

Superconductivity in rapidly quenched Mo-P-B alloys

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Superconducting transition temperatures (T_c) were measured for a series of Mo-P-B alloys in the Mo-rich corner of the ternary system. The alloys were studied in two forms: (a) slowly cooled after induction melting, and (b) rapidly quenched in an arc hammer apparatus. The rapid quenching produced an amorphous structure, but most of the alloys also contained some crystalline material, indicating that this system is not conducive to easy glass formation. Ternary slowly cooled crystalline alloys in the concentration range 20 to 30 at % phosphorus and 10 to 20 at % boron had relatively high T_c values of 9.6 to 9.9 K; higher than for either the Mo-P or Mo-B binary systems. T_c values up to 9.02 K were observed for completely amorphous foils, consistent with the previously reported maximum T_c values for amorphous alloys in this system. This remains the highest T_c reported for a metallic glass. All of the rapidly quenched foils were brittle.

1. Introduction

Interest in amorphous superconductors has included behaviour of the superconducting transition temperature, T_c , as a function of composition in the periodic table [1], explanations of the occurrence of superconductivity in amorphous alloys [2, 3], and information which superconductivity can give about the electronic [4] or defect [5] structure of amorphous alloys. It has been suggested that amorphous superconductors might find applications in superconducting magnet technology because of their good mechanical properties and their resistance to radiation damage [6, 7]. However, the values of T_c and H_{c2} , the upper critical field, of the best amorphous superconductors are only comparable to those for crystalline alloy superconductors such as NbTi, and fall short of those for compound superconductors like Nb₃Sn and Nb(CN). If ductile amorphous superconductors could be found with T_c and H_{c2} values greater than those of ductile alloys like NbTi, and if useful critical current densities could be achieved in them, for example, by partial crystallization, then a real interest in their practical use would arise. The amorphous alloys with the highest

reported values of T_c are based on molybdenum. A liquid-quenched alloy of Mo-10 at % B-10 at % P was reported [8] to have a T_c of 9.0 K: the highest value for a metallic glass yet observed. Molybdenum films ion implanted with nitrogen, sulphur or phosphorus at liquid helium temperatures had T_c values of 9.2 K for an "amorphous-like" phase [9].

There has been recent work [10] directed towards finding metallic glass superconductors with higher T_c values. None have been found to date. We report in this paper the results of experiments on rapidly quenched alloys in the Mo-rich corner of the Mo-P-B ternary alloy system. These experiments were conducted in an attempt to optimize T_c in the alloy system which now contains the metallic glass alloy with the highest value for T_c .

2. Experimental details

The Mo-P-B alloys were prepared from high purity powders which were mixed and pressed into pellets. The alloy pellets were sealed in quartz capsules under a partial pressure of pure argon and slowly heated in muffle furnaces to 1000°C to ensure reaction of the metalloid elements with

molybdenum. Alloy buttons with only modest losses of the volatile metalloid elements were prepared by levitation induction melting of the pellets in a water-cooled copper boat under an atmosphere of pure argon. Small samples (20 to 40 mg) were broken from the alloy castings and rapidly quenched from the liquid phase in an arc hammer apparatus described elsewhere [11].

Because of the volatility of boron and phosphorus, special care was taken to analyse the samples, both as alloy castings and as quenched foils. Three techniques were used: X-ray fluorescence, electron microprobe, and conventional wet chemical analysis. Only molybdenum and phosphorus could be analysed using the X-ray fluorescence and microprobe units available, so boron was obtained by the difference. In general, good agreement (~ 1 to 2%) with the nominal compositions was observed, and we will therefore use these compositions in the discussion of the experiments.

The rapidly quenched foils were characterized by X-ray diffraction on a Norelco automated diffractometer using $\text{CuK}\alpha$ radiation. Most of the as-

quenched foils were quite brittle. Some foils fractured in the arc hammer during the quench and were found as small fragments a few mm in diameter. There appeared to be a correlation between sample brittleness and structure. The most brittle samples were those containing the highest percentage of crystalline phase(s) as measured by the relative heights of the crystalline Bragg peaks in the X-ray diffraction patterns. Measurements of T_c were made by an inductive technique which has been described elsewhere [12, 13]. A calibrated germanium resistance thermometer was used to measure the temperature, and a pure lead sample was kept in the measuring coils for internal calibration.

