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Electron microprobe analysis of niobium-based superconducting materials

In this letter we report the results of our investigations to ascertain the accuracy of electron probe composition measurements in four superconducting materials when the standards used are pure elements; as for many superconducting systems compound standards are not easily available. The transition temperature, T_c, of a superconducting A-15 compound is very sensitive to composition variations. To illustrate this, in the V–Ga system the highest T_c is found for the A-15 phase compounds V_3Ga. Although the A-15 phase extends from 22 at.% Ga to 36 at.% Ga, T_c is maximum at exactly 25 at.% Ga and falls off at either side of this composition by about ~1 K per at.% change [1]. Further, many other superconducting properties may be related to the composition, or to small additions of a third or fourth element [2]. The electron microprobe is a useful tool for the characterization of superconducting materials because it provides a convenient, non-destructive means of obtaining their composition.

The accuracy of the composition measurement is related to the use of standards and the corresponding correction procedures used. In superconducting materials a compound standard with a composition known within 1% is difficult to make. On the other hand, if elemental standards (i.e. pure metals as standards) are used it is believed that the errors could be as large as 10%. For example Sweatman and Long [3] found that the use of pure aluminium as a standard for silicate analysis could lead to errors of about 8%. These errors are essentially due to excessive matrix corrections and large wavelength shifts due to the difference in chemical composition between the unknown and the standard. Clearly there is a need to determine accurately the error involved in the use of elemental standards in taking microprobe data. We report here the results on four systems, Nb–Al, Nb–Al–Si, Nb–Pt and Nb–Ir. The procedure used was to prepare a compound by the method described below, to determine its composition with the electron microprobe using elemental standards, and to compare the results with actual weight measurements and calculations from lattice parameter data.

The Nb–Al and Nb–Al–Si samples were prepared by melting pellets pressed from carefully weighed amounts of the powders in an argon-filled arc furnace. The niobium powder was necessarily coarser to reduce the oxygen contamination. The samples were turned over and remelted three to four times to assure homogeneity. Most of the samples were subjected to high temperature (~1850° C) heat treatments.

A Debye–Scherrer photograph was taken of the material evaporated and deposited on the hearth during this melting procedure and this material was found to be entirely aluminium, as

TABLE I Comparison of the composition of A-15 compounds as obtained by the three methods

Compound	Element	Composition (at.%)		
		Microprobe (computer corrected)	Nominal (obtained by weight measurements)	Theoretical estimate from lattice parameter
Nb_3Al	Nb	75.9 (± 0.5)	77.0 (± 0.1)	–
	Al	24.0 (± 0.3)	23.0 (± 0.1)	–
Nb_3Pt	Nb	75.3 (± 0.2)	75.9 (± 0.1)	76.0 (± 0.5)
	Pt	24.7 (± 0.2)	24.1 (± 0.1)	–
Nb_3Ir	Nb	75.7 (± 0.1)	75.0 (± 0.1)	75.1 (± 0.5)
	Ir	24.3 (± 0.1)	25.0 (± 0.1)	–
$Nb_3(AlSi)$ (1)	Nb	73.5 (± 0.5)	75.9 (± 0.1)	75.6 (± 0.5)
	Al	23.4 (± 0.3)	21.0 (± 0.1)	–
	Si	3.1 (± 0.1)	3.0 (± 0.1)	–
(2)	Nb	75.0 (± 0.5)	76.1 (± 0.1)	76.5 (± 0.5)
	Al	20.6 (± 0.3)	19.3 (± 0.1)	–
	Si	4.5 (± 0.1)	4.6 (± 0.1)	–

Note: All errors are estimates of precision only.

expected. Thus nominal compositions were determined from the weight losses (which could be as much as 20% of the aluminium) assuming the losses were only aluminium. In the Nb–Pt and Nb–Ir systems the weight loss was negligible during melting and the nominal values of the composition were calculated directly from the starting weights. The samples and elemental standards were prepared for the electron microprobe by the usual procedures. The elemental standards were of 99.9% purity or better.

Debye–Scherrer photographs were taken for all the samples in this study and they indicated that the predominant phase was A-15. The sharpness of the high-angle lines, in all but Nb_3Al, showed that the material was uniform. In addition, diffractometer scans and metallography were performed on a few of the samples. The diffractometer data with structure factor calculations gave a quantitative upper bound to the amount of second phase present of less than 2%, which agreed with the metallographs. By comparing the Debye–Scherrer photographs, an upper bound of 2% second phase could safely be assumed for all samples. This would result in an error in the A-15 composition of at most 0.2 at.% from unknown amounts of second phase. Further, weight loss measurements on the heat-treated samples indicated that the amount of material lost due to this treatment changed the A-15 composition by only a few tenths of at.%.

