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The thermodynamics of A15 compound formation by diffusion from ternary bronzes*

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The formation of high T_c Nb_3Al, Nb_3Ga, Nb_3Ge and V_3 (Ga, Si) has been attempted by solid state diffusion from ternary bronzes. None of the desired compounds were formed. The results are explained in terms of the thermodynamics of compound formation by solid state diffusion. Diffusion follows two-phase tie-lines; only those phases which lie on tie-line routes, and which are the most stable as defined by the stability index, are able to form. The addition of the third element to the bronze in general has little significant effect. There is no evidence to indicate that high T_c Nb_3Al, Nb_3Ga or Nb_3Ge can be produced by solid state reaction.

1. Introduction

The "bronze" process, in which filaments of niobium are drawn down in a copper–tin bronze matrix, and reacted to produce the A15 compound Nb_3Sn [1–3], is now an established production route for fully-stabilized, high-current density, multifilamentary superconducting wire. The "bronze" process has also beeen successfully applied to the vanadium-based A15 compounds V_3Ga [3, 4], V_3Si [4] and V_3Ge [6]. The niobium-based A15 compounds Nb_3Al, Nb_3Ga and Nb_3Ge all have higher critical temperatures, T_c and higher super critical fields, H_{c2}, than those of the four compounds previously mentioned. They thus have the potential to form conductors with performance superior to those presently available. Attempts to produce, by the bronze process, a conductor based on any of the above three compounds have not yet met with success. The major phases which do form in the various systems are; $Nb(Al_xCu_{1-x})_2$ in the niobium–aluminium bronze system, Nb_5Ge_3 in the niobium–germanium bronze system, and a series of Nb–Ga compounds, including non-stoichiometric, low T_c Nb_3Ga, in the niobium–gallium bronze system [7].

High T_c bulk samples of Nb_3Al, Nb_3Ga and Nb_3Ge cannot be produced by simple melting and solidification of the constituent elements. The reason is that the superconducting properties of A15 compounds are maximized in well-ordered, stoichiometric samples (see, for example, [8] for a review of the properties of A15 superconductors). In the Nb–Al, Nb–Ga and Nb–Ge systems the equilibrium A15 phase field does not include the stoichiometric composition. The presence of a stable σ or σ-related compound at a lower niobium composition pushes the range of homogeneity of the A15 compound to the niobium-rich side of the 3:1 composition, as shown in Fig. 9 of [8].

The addition of a third element can alter the relative stabilities of the A15 and σ-type phases, allowing the Nb-poor boundary of the A15 phase to advance to the stoichiometric composition. In the Nb–Al–Ge ternary system, an A15 compound, $Nb_3(Al_{0.8}Ge_{0.2})$ forms close to stoichiometry. This is believed to be due to a gap between the $Nb_2(Al, Ge)$ and $Nb_5(Ge, Al)_3$ phase fields which just allows the A15 phase field to advance to the stoichiometric composition [9]. A similar gap exists in the Nb–Al–Si system [10]. The existence of the gap between the σ-type phase fields has been related to

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TABLE I Possible A15 psuedo-binaries

Nb_3B	T_c(K)	a_0(Å)	Nb_3B'	T_c(K)	a_0(Å)	$\Delta a_0/a_0$	Eutectic at. % B	Possible T_c (estimate)	Measured T_c [§]
Nb_3Al	18.9	5.184	Nb_3Ga	20.3	5.165	0.004	9	19.0	19.4
			Nb_3Ge	23	5.14	0.009	70	21.0	20.7
			Nb_3In		5.303	0.023	4.7[‡]	18.0	
			Nb_3Si		5.08	0.020	89		19.2
			Nb_3Sn	18.3	5.30	0.022	2	18.4	18.6
Nb_3Au	13*	5.203	Nb_3Ge	23	5.14	0.012	73	16.0	
			Nb_3Si		5.08	0.024	69		
Nb_3Ga	20.3	5.115	Nb_3Ge	23	5.14	0.005	~100	21.5	
			Nb_3In		5.303	0.018	16.5	18.5	
			Nb_3Si		5.08	0.017	~100		
			Nb_3Sn	18.3	5.30	0.026	95	19.0	18.35[¶]
Nb_3Ge	23	5.14	Nb_3Sn	18.3	5.30	0.031	~0	18.5	
Nb_3In	8(?)	5.303	Nb_3Sn	18.3	5.70	0.001	52		18.3
Nb_3Si	(?)	5.08[†]	Nb_3Sn	18.3	5.30	0.042	~0		

*Muller *et al.* [14] extrapolation for stoichiometric Nb_3Au.

