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clearly perceptible and is sufficient to establish it as distinctly superior for use as the red-emitting component in cathode ray tubes for color television.

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METASTABLE PHASES AND SUPERCONDUCTORS PRODUCED BY PLASMA-JET SPRAYING[1]

($Ag_{0.6}Cu_{0.4}$ – a = 3.924 ±.001 Å, fcc, enhanced mutual solubility; $Ag_{0.74}Ge_{0.26}$ – a = 2.8995 ± .0008 Å, c = 4.7163 ±.0016 Å, c/a = 1.6266 ±.007, hcp, probable metastable compound; $Mo_{0.6}Ru_{0.4}$ – a = 2.7640 ±.0009 Å, c = 4.4621 ±.0017 Å, c/a = 1.6144 ±.0008, hcp, this is superconductor, T_c = 8.7°K; E)

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Metals and alloys may be quenched from the melt at rates estimated to be as high as 10^7 deg/sec, resulting in metastable phases which may be recovered at room temperature.

The principal advantages of the plasma-jet spraying technique described here are threefold: (1) Very high quench rates are possible; (2) large quantities of material may be easily produced in a continuous manner (the order of grams per minute); (3) refractory and reactive materials may be treated since there is no container problem.

The plasma-jet spraying technique consists in injecting powdered material (~325 mesh, or 44 μ) into a high-temperature plasma, and impinging the molten droplets at high velocity onto a cooled, roughened copper plate. In the present work this was accomplished with a Plasmadyne SG-1 hand spray gun.[2] The plasma may be generated in any of a wide variety of gases or gas combinations; helium or argon was used in these experiments. The residence time of a particle in the plasma is ~ 10^{-3} sec. The minute size of the droplet coupled with the intimate contact it makes with the copper target produces the very high cooling rate.

Ideally, the composition of each particle injected into the plasma should represent the bulk composition of the material being sprayed. To this end it is desirable, when treating a system of two or more phases, to prepare the powder from an alloy ingot of fine microstructure. A less desirable, but sometimes necessary, method is to inject mixed powders into the plasma. Only a limited amount of alloying can take place this way, but the deposited material may be removed from the copper target, pulverized, and recycled to achieve greater homogeneity. This might be done, for example, when the melting points of the alloy constituents are so different as to make the preparation of a master melt difficult.

The present work derives its inspiration from the rapid-quenching experiments on a variety of alloy systems being performed at the California Institute of Technology. Duwez and Willens describe how a small amount (about 100 mg) of material is melted in a graphite container, and then ejected through a small hole onto a curved copper target by means of a shock tube.[3] The drop smears to form a foil between 0.1 and several microns thick. Extension of solubility limits beyond equilibrium values, new phases not found under equilibrium conditions, and amorphous alloys have resulted from the Caltech experiments.

By means of plasma-jet spraying, two alloys, which have also been investigated by the Caltech workers,[4,5] were rapidly quenched. Complete mutual solid solubility in a $Ag_{0.6}Cu_{0.4}$ alloy (normal eutectic composition) was achieved. X-ray diffraction revealed the quenched material to be single phase, face-centered cubic; $a = 3.924 \pm .001$Å. This result is consistent with the experiment of Duwez, Willens, and Klement.[4]

A $Ag_{0.74}Ge_{0.26}$ alloy (eutectic composition) was plasma-jet sprayed to produce a metastable, single phase, hexagonal close-packed structure; $a = 2.8995 \pm .0008$ Å, $c = 4.7163 \pm .0016$ Å, $c/a = 1.6266 \pm .0007$. This agrees well with the result of Duwez, Willens, and Klement.[5] (Note a typographical error in this reference; the value of a for their $Ag_{0.743}Ge_{0.257}$ alloy apparently should be 2.897 Å, not 2.987 Å.) The same hcp phase, together with diamond-cubic germanium, was found in a sprayed $Ag_{0.26}Ge_{0.74}$ alloy.

The formation of metastable phases is not the only interesting feature of rapid quenching. Suppression of the normal formation of a phase has been accomplished by plasma-jet spraying, with an attendant enhancement of superconducting properties in an alloy of molybdenum and ruthenium. A $Mo_{0.6}Ru_{0.4}$ composition was melted in argon in a conventional arc-melting furnace, and the ingot was pulverized to 325 mesh. X-ray powder diffraction revealed an hexagonal phase – molybdenum dissolved in hexagonal ruthenium. In addition, as expected, the σ phase, Mo_5Ru_3, was identified.[6,7]

The technique of Schawlow and Devlin was used to determine the superconducting properties of the powder.[8] In this measurement, the powder is placed in the core of a solenoid whose inductance changes at the transition temperature. This change is reflected in a shift in frequency of an oscillator. The results are shown in Fig. 1; two distinct transitions are evident. Because the transitions are so broad, the superconducting transition temperatures are arbitrarily chosen at the points of inflection – $T_c = 6.3$ °K and $T_c' = 8.0$ °K. Very likely T_c corresponds to Mo_5Ru_3,[9,10] and T_c' to the molybdenum-ruthenium solid solution.[11]

The powder was plasma-jet sprayed, and the deposit was removed from the target and pulverized. X-ray diffraction revealed the same hcp phase (the molybdenum-ruthenium solid solution) as in the arc-melted material. The Mo_5Ru_3 phase, however, had disappeared. Figure 1 shows only one transition now – $T_c'' = 8.7$ °K. Presumably the absorption of the Mo_5Ru_3 into the solid solution sufficiently altered the valence electron/atom ratio to increase

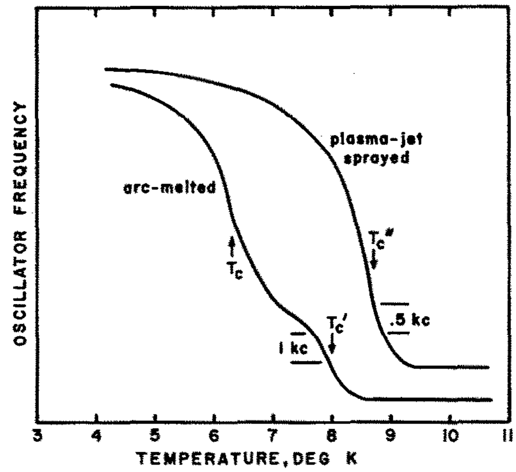

Fig. 1. Superconductivity of arc-melted and plasma-jet sprayed molybdenum-ruthenium. Schawlow and Devlin method of measurement at ~100 kc/sec.

the transition temperature by 0.7 °K. The lattice constants for the solid solution produced by spraying are $a = 2.7640 \pm .0009$ Å, $c = 4.4621 \pm .0017$ Å, $c/a = 1.6144 \pm .0008$. By extrapolation of existing data,[6] this corresponds to a solution of ~54 at.% Mo. Unfortunately the x-ray pattern for the arc-melted alloy was not very good, and the most that can be said is that the lattice constants for the arc-melted solid solution are approximately the same as for the sprayed alloy.

We thank B. T. Matthias for suggesting the molybdenum-ruthenium system as being potentially interesting in a rapid-quenching experiment.

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