

Ion mixing to produce amorphous Mo-Ru superconducting films

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Amorphous $\text{Mo}_{55}\text{Ru}_{45}$ alloy films were formed by ion mixing of multilayered samples. The ion mixed films, which contain no metalloid element, show excellent superconducting properties. The measured properties are correlated with the microstructure obtained by both x-ray diffraction and transmission electron microscopy.

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The Mo-Ru system has interested people in its superconducting properties, especially when the alloy is in the amorphous state. According to Collver and Hammond,¹ the superconducting to normal state transition temperature T_c of $\text{Mo}_{60}\text{Ru}_{40}$ amorphous alloy could be as high as 8.4 K. However, splat cooling technique has not been successful in producing this alloy. The addition of above 20 at. % of a metalloid element (e.g., B, P, Si, and As) is required by this technique to obtain an amorphous material.² The quenched amorphous alloy is therefore actually a ternary one and the metalloid elements decrease the transition temperature T_c considerably.³ It has been demonstrated that an amorphous phase will be formed by ion mixing using multilayered samples in those binary metal systems where two constituent metals are of different structures (structural difference rule).⁴ According, Mo-Ru amorphous materials should be obtainable by ion mixing, because Mo is of bcc structure and Ru has a hcp structure. However, at the composition of approximately $\text{Mo}_{60}\text{Ru}_{40}$, there is an equilibrium crystalline phase (σ phase) which might be expected to hamper the formation of a completely amorphous structure. In this letter we report the formation of Mo-Ru alloy films by ion mixing. These films consist of an amorphous matrix with crystalline phase inclusions. The superconducting properties as a function of ion dose have been measured and have been used to extract structural information which can be correlated to results from x-ray diffraction and transmission electron microscopy.

Multilayered samples were prepared by depositing Mo and Ru in alternating sequence on the inert substrate (SiO_2) to a total thickness of about 550 Å, which corresponds to the projected range R_p plus projected range straggling ΔR_p of the 300-keV Xe ions chosen for ion irradiation. The overall atomic composition ratio was controlled by varying the relative thickness of the Mo and Ru layers, and was designed to be $\text{Mo}_{55}\text{Ru}_{45}$. The samples consisted of four layers each of Mo and Ru, each about 50–90 Å with Ru at the top. The as-deposited samples were then irradiated at room temperature to the doses ranging from 3×10^{15} to 1.7×10^{16} Xe/cm².

As the mass numbers of Mo (96) and Ru (101) are very close, Mo and Ru signals in the backscattering spectrum will

be overlapped. Nevertheless, by adjusting the tilt angle to overlap the signal of the first Mo layer with that of the second Ru layer and so on, one is able to see the discrete structure of the Mo-Ru multilayers. From the backscattering spectra taken before and after irradiation to various doses, it was found that a dose of 7×10^{15} Xe/cm² was needed to induce more or less uniform mixing (see Fig. 1).

For those samples irradiated to doses of 7, 10, 13, and 17 in units of 10^{15} Xe/cm², x-ray diffraction patterns (Read camera) showed an amorphous band with occasional evidence for crystalline phase. Table I summarized the observations from x-ray diffraction. Some samples were examined by TEM. Figure 2 shows (a) a typical electron micrograph and (b) an electron diffraction pattern. One can see that the structure consists mainly of grey amorphous matrix with 50–100 Å crystals (light and dark regions) interspersed throughout. A careful examination of the grey amorphous matrix reveals lighter features about 10 Å across which probably are Xe gas bubbles. We conclude from the observations that an amorphous matrix was formed by ion mixing in all those four samples, which was interspersed by the crystalline inclusions as well as Xe gas bubbles. In other words, the ion mixed films are very inhomogeneous, which should be responsible to their superconducting properties discussed later.

The superconducting measurements performed were transition temperature, upper critical field, and critical current. The transition temperature and upper critical field

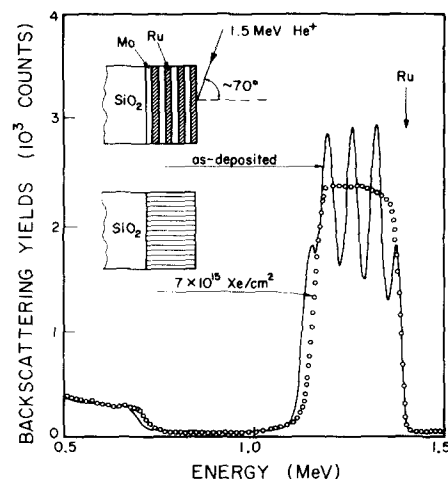


FIG. 1. MeV $^4\text{He}^+$ backscattering spectra of Mo-Ru multilayered sample and the sample irradiated to a dose of 7×10^{15} Xe/cm².

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TABLE I. X-ray diffraction results from the ion mixed films.

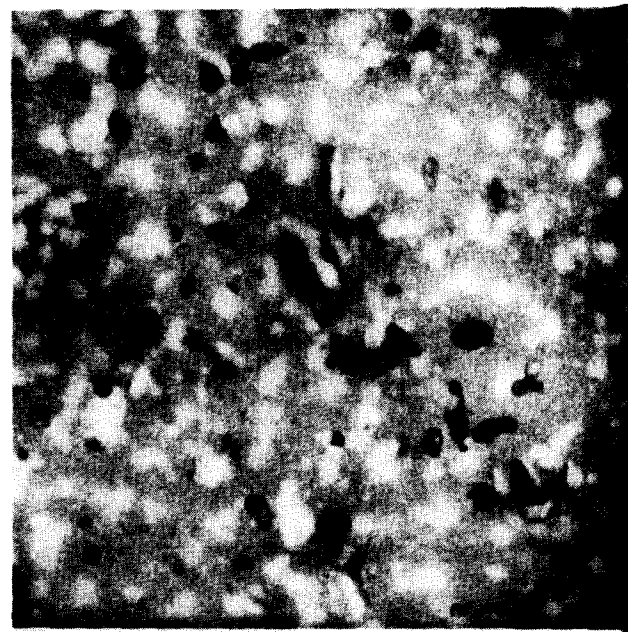
Ion dose (Xe/cm ²)	Amorphous phase	Crystalline phase	Comment
7×10^{15}	a diffuse band	some weak Mo and Ru lines	Amorphous + Mo + Ru
1×10^{16}	an intense diffuse band	weak lines probably Mo	almost totally amorphized
1.3×10^{16}	a diffuse band	Mo or σ phase	Amorphous + (Mo or σ phase)
1.7×10^{16}	a diffuse band	Mo or σ phase	Amorphous + (Mo or σ phase)