[†] Lattice parameter for Nb_3Si calculated on Johnson and Douglass [15] modification of Geller [16] scheme.

[‡] Monotectic

[§] See [8], Table IV.

[¶] Horigami *et al.* [17].

the presence of a eutectic in the Al–Ge and Al–Si systems [8]. There is also a eutectic in the Al–Ga system, and a gap between Nb_2(Al, Ga) and Nb_5(Ga, Al)$_3$ [11]. Machlin [12] has pointed out that the existence of a eutectic indicates that the two elements do not like to be associated as nearest neighbours in a crystal, and that, whereas B-sites in the σ-type phases do have other B-sites as nearest neighours, this does not occur in the A15 structure. Thus A15 Nb_3(Al, Ge) will not have Al and Ge atoms as nearest neighbours, but Nb_2(Al, Ge) and Nb_5(Ge, Al)$_3$ will, and their stability is accordingly reduced.

Given the above considerations, it should be possible to predict systems in which stoichiometric ternary A15 phases might be found. For the three elements, Nb, B, and B$'$, Nb + B and Nb + B$'$ should both form, or, as in the case of Nb + Si, be on the verge of forming A15 compounds Nb_3B and Nb_3B'; the difference in lattice parameter between these two A15 compounds should not exceed 3 per cent, to ensure complete miscibility [13]; and the BB$'$ binary system should be a simple eutectic. A list of potential systems based on Nb and satisfying these criteria is given in Table I. Also included in the table are Nb_3Ge–Nb_3Sn, and Nb_3Si–Nb_3Sn, whose lattice parameter differences exceed the three per cent limit. The possible superconducting critical temperature, T_c, is estimated from an average of the T_cs of the constituent binary A15s, appropriately weighted to correspond to the eutectic composition.

No published attempt has yet been made to verify the above ideas. The only Nb-based ternary systems investigated in any detail are Nb–Al–Ge and Nb–Al–Si, by Muller, the results of which initiated the formulation of these concepts, and the Nb–Al–Ga system by Drys.

The inability to produce stoichiometric, high T_c, Nb_3Al, Nb_3Ga or Nb_3Ge by the bronze process is due to the interference of a more stable phase or phases. The stabilities of these phases relative to the A15 phases could be susceptible to alteration by the addition of an appropriate third element. It might be possible, using the correct ternary bronzes as a starting matrix, to produce wires of ternary A15 compounds by solid state diffusion. It is the quaternary system, NbBB$'$Cu, that should be considered in the bronze process, rather than just the ternary Nb, B, B$'$. It is not at all clear how the addition of copper will modify the ternary phase diagrams. In Nb–(Cu, Ga), V–(Cu, Ga) and V–(Cu, Si) ternary diffusion couples the A15 compound, with negligible copper content, is formed instead of the compounds rich in Sn, Ga or Si which normally occur in the binary diffusion couples [7]. The presence of copper in these ternary diffusion couples is beneficial.

Horigami *et al.* [17] have previously examined the Nb–Ga–Sn system. Using a Nb–1 wt%Zr filament in a Cu–8.5 wt% Ga–5 wt% Sn matrix, a maximum T_c of 18.35 K was measured in a sample reacted for 12 h at 800° C. Microprobe and X-ray lattice parameter data indicated that the compound formed was $Nb_3(Ga_xSn_{1-x})$ in which x lies between 0.04 and 0.12. This small amout of gallium in the Nb_3Sn is insufficient to have a significant effect on T_c, but does produce a considerable increase in H_{c2} over that of pure Nb_3Sn made by the same process [18].

In the light of these arguments, it was thought worthwhile to attempt A15 compound formation from ternary copper bronzes. The constituents of the bronzes, chosen by the critera given above, were based on those listed in Table I. Of the 14 systems in the table, 10 were investigated in the form of single-filament niobium in bronze matrix wire. The V_3Ga–V_3Si psuedo-binary was also studied, as a maximum T_c of 18.6 K had been reported for this sytem [19].

2. Experimental prodcedures

Samples were prepared from cast bronze rods 15.9 mm in diameter, swaged to either 12.7 or 6.35 mm diameter, then drilled with a hole along the axis either 6.35 or 3.18 mm diameter, and homogenized. Into the hole was inserted a niobium, or in two cases vanadium, core rod, of the same diameter as the hole. The composite specimens were then drawn down to a final wire diameter of 0.635 mm, with intermediate anneals as necessary. The compositions of the samples thus prepared are given in Table II.

