Stress-induced enhancement of T_c in bronze-processed V_3Ge[a)]

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Compressive stresses arising from differential contraction of the bronze matrix were found to cause an increase in the critical temperature, T_c, of bronze-processed V_3Ge. This unusual behavior for an A-15 compound is in qualitative agreement with Testardi's theory, although the enhancement of T_c does not increase parabolically with strain and saturates at strains of $\sim 0.5\%$.

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The formation of A-15 V_3Ge by a solid-state diffusion process (i.e., the "bronze process") has recently been reported by Tachikawa *et al.*[1] Onset superconducting transition temperatures, T_c, in the range 6.6–7.1 K were obtained. These values are higher than those obtained with arc-melted V_3Ge ($T_c = 6.35$ K [2]), and it was argued that the higher T_c may possibly be due to achieving better stoichiometry in the formation of the compound by the solid-state process.

However, elastic strains in A-15 superconductors, as well as deviations from stoichiometry, can cause significant changes in the superconducting properties[3] and it has been shown[4] that the residual elastic strains inherent to the bronze process, because of differential thermal contraction between the bronze matrix and the core, cause measurable changes in T_c in some composite A-15 superconductors. Data are presented below which show that the enhancement of T_c in bronze-processed V_3Ge composites is the result of such residual elastic strains.

Noncubic strains, e.g., uniaxial, tetragonal, etc., generally *lower* the T_c in A-15 superconductors. However, Testardi has predicted,[5,6] on the basis of a phenological theory with parameters derived from measurements of single-crystal elastic constants in the vicinity of T_c, that for V_3Ge, T_c *increases* quadratically with both volumetric and tetragonal components of strain. The observed change in T_c upon removing the bronze matrix is compared below with values derived from Testardi's theory.

Single-core wires were prepared from pure vanadium cores, 3.2 mm in diameter, in nominally Cu–10 wt% Ge ("bronze") matrices, with outer diameters ranging from 5 to 13 mm. This resulted in varying bronze-to-core ratios, nominally 2, 3, 8 and 15, and thus in varying residual strains induced by differential thermal contraction. The resulting composite single-core wires were then drawn to final diameters between 0.64 and 1.3 mm and reacted in quartz tubes at 800 and 850 °C for periods of 200 or 400 h. These treatments resulted in V_3Ge layers 5–40 μm thick, as well as a Ge-rich second phase[1] of ~15–50 μm thick. The actual bronze-to-core ratio, referred to henceforth as R_v, was measured for each specimen from optical photomicrographs of the reacted composite wires. (The volume of the core includes V, V_3Ge, and the Ge-rich phase.)

Superconducting transition temperatures were measured inductively, using a lock-in amplifier technique, both before and after removing the bronze matrix. The bronze matrix was removed by dissolution in molten tin, followed by etching away the excess tin in concentrated hydrochloric acid. Typical transition temperature data are shown in Fig. 1. In some specimens, especially those with large values of R_v, there appear to be two transitions in the composite conductor. As shown in Fig. 1(b), the smaller of the two transitions is always essentially unshifted with respect to the transition temperature of the matrix-free, presumably unstressed, V_3Ge and is probably due to end effects in the wire specimens which were cut into ~6-mm-long segments after drawing but prior to reacting. The critical temperature was taken to be the midpoint of the transition (that of the shifted transition in those specimens exhibiting two transitions).

Critical temperatures obtained before and after removal of the bronze matrix are shown in Fig. 2 as a function of the volume ratio of matrix to core, R_v. Note that for both reaction temperatures (800 and

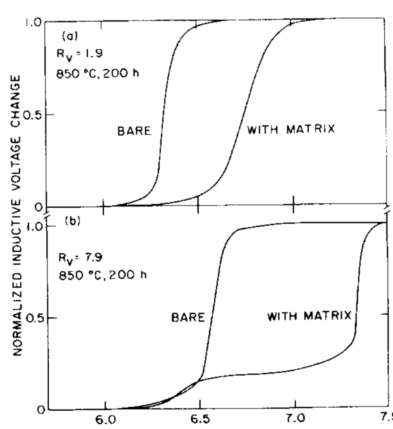

FIG. 1. Typical inductance data at the superconducting transition of bronze-processed V_3Ge, both in the bronze matrix and with the matrix removed. Data are shown for two matrix to core volume ratios, R_v.