3. Results and discussion

The results of the X-ray diffraction and T_c measurements are given in Table I. The relative fractions of the amorphous and crystalline phases were estimated from intensities of the broad amorphous peaks and the sharp crystalline Bragg peaks in the X-ray diffraction patterns. Examples of the diffraction patterns for rapidly quenched foils of

TABLE I Structure of rapidly quenched foils by X-ray diffraction

Alloy	Predominantly crystalline	Predominantly amorphous	Amorphous	T_c of quenched foils (K)	T_c of ingots (K)
Mo + 5P + 10B	0			8.49	3.64
Mo + 5P + 15B	0			7.98	5.56
Mo + 5P + 20B	0			7.47	5.62
Mo + 10P + 5B	0			7.50	3.85
Mo + 10P + 10B		0		8.00	5.59
Mo + 10P + 15B			0	7.70	5.56
Mo + 10P + 20B		0		7.20	5.63
Mo + 15P + 5B	0			8.20	3.46
Mo + 15P + 10B			0	8.10	5.50
Mo + 15P + 15B		0		8.02	7.88
Mo + 15P + 20B	0			7.70	8.89
Mo + 20P		0		8.61	5.97
Mo + 20P + 10B		0		7.60	9.32
Mo + 20P + 15B			0	9.02	9.62
Mo + 20P + 20B		0		9.62	9.75
Mo + 25P		0		8.37	5.68
Mo + 25P + 5B	0			7.47	5.67
Mo + 25P + 10B		0		7.30	9.89
Mo + 25P + 15B	0			9.30	9.89
Mo + 30P	0			8.07	4.20
Mo + 30P + 5B		0		6.85	5.49
Mo + 30P + 10B		0		6.80	9.75
Mo + 30P + 15B	0			9.44	8.32

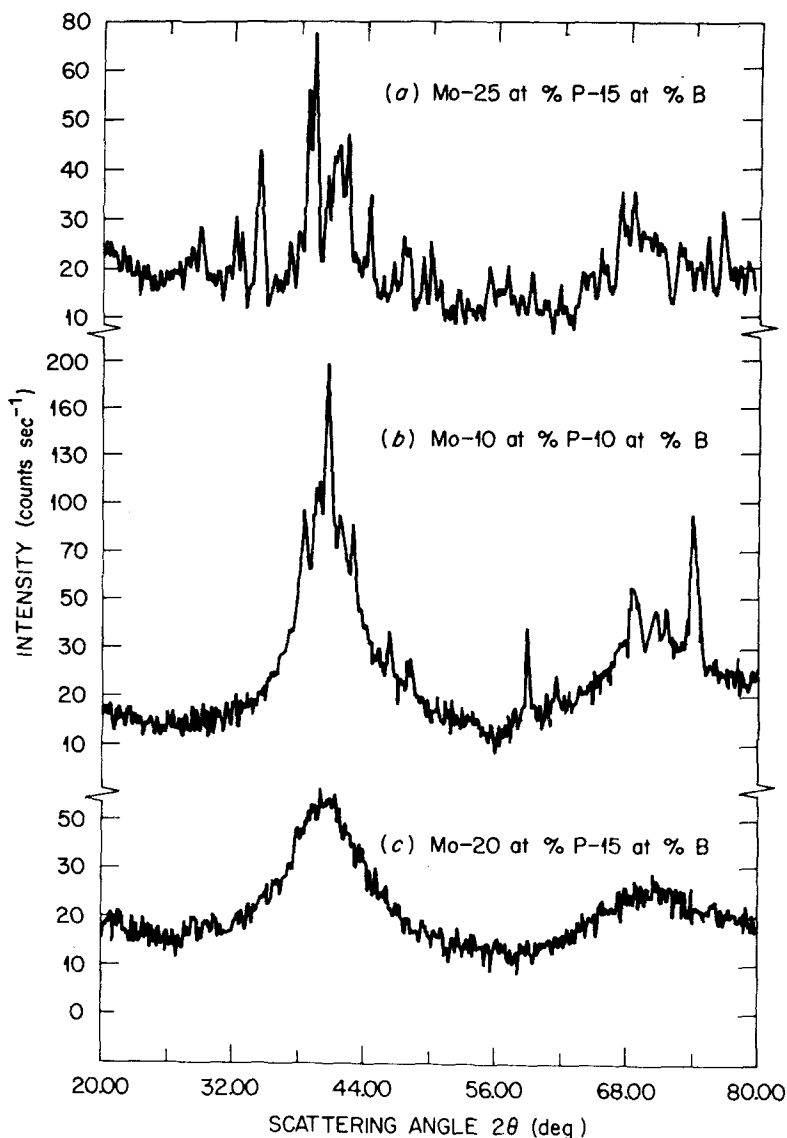


Figure 1 Diffracted intensity against scattering angle 2θ for rapidly quenched foils of: (a) Mo-25 at% P-15 at% B, (b) Mo-10 at% P-10 at% B, (c) Mo-20 at% P-15 at% B.