Specimens of the drawn wire, 0.2 m long, were encapsulated in silica tubes under a vaccum of 10^{-6} Torr, and reacted for various times up to 300 h at temperatures between 600 and 900° C. Superconducting critical temperatures of the reacted specimens were measured inductively, to an accuracy of 0.1 K. The composition of any compound formed was determined on metallographic cross-sections of selected samples using an ARL model EMX 21000 electron beam microprobe. Computer corrections for absorption, fluorescence, etc. were made on spot readings in the reacted layer to give reasonably accurate estimates of compound composition.

3. Results

The results of the superconducting critical tempera-

TABLE II

Specimen no.	Core/matrix composition (wt %)	Maximum T_c (K)	Heat treatment	Layer composition (microprobe)
1	Nb/Cu–2 Al–13.5 Ga	9.2		NbGaCu compound
2	Nb/Cu–4.5 Al–9 Ga	9.2		
3	Nb/Cu–7 Al–2.5 Ge	9.2		Nb_3Ge_2 with trace of Al
4	Nb/Cu–6.5 Al–3 Ge	9.2		
5	Nb/Cu–6 Al–3.5 Ge	9.2		
6	Nb/Cu–4 Al–6 In	9.2		NbAlCu compound
7	Nb/Cu–6 Al–4 In	9.2		
8	Nb/Cu–3 Al–2 Si	9.2		Nb_3Si_2
9	Nb/Cu–2 Al–3 Si	9.2		Nb_3Si_2
10	Nb/Cu–2 Al–9 Sn	17.8	86 h 800° C	Nb_3Sn with no trace of Al
11	Nb/Cu–3 Al–5 Sn	17.8	48 h 800° C	
12	Nb/Cu–4 Al–6 Sn	17.9	96 h 800° C	
13	Nb/Cu–6 Al–3 Sn	17.7	192 h 750° C	
14	Nb/Cu–10 Au–1 Si	9.2		Nb_3Si_2
15	Nb/Cu–9 Ga–6 In	9.2		NbCuGaIn compound
16	Nb/Cu–13.5 Ga–3 In	9.2		
17	Nb/Cu–5 Sn–5 Ge	9.2	24 h 850° C	Nb_3Ge_2 containing some Cu
18	Nb/Cu–3 In–9 Sn	17.8	192 h 750° C	Nb_3Sn with no trace of In
19	Nb/Cu–6 In–6 Sn	17.4	96 h 800° C	
20	Nb/Cu–9 In–3 Sn	16.6	192 h 750° C	
21	Nb/Cu–1 Si–9 Sn	9.2		Nb_3Si_2
22	Nb/Cu–3 Si–6 Sn	9.2		$Nb_{0.4}Si_{0.36}Cu_{0.24}$
23	V/Cu–13.5 Ga–1 Si	~13 very broad	100 h 700° C	$V_5Si_3 + V_3Si$ with trace of Ga, Cu
24	V/Cu–9 Ga–2 Si	~14 and weak	100 h 700° C	

ture and microprobe measurements are summarized in Table II. These are extremely disappointing. Nowhere can be seen any indication of the formation of an A15 compound other than Nb_3Sn, or V_3Si in the case of the vanadium-based specimens. Nor does the Nb_3Sn, layer formed from tin-containing bronzes ever show the presence of the third element from the original bronze. This is discouraging, as additions of third elements to bulk Nb_3Sn have been shown to enhance superconducting properties [8]. In the samples which did not form Nb_3Sn, or V_3Si, the highest observed transition temperature is 9.2 K, that of the unalloyed niobium core. A more stable, non-A15 compound, is preferentially formed in these samples. The stable compounds are usually binary compounds with niobium and one of the two elements added to the copper matrix; occasionally they contain a trace of the third element or of copper. Exceptions are the following: samples 1 and 2 from Cu–Al–Ga matrices in which the layer is a NbCuGa compound; samples 6 and 7 from Cu–Al–In matrices in which the layer is a NbAlCu compound; samples 15 and 16 from Cu–Ga–In matrices in which the layer is a NbCnGaIn compound. The exact composition of these compounds is uncertain as it changes with initial matrix composition and position in the layer; presumably the compounds possess a wide range of homogeneity.

