Letters

Magnetisation of Superconducting Carbides

Reported values of the critical temperature, T_c, for superconducting transition-metal carbides show considerable disagreement [1]. These carbides exist over a wide homogeneity range, and it is now known that their critical temperatures vary with carbon content. For niobium and tantalum monocarbides, T_c is a maximum for the stoichiometric composition, and falls off rapidly with decreasing carbon content. T_c for $NbC_{0.977}$ is 11.1° K, falling to 1.05° K for $NbC_{0.829}$, and is 9.7° K for $TaC_{0.987}$, falling to 2.04° K for $TaC_{0.848}$ [2].

Samples of niobium and tantalum carbides deficient in carbon, prepared by conventional hot-pressing techniques, were supplied by Murex*. The samples were in the form of rectangular strips measuring 20 × 2 × 0.4 mm. Samples were investigated both in the as-received condition and after annealing for 1 h at 2250° C in a carbon tube furnace. Chemical analyses (table I, p. 498) and stress/strain curves indicated that the samples picked up carbon during the annealing treatment [3]. Specimen magnetisation was measured at 4.2° K by moving the specimen axially from one search coil to another, wound in opposition, inside a uniform magnetic field provided by a superconducting solenoid. The change in magnetic flux as the specimen was moved from one coil to the other was measured with a ballistic galvanometer.

The magnetisation curves of the as-received and the annealed niobium carbide specimens are shown in fig. 1. Compared to the as-received specimen, the magnetisation curve of the annealed sample shows a decrease in the magnetic hysteresis. This decrease is believed to be due to a removal of the barriers causing hindrance to flux movement. It is now known that various crystal imperfections, such as dislocations, precipitates, etc., can interact with Abrikosov's supercurrent vortices (see outline in reference 4) and cause flux pinning [5]. Figs. 2 and 3 are the photomicrographs of the specimen before and after annealing [3]. The dark dots seen at the grain boundaries are the holes and cavities produced during sintering. After annealing, there is a reduction in the number and size of holes. Measurements indicated an

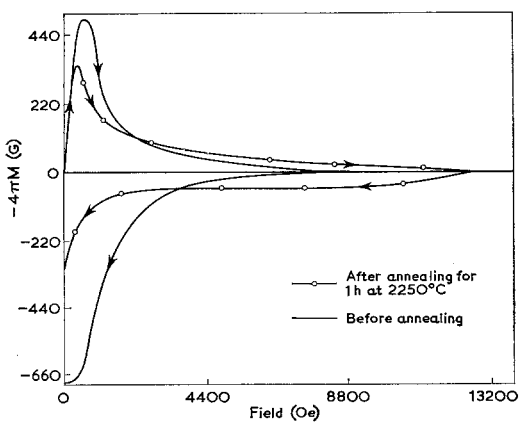

Figure 1 Magnetisation curves of niobium carbide before and after annealing.

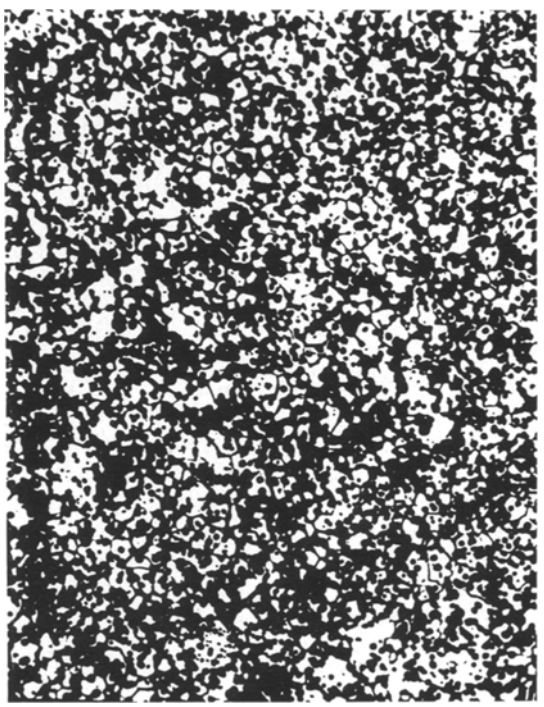

Figure 2 Photomicrograph of niobium carbide before annealing (×210).