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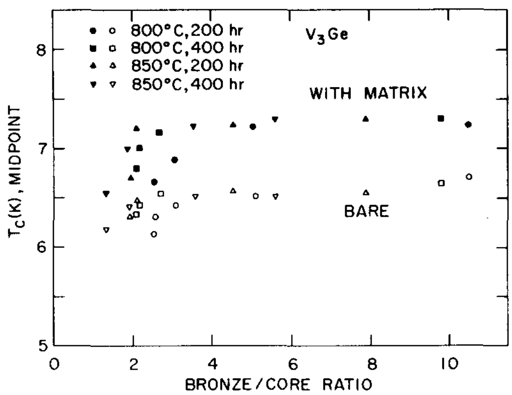

FIG. 2. Superconducting transition temperature for bronze-processed V_3Ge, both as-processed (with matrix) and with the bronze matrix removed (bare).

850 °C) and times (200 and 400 h), removing the bronze matrix, thus presumably removing the elastic strain, produces a significant *drop* in T_c for V_3Ge. This result is consistent with the predictions of Testardi[5,6] and is opposite to the behavior of bronze-processed Nb_3Sn for which T_c *increases* when the bronze is removed.[4,7]

There are other differences between the behavior of V_3Ge and of Nb_3Sn as well. For small values of the ratio R_v, the magnitude of the change in T_c upon removal of the bronze matrix ($|\Delta T_c|$) is larger for V_3Ge than for Nb_3Sn, e.g., ~0.6 K for V_3Ge compared with ~0.3 K for Nb_3Sn [7] at $R_v \cong 2$. However, for V_3Ge, $|\Delta T_c|$ saturates with increasing R_v at a lower level and for smaller R_v than it does for Nb_3Sn. For Nb_3Sn, $|\Delta T_c|$ saturates at a value of ~1.2 K for ratios $R_v \gtrsim 15$.[7] By contrast, $|\Delta T_c|$ saturates at ~0.7 K for $R_v \gtrsim 3$ for V_3Ge.

It is of interest to compare the observed values of ΔT_c with values predicted by Testardi's phenomenological theory of the strain dependence of the critical temperature. In order to do this, Testardi's theory, originally for single-crystal cubic superconductors, must be adapted to the case of polycrystalline composite wires, and an estimate must be made of the thermally induced strains in the composite wire.

To estimate the axial and radial strains present in the superconductor, we approximate both the matrix and core as isotropic elastic solids, treat the core as thermoelastically homogeneous[8] (even though it consists of a vanadium interior covered with thin layers of V_3Ge and a Ge-rich phase), and take the axial strain in the matrix to be constant across its diameter. Appropriate solutions to the equations of elastic equilibrium can be found in the work of Love[9]; combining these with the requirements of stress equilibrium and strain continuity between the two elements of the composite yields the strains in the composite. To the neglect of a small term proportional to the difference in the Poisson ratios of the core and matrix, the axial strain is

$$e_{zz} \cong \frac{\delta R_v E_m/E_c}{1 + R_v E_m/E_c}, \tag{1}$$

where E_m and E_c are the Young's moduli of the matrix and core. The analogous equation for the radial strain is somewhat complex and will not be reproduced here. Finally, the differential thermal contraction parameter δ is defined as

$$\delta = \int_{T_{\mathrm{measurement}}}^{T_{\mathrm{reaction}}} (\alpha_c - \alpha_m)\, dT, \tag{2}$$

where the limits on the integral are the temperatures of the measurement of superconductivity and of the bronze-process reaction, and where the α's are the linear coefficients of thermal expansion.

In the absence of data on the thermal expansion coefficient of Cu-Ge bronze, this was approximated by values for Cu from 4 to 293 K and by values for Cu + 10% Sn from 293 to 1200 K.[10] These data, together with the thermal expansion coefficient of V, [8,10] were used to calculate the differential thermal contraction parameter δ, yielding 0.925 and 0.984% for reaction temperatures of 800 and 850 °C, respectively.

In addition to δ, values of the Young's modulus ratio, E_m/E_c, are required, An analysis[11] of more extensive data available for Nb_3Sn-bronze composites, where the dependence of T_c on externally applied stress has been measured,[7] suggests that plastic yielding in the bronze matrix occurs on cooling and that this can be accounted for approximately by using a lower value of E_m/E_c than the elastic value. In particular, the R_v dependence of the residual axial strain obtained from the applied stress experiments with Nb_3Sn composites is fit quite well for $1 < R_v < 44$ with Eq. (1), provided E_m/E_c is taken as 0.29 rather than the value of approximately unity which results from the actual elastic constants. (With $E_m/E_c \cong 1$, values of e_{zz} are shifted by at most 0.1%.) In the absence of any other information, we take this value to be at least approximately correct for V_3Ge-bronze composites and, together with the values of δ above, with Eq. (1) we obtain the axial strains shown together with their associated T_c enhancement in Fig. 3. Results of an applied stress experiment[12] on a V_3Ge-bronze composite with $R_v = 2.3$, reacted for 48 h