The reaction layer formed from a Cu–5 wt% Ge–5 wt% Sn bronze, sample 17, just as for all of the other combinations tested with germanium present in the bronze, is the compound Nb_3Ge_2. Zwicker *et al.* [20] claim that if the Cu–Sn–Ge bronze contains 1% or more of germanium, the reaction layer is the A15 compound Nb_4Ge. This is the equilibrium, A15 phase in the Nb–Ge binary system, which has a $T_c \sim 6$ K. They further claim that when the germanium content of the bronze is reduced to 0.5%, ,the layer formed is Nb_3Sn (plus some Ge) and its $T_c = 19.3$ K. (They also claim a T_c of 19.0 K for Nb_3Sn grown from a straight tin bronze, which is ~ 1.5 K higher than the best T_c usually claimed for bronze process Nb_3Sn. This suggests that their thermometry may be questionable). Further work by one of the authors (TSL [21]) shows that, as the germanium content of the bronze is reduced, and the tin content correspondingly increased, the resultant Nb_3Ge_2 layer thickness decreases, now allowing diffusion of tin through the layer and the formation of some Nb_3Sn containing a very small amount of Ge wtih a maximum T_c of 18.0 K.

When silicon is present, the preferred compound, with the one exception of sample 22 mentioned above, has the composition Nb_3Si_2. This compound has not been reported in any investigation of the Nb–Si binary phase diagram [22], but by analogy with the Nb–Ge system is not entirely unexpected. The bronze was removed from a portion of sample 21 by dissolution in nitric acid, and an X-ray powder pattern taken of the reacted layer. After deletion of all of the lines which could be identified as being due to the pure niobium bcc phase or the tetragonal Nb_5Si_3 phase (some of the latter phase must have formed though not detectable from the microprobe trace) several prominent lines remained. These lines could not be identified with any known structure and are presumed to originate from the Nb_3Si_2 phase; their *d*-spacings are listed in Table III.

V_5Si_3 forms in systems between vanadium and bronzes containing silicon. The superconducting measurements indicate the presence of an A15 compound, probably V_3Si containing some Ga or Cu. The V_3Si layer is too thin to be detected by microprobe analysis. This is similar to what happens between vanadium and a straight Cu–Si binary bronze where both V_5Si_3 and a generally much thinner layer of V_3Si are formed [5]. Livingston [23] has similarly found that the reaction layer between vanadium and mixed Cu–Ga–Si bronzes is dominated by vanadium–silicon compounds. In all other specimens studied, in which the bronze contains tin and a third element which is neither germanium nor silicon, the major compound formed is Nb_3Sn. When the third element is aluminum or indium, it is not, insofar as can be detected by the microprobe, incorporated into the Nb_3Sn layer.

TABLE III Unidentified prominent X-ray lines – sample 21

d-spacing (Å)	Intensity
2.82	Strong
2.19	Medium
2.06	Medium – strong
1.48	Medium – strong
1.43	Medium
1.34	Medium – strong

4. Discussion

The formation of phases by diffusion between elements or other phases is governed by thermodynamic considerations. In multi-component systems, diffusion follows the two-phase tie-lines [24]. The only phases that will form in a diffusion couple are those phases which lie on the most direct route, following the two-phase tie-lines, between the two initial components of the couple. Of the phases which can form, the ones most likely to form are those with the highest relative thermodynamic stability [7]. The most stable phases will generally have larger homogeneity ranges and will be the termini for more tie-lines than will be the less stable phases. This will tend to ensure that the more stable phases are most likely to be encountered on the tie-line routes.

The stability index, S.I., as introduced by Raynor [25] is, in practice, a good measure of the relative thermodynamic stability of phases. The stability index, for a compound $A_xB_{(1-x)}$, is the ratio of the compound's melting point to the appropriately weighted average of the melting points of the elements. It is defined by:

$$\text{S.I.} = T_m[T_A - (T_A - T_B)(1-x)]^{-1} \qquad (1)$$

where T_m is the melting point of the phase, T_A and T_B are the melting points of the pure elements A and B ($T_A > T_B$), and x is the atomic fraction of A in the phase corresponding to its maximum melting point. Hartsough [26] has used a similar concept, the formation temperature ratio (FTR), to compare the stability of a phase relative to the two phases either side of it. The formation temperature ratio for the β-phase, relative to the α- and γ-phases, is again the ratio of the melting point of the β-phase to the weighted average of melting points of the other phases, and is given by:

$$\text{FTR} = T_\beta[T_\alpha - (T_\alpha - T_\gamma)(C_\alpha - C_\beta)/(C_\alpha - C_\gamma)]^{-1} \qquad (2)$$

where T_α, T_β and T_γ are the melting points ($T_\alpha > T_\gamma$), and C_α, C_β and C_γ are the compositions, of the α-, β- and γ-phases, respectively.