The results from the microprobe measurements compared to elemental standards and after correction using the Magic IV computer program [4] are given in Table I. The computer program essentiallt corrects for such factors as difference in absorption, atomic number and fluorescence between the standards and the samples and has no adjustable parameters. The nominal compositions are listed as a check on the accuracy of the results. All errors include precision only and do not include estimates of the accuracy of the models in correcting the microprobe results or assumptions in obtaining the nominal composition. In the Nb_3Al case, where the sample was less uniform (± 2 at.%), sufficient data were taken to ensure a good average.

For the binary compounds the agreement between the microprobe results and the nominal concentrations is encouraging, as it is better than 1 at.% in all cases. In the Nb_3Al case, the justification for comparison with the nominal concentrations – even though the weight losses were large – lies in the fact that this sample was one of a series of Nb_3Al samples for which the lattice parameter data (lattice parameter as a function of nominal concentration) agreed well with the data of Muller [5]. The Nb_3Pt and Nb_3Ir comparisons can be justified on the basis of the negligible weight losses during arc melting.

For the ternary compounds (see Table I) the agreement for niobium is not as good, which may be a result of the additional complication of the ternary alloy. There are no lattice parameter data as a function of Nb, Al, and Si composition with which to compare our lattice parameter data. However, we can with some reliability calculate the niobium concentration for an off-stoichiometry compound, $Nb_{3+y}(AlSi)_{1-y}$ from the lattice parameter and aluminium to silicon ratio assuming a Geller [6] type scheme. Let r be the radius of an Nb or Al atom, on the A or B site, then the lattice parameter

$$a_0 = \frac{4}{\sqrt{5}}(r^{A}_{Nb} + yr^{B}_{Nb} + (1-y)r^{B}_{Al+Si}),$$

where

$$r^{B}_{Al+Si} = \frac{(\text{Al con.})r^{B}_{Al} + (\text{Si con.})r^{B}_{Si}}{(\text{Al con.}) + (\text{Si con.})}$$

is an effective radius on the B site due to aluminium and silicon. a_0 was measured; for r^{A}_{Nb} and r^{B}_{Si} we used the Johnson–Douglass [6] radii of 1.51 Å and 1.33 Å, respectively; for r^{B}_{Al} we calculated a value of 1.3875 Å assuming that $a_0 = 5.183$ Å for stoichiometric Nb_3Al; and for r^{B}_{Nb} we used a value of 1.44 Å calculated from the slope of the Nb_3Al a_0 versus composition data on the Nb-rich side. From these numbers we obtain y and thus the calculated values of Nb concentration. The values so obtained agreed closely with the nominal values (as also with the microprobe values, see Table I). In addition we performed a similar calculation for the Nb–Pt and Nb–Ir systems, with equally good agreement (see Table I).

The agreement between calculated and nominal values with the computer corrected microprobe values (within 1 to 2% for Nb) justifies the use of elemental standards for characterizing these compounds. Such good agreement is probably fortuitous to some extent as all the superconductors have a high concentration of one of the elements (i.e. Nb). However, this will usually be the case with most of the A-15 superconductors with a chemical composition roughly A_3B. Based on these tests it seems reasonable to speculate that A-15 superconducting compounds can be analysed using elemental standards with an accuracy of a few percent in A. If, however, a higher accuracy is desired, the procedure outlined for preparing the multicomponent standards can be used. Further, such multicomponent standards can be very useful for characterizing vapour-grown A-15 materials whose composition cannot otherwise be determined accurately.

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The effect of carbide particle size on the initiation of recrystallization of a hypoeutectoid steel

It is well established that dispersed, hard, incoherent particles can either retard or accelerate recyrstallization of a metallic matrix [1, 2]. Retardation can be explained by the "Zener-force", $-F$, caused by a volume portion, f_p of spherical particles with radius r_p interacting with a moving reaction front of specific energy γ [3]:

$$-F = \frac{3\gamma f_p}{2r_p}. \quad (1)$$

Particle size dependence of acceleration of recrystallization can be explained at least in principle by enhanced nucleation at particles. A necessary condition for the motion of a recrystallization