent examination of the Cu–Nb–Ge phase diagram [6] indicates that no two-phase tielines exist between the Nb_3Ge and Cu(Ge) phases. A two-phase region between the Nb and Nb_5Ge_3 phases apparently isolates the Nb_3Ge from equilibrium with any but these two neighboring phases. The published Cu–Nb–Al diagram [20] indicates that the Nb_3Al phase is similarly isolated, and the existence of two ternary compounds further interrupts the diffusion path between Nb and Cu(Al). Information is not yet available on the Cu–Nb–Ga diagram, and the possibility remains that Cu(Ga) solid solutions of sufficiently low Ga concentration may be in equilibrium with the Nb_3Ga phase.

5. Summary

Earlier studies [3–5] of the reaction between V and Cu–Si reported that, for Si concentrations ranging from 5 to 30 at.% Si, the V_3Si layers formed were much thinner than the accompanying V_5Si_3 layers. We have found that further reduction of Si concentration gradually suppresses V_5Si_3 and makes V_3Si formation more favourable.

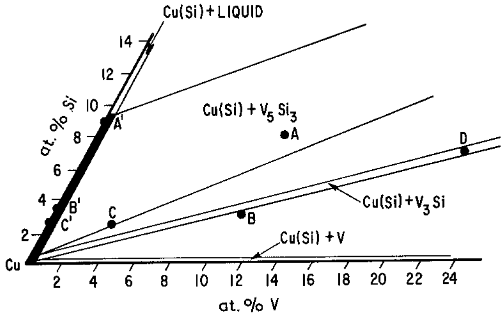

Figure 2 Cu-rich corner of the Cu–V–Si phase diagram at 900° C as suggested by the results of the present experiments. Points A, B, C, D represent overall compositions of various multifilamentary composites, and points A', B', and C' represent average initial matrix compositons, as discussed in text. Initial matrix compositions determine relative thicknesses of initial reaction layers, as reaction with V proceeds along appropriate tielines to the V_5Si_3 phase. Overall conductor compositions determine equilibrium phase distribution, approached at long reaction times.

Although V_5Si_3 layers are formed for matrix compositions at least as low as 1 at.% Si, the proportion of V_3Si produced increases as the Si concentration in the matrix decreases. Our studies have also shown that the overall Si to V ratio in the composite is an important parameter. If this ratio is kept sufficiently low, the V_5Si_3 formed is eventually converted to V_3Si as the matrix Si concentration drops. These various results are incorporated in the proposed partial phase diagram shown in Fig. 2.

Acknowledgments

We are grateful to Dr R. A. Sigsbee for co-operation and use of his equipment in measuring critical temperatures, to S. Alessi, I. Mella, and J. Methe for metallography, and to M. McConnell for microprobe measurements. This work was supported in part by the Air Force Office of Scientific Research.

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Received 14 December 1976 and accepted 28 January 1977.