For an intermetallic phase to form in a diffusion couple between two elements, A and B, its stability index should be >1 and higher than that of any other phase in the system. Once the phase, γ, with the highest S.I. has formed, if any other phase has an FTR between γ and one of the pure elements which is greater than 1, it too will be able to form. In this way several phases may appear in a diffusion couple. Clearly for any phase to have an FTR >1 requires also that its S.I. be >1. Phases with an S.I. <1, and even those whose S.I. >1 if adjacent to a very stable phase, are not expected to form. In practice there are some exceptions to this rule, but in general it is a very good guide as to the phases that are likely to form in a solid state diffusion couple between the pure elements.

The concepts of stability index and formation temperature ratio, defined above for binary systems, can in principle be extended to ternary systems. This was done by Luhman *et al.* [7] for the six ternary systems Nb–Cu–X (X = Sn, Al, Ga, Ge) and V–Cu–Y (Y = Ga, Si) of interest in the bronze method for preparing A15 compounds. They recalculated the Nb–X and V–Y binary S.I. values, replacing T_B in Equation 1 by a temperature, T_B', appropriate to the Cu–X (Y) solid solution. T_B' was chosen to be the liquidus corresponding to the initial composition of the bronze. The S.I. values should have been calculated along the two-phase tie-line diffusion routes of the ternary diagrams. As these were not known, the calculations were done using the Nb–X or V–Y binary diagram. This procedure implicitly, and almost certainly incorrectly, assumes that copper does not dissolve in and does not affect the melting points of the intermediate phases. Nevertheless the predictions of this method were in good agreement with what was found experimentally.

Recently portions of some of the relevant ternary diagrams have become available, and a better understanding of the bronze process is now possible. In as much as they relate to the formation of the A15 compound, at least four types of ternary phase diagram can be recognized.

(a) Those in which the A15 phase is the only relevant stable phase, other than the terminal Nb(V) and Cu-based solid solutions. The Nb–Sn–Cu diagram, of which the preferred version is that due to Hopkins, Roland and Daniel [27], is an example of this type. Fig. 1 is an estimate of the 700° C isotherm for this system, deduced from the 1100° C section of Hopkins *et al.* This diagram shows that the diffusion path from the Cu–Sn solid solution to the Nb–Sn solid solution passes through the A15 Nb_3Sn phase field. The stability index of this compound, calculated from Equation 1 with T_B replaced by the melting point of the bronze, is just >1 (the actual value depends upon the assumed composition of the bronze) and thus

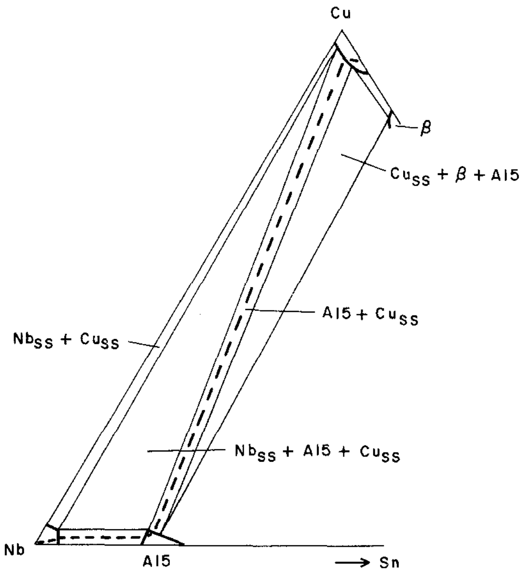

Figure 1 Part of a section of the Nb–Cu–Sn ternary phase diagrams, at ~700° C This is deduced from the 1100° C section of Hopkins *et al.* [27]. The dashed line indicates the solid state diffusion path between Cu–Sn solid solution and pure Nb.

