Superconductivity of Nb–Ru alloys synthesized at high pressure

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We synthesized at high pressure two intermetallic phases with composition close to $NbRu_3$, an α phase with structure of the Cu_3Au type ($a = 3.88$ Å), and a γ phase with hexagonal close-packed structure ($a = 2.74$ Å, $c = 4.40$ Å). The superconducting-transition temperatures of the α and γ phases were $T_c = 15$–16 °K and 11–12 °K respectively.

The system Nb-Ru was investigated at normal pressure by several workers. In spite of some differences in details, the main features of its structure can apparently be regarded as reliably established. The system covers a wide range of solid solutions based on the bcc lattice of Nb (up to 55 at.% Ru),[1] which undergoes a martensitic transformation when the Ru concentration exceeds 40 at.%. The solid-solution lattice then becomes tetragonal[1] or orthorhombic.[2,3] The solid-solution region based on the hcp lattice of Ru is narrower (up to 29 at.% Nb).[1] The system contains only one intermediate phase with composition near $NbRu_3$ with hcp structure,[1] which has, according to the data of[4], a high-temperature modification with a more complicated hexagonal structure.

The superconducting properties of the Nb-Ru alloys were investigated in[5,6]. In the region of the cubic solid solution, the critical temperature decreases rapidly (0.65 °K per at.% of Ru) down to $T_c < 1$ °K, and further increase of the Ru concentration leads to a certain increase of the critical temperature, to $T_c > 1$ °K in the region of the tetragonal solid solution[5] and to $T_c = 2.5$ °K for alloys with composition Nb_2Ru_3.[6]

We investigated the structure and superconducting features of Nb-Ru alloys (from 66 to 90 at.% Ru) prepared from powders of the constituent metals at a pressure of 100 kbar (the calibration was against the polymorphic transitions of bismuth at 25.4, 26.9, and 89 kbar and of tin to 112 kbar) and temperature from 1200 to 1350 °C. The samples were sintered in a boron nitride ampul placed in a heater made of metallic niobium. The temperature was measured with a chromel-alumel thermocouple, the junction of which was located near the outer wall of the niobium heater. The samples were kept at the set values of P and T for 2—10 minutes and were then rapidly cooled to room temperature at constant pressure. After removal of the load, the samples were taken out of the chamber and powder debyegrams were obtained in copper-filtered radiation in RKD-57 and RKU-114 cameras. The superconducting properties of the samples were measured by a magnetic method.

The alloys investigated in greatest detail were those with composition $NbRu_3$; they were all polyphase, apparently as a result of the presence of a temperature gradient in the reaction ampul as well as because of the non-equilibrium conditions under which the experiment was performed (short exposure times, rapid cooling to room temperature). Two intermediate phases were found in the samples of this composition, a γ phase with hexagonal close-packed structure, having unit-cell parameters $a = 2.74 \pm 0.01$ Å, $c = 4.40 \pm 0.02$ Å, and $c/a = 1.60$, and a cubic α phase with Cu_3Au structure and $a = 3.88 \pm 0.02$ Å.

The samples are usually mixtures of both phases, and in some cases a third phase is observed, namely a solid Ru(Nb) solution based on the hexagonal close-packed structure of Ru with unit-cell parameters $a = 2.71 \pm 0.01$ Å, $c = 4.29 \pm 0.02$ Å, and $c/a = 1.58$. From the measured parameters, in accordance with the data of[1], we can estimate the amount of dissolved Nb, which does not exceed 3—5 at.%.

The formation of a hexagonal close-packed phase with $NbRu_3$ composition and with unit cell parameters $a = 2.75$ Å, $c = 4.418$ Å, and $c/a = 1.607$ at atmospheric pressure was noted in[1], and an α phase with structure of the Cu_3Au type is apparently produced as a result of the high pressure. The x-ray patterns of the samples containing the α phase reveal no superstructure lines, but the question of the ordering of this phase cannot be solved by x-ray analysis, since the near equality of the atomic factors of the niobium and ruthenium scattering should make the intensity of the superstructure reflections very small even in the case of complete ordering. If the intensity of the strongest reflection is assumed to be $I_{111} = 100$, then the intensity of the strongest reflections produced after ordering is smaller by a factor of almost 200: $I_{100} = 0.6$ and $I_{111} = 0.4$.

Measurement of the superconducting properties of the $NbRu_3$ alloys have revealed that all have rather high superconducting-transition temperatures. The mean critical temperature is ~13 °K and the width of the transition is 2—4 °K. A comparison of the critical temperatures and of the phase composition of the samples gives grounds for assuming that both phases are superconducting, but the cubic phase is characterized by a somewhat higher value $T_c = 15$—16 °K, whereas the hexagonal phase has $T_c = 11$—12 °K.

As is well known, many phases with hexagonal close-packed structure and with cubic structure of the Cu_3Au type have superconducting properties, but their critical temperatures usually do not exceed 10 °K.[7,8] Judging from the critical temperatures obtained for the $NbRu_3$ alloys prepared at high pressure, one could more readily assume that a phase with structure of the Cr_3Si is produced, but x-ray diffraction did not reveal this phase in any of the samples.

Alloys obtained at high pressure were annealed in vacuum at temperatures 1000 °C (for 2 hours) and 1200 °C (for 5 hours). No significant change in the phase composition and in the superconducting properties was observed.

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