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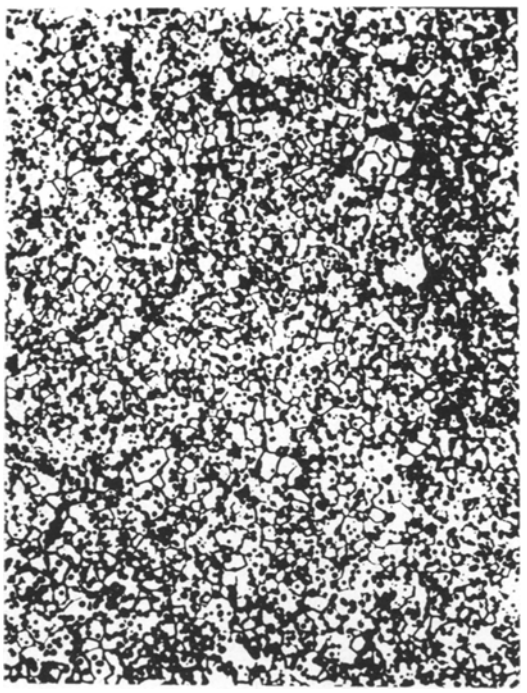

Figure 3 Photomicrograph of niobium carbide after annealing for 1 h at 2250° C (×210).

increase in the density of the specimen (table I). This reduction in the density of holes and cavities after annealing is perhaps the most significant cause of the observed decrease in the hysteresis. The mechanism of flux pinning by a hole or cavity should be similar to that due to a non-superconducting particle, where the pinning arises because of the existence of the surface barrier to vortex entry [6, 7]. The magnitude of the interaction of a vortex with a hole will be proportional to the difference between the equilibrium magnetisation of the hole and the superconductor. Because of the lack of success in preparation of suitably thin specimens for transmission electron microscopy, the part played by dislocations and other imperfections remains unclear.

A more interesting feature of the magnetisation curves of fig. 1 is the increase observed in the upper critical field, H_{c_2}, after annealing. H_{c_2} is increased from the initial value of 8000 Oe to a value greater than 12 000 Oe. This must be due to the increased carbon content after annealing, which will increase T_c and hence the critical field.

Similar studies were made on tantalum carbide specimens. Fig. 4 gives the magnetisation of the

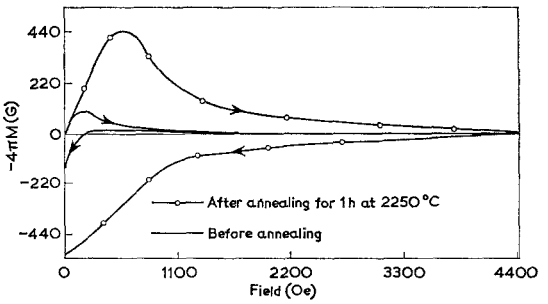

Figure 4 Magnetisation curves of tantalum carbide before and after annealing for 1 h at 2250° C.

specimen before and after annealing. In contrast to niobium carbide, the specimen after annealing shows a considerable increase in the magnetic hysteresis. As before, there is also a large increase in H_{c_2}. This increase is again due to the increased carbon content. Photomicrographs of the tantalum carbide were similar to those for the niobium carbide; but there is evidence that in the annealed specimen the carbon content was in excess of that required for stoichiometry, and that this excess carbon had precipitated out [3]. These carbon precipitates may account for the increased hysteresis of the annealed specimen. Again, it was not possible to produce thin specimens for transmission electron microscopy.