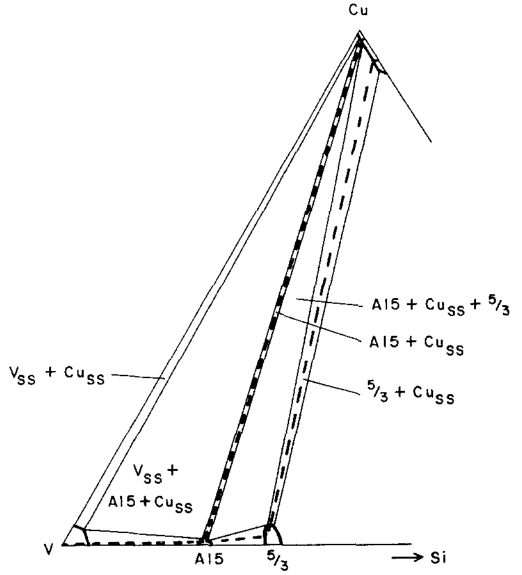

Figure 2 Part of a hypothetical section of the V–Cu–Si ternary phase diagram at ~700° C, deduced from the work of Livingston [29]. The dashed lines indicate diffusion paths between two concentrations of Cu–Si solid solution and pure V.

the A15 compound is able to form. Suenaga *et al.* [28] have shown that the rate of Nb_3Sn formation increases with increasing tin content of the bronze until the solid solution limit is exceeded and the β-phase if formed. The activity of tin in the α-phase increases with increasing tin concentration to cause this increase in compound layer growth rate. Because of the shape of the A15 compound phase field, the final composition of the Nb_3Sn formed is little affected by the initial tin concentration. V_3Ga is formed with the same readiness as Nb_3Sn, and the V–Ga–Cu ternary diagram, is similar to that of Nb–Sn–Cu [29]. V_3Ge has also been formed from Cu–Ge bronze [6] and Nb_3Ge from Ag–Ge solid solution [30]. The appropriate ternaries for these systems are presumed to be of this type.

(b) Those in which there are two stable phases, the A15 and one other (usually a σ-related 5/3 compound). An example of this type is the V–Si–Cu diagram [31], a deduced section of which at 900° C is shown in Fig. 2. Two diffusion paths are indicated. One, from low Si bronze (< 1 at.% Si) goes directly to V_3Si; the other, from bronze with higher silicon content, goes to V_3Si via V_5Si_3. The stability indices are ~ 1.22 for V_3Si and ~ 1.35 for V_5Si_3. V_3Si is expected, and is indeed found, to form directly from a low silicon bronze. With more silicon present, V_5Si_3, with its higher S.I., is expected to be the only product. In practice, a double layer of V_5Si_3 and V_3Si is formed [5, 31], the relative proportions of the former increasing with increasing Si content of the starting bronze. Once a layer of V_5Si_3 has formed, it is necessary to consider the diffusion couple pure V/V_5Si_3. In this situation, the formation temperature ratio calculated from Equation 2 is 0.98. However, V_5Si_3 will not be in equilibrium with pure vanadium, but with a solid solution of silicon in vanadium. Replacing the melting point of pure V by the solidus temperature for a V–2 at.% Si solid solution in Equation 2 raises the FTR for V_3Si to 1. All that is required for the formation of a layer of V_3Si is that, at the V/V_5Si_3 interface, the concentration of Si dissolved in the V should exceed 2 at%. If vanadium is present in excess, all of the V_5Si_3 will ultimately convert to V_3Si; if Si is present in excess, the final layer will be V_5Si_3. In practice the reaction times are usually such that neither component is exhausted, and, as mentioned above, both compounds are formed.

(c) In the third type of diagram, the most stable phase is one in the Nb(V)–X binary, with a lesser Nb(V) content than the A15 phase. There is no direct tie-line to the A15 phase, and the A15 may not even lie on the direct tie-line route from the

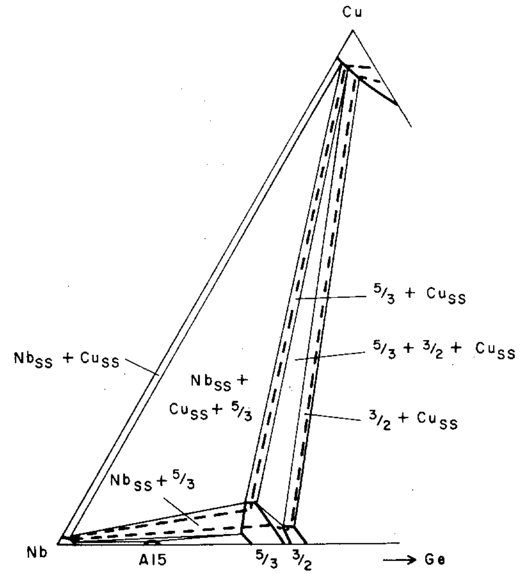

Figure 3 Part of a section of the Nb–Cu–Ge ternary phase diagram, at ~700° C, deduced from the 1100° C section of Hopkins *et al.* [27]. The dashed lines indicate diffusion paths between two concentrations of Cu–Ge solid solution and pure Nb.