measurements were performed resistively using a standard four-point probe. This type of measurement requires percolation of a supercurrent through the sample which in turn requires that about 15% of the sample be superconducting.⁵ Thus, in inhomogeneous materials such as these, the T_c measurements may reflect only about the 15% of the sample having the highest T_c . On the other hand, critical current measurements generally represent the superconducting properties of the bulk of the sample. From critical current measurements, we can obtain the flux pinning force density. By measuring critical current as a function of field and extrapolating to zero current we can find the bulk upper critical field.

A scaling relationship exists between primary force density and upper critical field of the form $F_p \propto H_{C_2}^n$; $n \sim 2$.⁶ Thus, the critical parameter for evaluating the relationship between a change in pinning force and a change in microstructure is $F_p/H_{C_2}^2$.

Table II summarizes the superconducting properties measured on these samples. The transition temperature and upper critical field behavior is complicated by the inhomogeneous nature of these samples. It is not clear which phase is dominating the superconducting behavior. However, there are some points worth mentioning. The transition temperature first rises then drops as a function of irradiation dose. Purely amorphous films of Mo-Ru alloys have been previously prepared by coevaporation of the metals.¹ For comparison, the T_c of evaporated amorphous Mo-Ru phase of this composition was found to be about 8 K, while T_c for σ -phase $\text{Mo}_{60}\text{Ru}_{40}$ is known to be 7.1 K.⁷ Thus, the transition temperature behavior would suggest that as ion mixing progresses, the sample first transforms to an amorphous structure, but with further irradiation transforms to a σ -phase crystalline structure.

The upper critical field was linear with temperature over the measured range for all these samples. The field gradients $(dH_{C_2}/dT)_{T=T_c}$ are all fairly high (~ 24 kOe/K) which is characteristic of a disordered material. There is a large difference between the resistively measured upper critical field and that found by extrapolating the critical current measurements. This reflects the inhomogeneous nature of



(a)

1000 Å



(b)

FIG. 2. TEM results of structural analysis of ion mixed $\text{Mo}_{55}\text{Ru}_{45}$: (a) electron micrograph; (b) electron diffraction pattern.

these samples. The maximum pinning strength $F_{pm}/H_{C_2}^2$ decreases then increases as a function of irradiation dose. The decrease in pinning force from sample 7×10^{15} to sample 10×10^{15} Xe/cm² is most likely due to the destruction of the remnants of the original layered crystalline structure. The increase in pinning force following doses greater than 10×10^{15} Xe/cm² may be due to the formation of the crystalline σ phase, which is likely formed by a polymorphic transformation of the amorphous phase.⁸ This interpretation is

TABLE II. Xenon ion dose, transition temperature, critical field gradient, critical field at 4.2 K determined from resistive measurements [H_{C_2R} (4.2)] and flux pinning measurements [H_{C_2p} (4.2)], and flux pinning force parameter for ion beam mixed Mo₅₅Ru₄₅ samples.

Ion dose (ions/cm ²)	T_c (K)	$\left. \frac{dH_{C_2}}{dt} \right _{T_c}$ (kOe)/K	H_{C_2R} (4.2) (kOe)	H_{C_2p} (4.2) (kOe)	$F_{P_m}/H_{C_2}^2$ (N/m ³ Oe ²)
0 (initial layers)	0.92 [Mo(bcc)] 0.49 [Ru(hcp)]
7×10^{15}	7.66	24.1	83.4	67	0.111
10^{16}	7.72	22.5	79.2	63	0.099
1.3×10^{16}	7.42	25.0	80.5	60	0.107
1.7×10^{16}	7.17	25.4	75.4	59	0.124

consistent with the x-ray results and T_c behavior. Transmission electron microscopy did not reveal significant morphological changes, suggesting that critical current measurements are more sensitive to subtle changes in the microstructure than TEM.

The critical current densities measured in these samples were comparatively large. For example, at field of $\frac{1}{2} H_{C_2}$ and a temperature of 4.2 K (reduced temperature $T/T_c \sim 0.6$) the critical current was above 1×10^4 A/cm². This large critical current density again reflects the inhomogeneous nature of these samples and suggests that this sample fabrication technique results in a sample microstructure which is very favorable to obtaining strong flux pinning effects.

In conclusion, partially amorphous Mo-Ru films have been produced by ion mixing of multilayered samples without adding any metalloid element. The microstructure is shown by TEM, x-ray diffraction, and superconducting measurements to be very inhomogeneous and consists of an amorphous matrix with crystalline inclusions. Critical current measurements have demonstrated that flux pinning intersections and thus the inhomogeneity first decreases and then increases as a function of irradiation dose. This is interpreted as resulting from the change in sample microstructure with progressive ion irradiation. The high critical cur-

rent observed suggests that this sample fabrication technique might be employed in other high T_c superconductors to produce a microstructure favorable for strong flux pinning and subsequently high current carrying capacity.

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