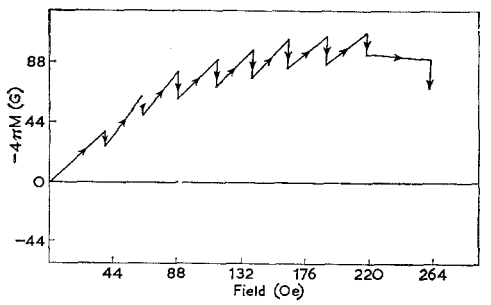

Figure 5 Magnetisation curve of tantalum carbide before annealing, showing flux instabilities.

The detailed magnetisation studies of the as-received specimen showed an interesting effect (fig. 5). Flux jumps were observed at fields much smaller than the field for largest magnetisation. The occurrence of instabilities at such an early stage in the magnetisation curve is most unusual. It suggests that the as-received material is very inhomogeneous and contains large volumes whose composition is such that the critical temperature is below 4.2° K. The jumps in the magnetisation curve correspond to the flux

TABLE I [3]

Material	Carbon content (wt %)	(at. %)	Density (% theoretical)	T_c (° K) [2]
NbC, as-received	10.00	46.2	91.5	7
NbC, annealed	10.90	48.6	92.5	11
TaC, as-received	6.28	50.1	83.8	10
TaC, annealed	6.50	51.1	89.3	10

rapidly penetrating across these non-superconducting regions. The annealing treatment removes these inhomogeneities and the annealed specimen does not show flux jumps. It is concluded from these results that niobium and tantalum carbides are type-II superconductors, whose critical temperature, upper critical field, and degree of irreversibility are strongly affected by carbon content and microstructure.

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References

1. B. W. ROBERTS, *Progress in Cryogenics* **4** (1964) 159.
2. A. L. GIORGI, E. G. SZKLARZ, E. K. STORMS, A. L. BOWMAN, and B. T. MATTHIAS, *Phys. Rev.* **125** (1962) 837.
3. D. J. ROWCLIFFE, (Lockheed Missile and Space Corp, Palo Alto, California), private communication.
4. A. V. NARLIKAR and D. DEW-HUGHES, *J. Matls. Sci.* **1** (1966) 317.
5. D. DEW-HUGHES, *Matls. Sci. and Eng.* **1** (1966) 2.
6. A. M. CAMPBELL, Ph.D. thesis, Cambridge (1966).
7. J. E. EVETTS, Ph.D. thesis, Cambridge (1966).

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The Vertical Pulling of $MgAl_2O_4$ Single Crystals

This note describes a technique which allows single crystals of spinel, $MgAl_2O_4$ (melting point 2105° C), to be pulled from the melt, and such a crystal is shown in fig. 1. This is the first reported growth of spinel using this method. Hitherto, it has been grown by either flux or flame-fusion methods.

The main difficulties in growing high-melting-point oxides such as spinel by the vertical-pulling technique arise because iridium, which is the only suitable crucible material chemically compatible with the molten oxide, has a melting point (2410° C) only slightly higher than the oxide itself. Because of the insulating nature of oxide melts, the crucible wall must be at a considerably higher temperature than 2105° C in order to keep the material molten in the crucible centre. As a consequence, the iridium is at a temperature approaching its own melting point, and any inhomogeneity in the crucible, such as a deviation in wall thickness or an impurity inclusion, leads to localised overheating and catastrophic failure of the crucible. In the present work, these difficulties have been overcome by using a crucible with a wall thickness of 0.125 in. (1.0 in. = 25.4 mm), twice the thickness used in the growth of sapphire [1], and by placing an iridium disc above the crucible as near to the melt surface as possible. Although a small viewing slot is necessary in the disc for the operator to see the growing crystal, this latter measure considerably reduces the radial temperature gradients.

The general arrangement of the crystal-growing apparatus is similar to that used already for sapphire [1], but, as it is the detailed changes made during the present work which