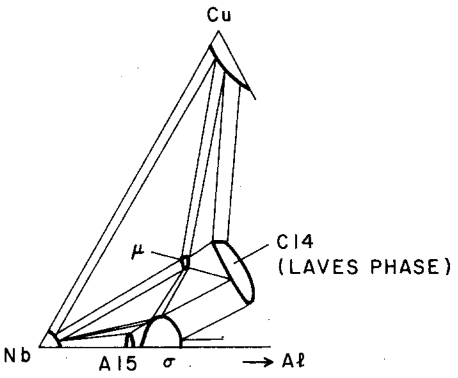

Figure 4 Part of a section of the Nb–Cu–Al ternary phase diagram, at 1000° C [32]. The μ and Laves phase block diffusion paths between the Cu–Al solid solution and pure Nb.

most stable phase to the Nb–X solid solution. An example of this type is the Nb–Ge–Cu diagram, a section of which, again from the work of Hopkins *et al.* [27], is shown in Fig. 3. There are in fact two stable phases, Nb_5Ge_3 and Nb_3Ge_2, whose S.I.s are respectively ~1.16 and ~1.09, compared to ~0.96 for the (non-stoichiometric) A15 phase. Two possible diffusion paths are indicated, depending upon the initial concentration of germanium in the bronze. In both cases the resultant reaction layer is expected to be Nb_5Ge_3, as is found experimentally [27].

(d) In the final type of system, the most stable phase is a new, ternary phase which bears no relation to, and whose existence cannot be predicted from, any of the three constituent binary systems. The example here is Nb–Al–Cu [32]; a 1000° C isothermal section of this diagram is shown in Fig. 4. Two ternary compounds, χ phase and a Laves phase $Nb(Al_xCu_{1-x})_2$, block the tie-line routes between the Cu–Al bronze and the Nb–Al solid solution. Which one of these is acutally formed can be seen to depend upon the starting composition of the bronze. The wide homogeneity range of the Laves phase suggests that it is very stable; this is the phase found by Luhman *et al.* [7] for their Nb/Cu–Al diffusion couple. The Nb–Ga–Cu ternary, though not yet published, must have features of types (b) and (d). Both low T_c, non-stoichiometric A15 and Nb_3Ga_2 are formed in Nb/Cu–Ga bronze couples [7]; a C14 Laves phase, $Nb(Cu, Ga)_2$ [33], and a μ-phase, Nb_2CuGa [34], have been reported in this sytem.

It can be seen from the foregoing that a knowledge of the appropriate ternary phase diagram, coupled with an estimate of relative phase stability, enables the accurate prediction of the phases that will be formed by reaction of Nb or V with a binary bronze alloy. These ideas are now extended to the explanation of the diffusion results from ternary bronzes. An examination of the final column of Table II indicates that, in most cases, the addition of a third element to the bronze appears to have had little effect. The fact that the quaternary diagrams have not yet been determined does not seem to be a serious obstacle to understanding the results reported here. The compounds actually formed could, in most cases, have been predicted from a knowledge of Nb(V)-based binary phase diagrams only, occasionally supplemented with help from the Nb(V)–Cu–X ternary diagrams.

Table IV lists all of the intermetallic phases known to be present in the Nb(V)-based binaries appropriate to the samples studied. The stability indices for these phases, calculated from Equation 1, are also given. It is not quite clear what quantity should be used for T_B in Equation 1 when the couple is between a pure element and a bronze. Luhman *et al.* [7] previously used the liquidus temperature of the bronze; the solidus temperature might equally well have been chosen. The situation is complicated by the changing composition of the bronze during the course of the reaction. The S.I.