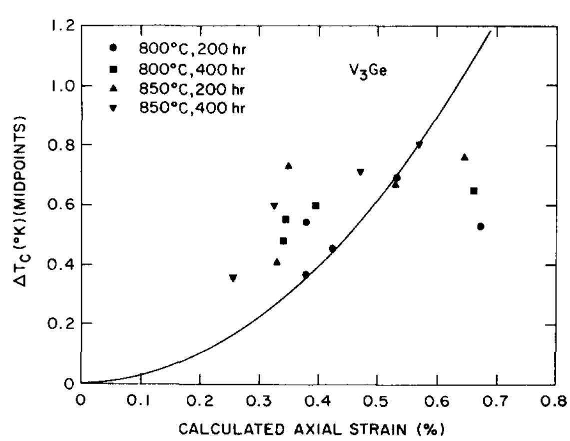

FIG. 3. Increase in the superconducting transition temperature of bronze-processed V_3Ge due to the presence of the bronze matrix as a function of the calculated differential thermal contraction-induced compressive axial strain. Also shown, as the solid curve, is a prediction based on Testardi's phenomenological theory.

at 750 °C, suggests that $e_{zz} \cong 0.2-0.3\%$, compared with a value of 0.34% calculated from Eq. (1), as described above. The measured ΔT_c is 0.9 K, somewhat larger than the values shown in Fig. 3 at the same strain.

Also shown in Fig. 3 is the predicted strain dependence of the T_c enhancement based on Testardi's theory. This curve was obtained by averaging Testardi's expression for cubic single crystals over crystal orientation for a texture-free polycrystal. Using Testardi's experimental phenomenological constants for V_3Ge [5,6] and neglecting the term linear in dilatation (which is small and of unknown sign), one obtains for cylindrically symmetric strains

$$\Delta T_c^{V_3Ge} \cong e_{zz}^2[0.965(1+2\xi)^2 + 1.53(1-\xi)^2] \times 10^4 \text{ K}, \tag{3}$$

where e_{zz} is the axial strain and ξ is the ratio of radial to axial strain. (Based on solutions to the elastic equilibrium equations for conditions appropriate to this experiment, we take ξ to be -0.1.) It may be seen that Eq. (3) yields the correct sign and order of magnitude of the change in T_c due to elastic strain, but the experimental data, even though scattered, appear to show a saturation in ΔT_c with increasing strain, inexplicable by Eq. (3). This may be a consequence of the rather rough nature of the approximations used in the estimation of the residual strain; however, it should be noted that our analysis[11] of the behavior of Nb_3Sn-bronze composites shows that the form of Eq. (3) (quadratic in e_{zz}) describes the data for ΔT_c quite well over the same range of residual strains shown in Fig. 3 for V_3Ge.

Thus, we have found that nonhydrostatic elastic strain *increases* the superconductivity transition temperature of V_3Ge, in contrast to the behavior of most A-15 superconductors, and that the sign and order of magnitude of this effect are correctly predicted with the use of Testardi's[5,6] theory. However, in contrast to these predictions, and to the behavior of Nb_3Sn, the experimental data suggests that ΔT_c does not increase parabolically with strain and saturates at strains of ~0.5%. This apparent saturation may be due to elastic strain relief by interfacial fracture in the three-phase composite or to an inherent characteristic of V_3Ge.

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Origin of coercivity in a Cr-Co-Fe alloy (chromindur)

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Lorentz microscopy and magnetization and Mössbauer effect measurements have been performed on a Cr-Co-Fe alloy having a two-phase microstructure. Domains spanning many particles have been seen in samples whose H_c's vary between 200 and 420 Oe. Walls appear to be ragged and are held back by particles. Magnetization and Mössbauer effect measurements indicate that the two phases constituting the microstructure in each of the three situations examined are ferromagnetic at ambient temperature. Based on these results it is inferred that domain-wall–particle interaction is responsible for H_c.

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Following the pioneering work of Kaneko and his co-workers on permanent magnets based on the Fe-Cr-Co alloy system,[1–4] a ductile cold-formable permanent magnet containing Fe–27 wt% Cr–15 wt% Co and minor additions of Zr and Al has recently been developed by Chin, Plewes, and Wonsiewicz[5] for telephone receiver applications. In optimally aged condition, the energy product $BH_{max} \sim 1.5 \times 10^6$ GOe can easily be achieved. In fact, Kaneko *et al.*[4] have successfully attained values as high as $BH_{max} \sim 8 \times 10^6$ GOe in a ⟨100⟩ single crystal by incorporating an additional anneal in a magnetic field followed by swaging. It has been assumed previously that, as in Alnico, domain rotation of single domain magnetic particles within a nonmagnetic matrix is