TABLE IV

Binary system	Phase diagram reference	Phases	S.I.
Nb–Al	Lundin and Yamamoto [35] modified by Moehlecke [36]	A15	0.84–0.83
		Nb_2Al	0.95–0.93
		$NbAl_3$	1.13–1.10
Nb–Au	Muller *et al.* [14]	A15	0.86–0.85
Nb–Ga	Feschotte and Spitz [37]	A15	0.90–0.89
		Nb_3Ga_2	0.96–0.93
		$NbGa_3$	0.95–0.88
Nb–Ge	Moffatt [38]	A15	0.97–0.94
		Nb_5Ge_3	1.14–1.09
		Nb_3Ge_2	1.11–1.06
		$NbGe_2$	1.19–1.08
Nb–Si	Deardorff *et al.* [22]	Nb_3Si (tet)	0.95–0.93
		Nb_5Si_3	1.29–1.24
		$NbSi_2$	1.32–1.21
Nb–Sn	Shunk [39]	A15	1.04–1.01
		Nb_6Sn_5	0.60–0.57
		$NbSn_2$	0.68–0.61
V–Ga	Shunk [40]	A15	0.83–0.81
		V_6Ga_5	0.81–0.78
		V_6Ga_7	0.88–0.83
		V_2Ga_5	0.93–0.86
V–Si	Hansen [41]	A15	1.24–1.20
		V_5Si_3	1.38–1.32
		VSi_2	1.38–1.26

values in Table IV were calculated with two values of T_B; that of the bronze peritectic (the lowest temperature of both liquidus and solidus) and that of pure copper. The range of values thus produced must include the value appropriate to the particular situation.

As a starting point it is assumed that the phase most likely to be formed from a ternary bronze, Cu–B–B′, is that which appears to be most stable in either of the Nb(V)–B and Nb(V)–B′ binary phase diagrams. Stability is that calculated for diffusion from a bronze; and compounds with less than 50% Nb(V) are deleted, as they will not lie on direct diffusion paths. Table V gives the 10 niobium-based and one vanadium-based ternary combinations investigated. In the second column is listed, for each combination, the most stable binary phase, that is the phase with the highest S.I. from Table IV, in either of the two binaries, as defined above. The final column shows the phase actually found.

A first impression is that the scheme followed is not a very good predictor, with only 3 clear successes out of 11. The discrepancies can, however, be explained. In the Nb–Al–Ga sample, the compound formed contains Nb, Ga, Cu. Its exact composition was not determined, but it could be Nb_3Ga_2, as predicted, in which some of the Ga, and possibly some of the Nb, is replaced by Cu. In both the Nb–Al–Ge and Nb–Ge–Sn samples, Nb_5Ge_3 is prediced, Nb_3Ge_2 is found. The S.I.

TABLE V

Ternary system	Most stable binary phase	Phases actually formed
Nb–Al–Ga	Nb_3Ga_2	NbGaCu compound (Nb_3Ga + Cu?)
Nb–Al–Ge	Nb_5Ge_3	Nb_3Ge_2
Nb–Al–In	Nb_2Al	NbAlCu phase of varying composition (Laves phase?)
Nb–Al–Si	Nb_5Si_3	Nb_3Si_2
Nb–Al–Sn	Nb_3Sn	Nb_3Sn
Nb–Au–Si	Nb_5Si_3	Nb_3Si_2
Nb–Ga–In	Nb_3Ga_2	NbCuGaIn compound of variable composition [$Nb_3(GaCuIn)_2$?]
Nb–Ge–Sn	Nb_5Ge_3	Nb_3Ge_2
Nb–In–Sn	Nb_3Sn	Nb_3Sn
Nb–Si–Sn	Nb_5Si_3	Nb_3Si_2 or NbSiCu phase
V–Ga–Si	V_5Si_3	V_5Si_3 + trace of V_3Si

values for both compounds are close. The liquidus and solidus of the ternary bronze are expected to be lower than those of either binary bronze; a not much lower value of T_B used in determining the S.I. could easily reverse the relative positions of Nb_5Ge_3 and Nb_3Ge_2. The Nb_2Al phase is predicted for the Nb–Al–In combinations. However, a straight Cu–Al bronze gives the $Nb(Al_xCu_{1-x})_2$ Laves phase, and this appears still to be what actually forms when In is added to the bronze. The combinations containing silicon all should produce Nb_5Si_3, but apparently give Nb_3Si_2. As this phase does not appear in the published phase diagram from which the S.I. is calculated, predictions based on these calculations must be regarded as invalid. Finally, Nb_3Ga_2 is predicted for the Nb–Ga–In system. The phase that is formed, which contains about 50 wt % Nb with variable amounts of Ga, In and Cu, could be $Nb_3(Ga, In, Cu)_2$.

In the main, the addition of a third element to the bronze has altered only slightly the melting points and compositions of the phases formed by solid state diffusion. There is no indication at all, that, by finding a suitable starting composition for the bronze, multifilamentary conductor of high T_c Nb_3Al, Nb_3Ga or Nb_3Ge can ever be fabricated by this process.

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