Mo-25 at% P-15 at% B, Mo-10 at% P-10 at% B, and Mo-20 at% P-15 at% B are presented in Figs. 1a, b and c, respectively, for samples which are (a) predominantly crystalline, (b) predominantly amorphous, and (c) amorphous. This qualitative description of the structure of each alloy is indicated in Table I. In many cases, quenched foils from the same alloy had different ratios of amorphous to crystalline phases. Samples with the greatest percentage of amorphous phase are reported in Table I for each alloy. Most of the Mo-P-B alloys rapidly quenched exhibited a mixed structure (i.e. amorphous and crystalline). Cooling rates have been estimated to be 10^6 to 10^7 K sec^{-1} [11] for the conditions employed in the arc hammer apparatus used for rapid quench-

ing. Since completely amorphous structures were not generally obtained at these cooling rates, the Mo-P-B alloys studied cannot be considered easy glass formers. Because of the mixed-phase nature of most of the alloys, it was not always possible to determine whether the maximum measured T_c corresponded to the amorphous structure or to some crystalline phase. The T_c values listed in Table I and plotted in the figures represent the temperature for the onset of superconductivity.

In order to distinguish between the T_c values of the amorphous and crystalline phases, T_c measurements were made on the induction melted pellets, which had been relatively slowly cooled and were entirely crystalline in structure. The

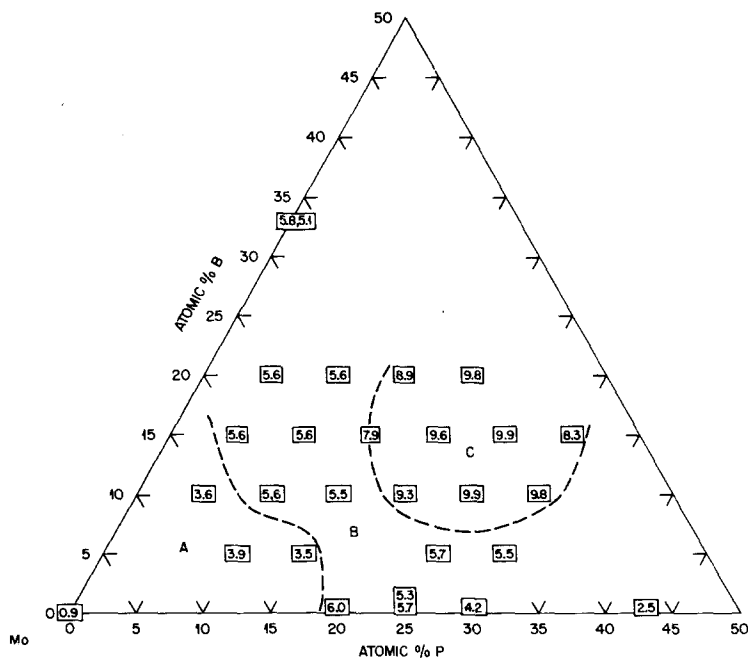


Figure 2 T_c values for slowly cooled crystalline Mo-P-B alloys. Regions A, B, and C are delineated to aid in the discussion (see text).

results of the T_c measurements are included in Table I and also illustrated in Fig. 2. Here the Mo-rich corner of the Mo-P-B composition diagram is given with the onset T_c for each alloy ingot. For mixed structures in this region, it is therefore likely that the amorphous phase has the higher T_c , approximately by a factor of two. As the metalloid concentration increases (region B), the foils continue to have higher T_c values (e.g. Mo-15at% P-10at% B, T_c of the amorphous foil = 8.1 K compared to 5.5 K for the crystalline casting). However, at higher metalloid concentrations (region C), the T_c values become comparable and finally the crystalline castings exhibit somewhat higher values. Thus, for mixed structures in the rapidly quenched foils in this composition range, it becomes difficult to distinguish which phase is responsible for the onset T_c .

A T_c of 8.0 K was observed for our Mo-10at% P-10at% B quenched foil, compared to 9.0 K for the same nominal composition reported by Johnson *et al.* [8] and the 8.1 K reported by Strudthoff *et al.* [16]. However, we did find a T_c of 9.02 K for our amorphous Mo-20at% P-15at% B alloy. Thus the present study has produced an amorphous Mo-P-B alloy which has the same maximum T_c previously reported for this system, albeit at a somewhat different nominal metalloid composition. This value for T_c remains the highest reported for a metallic glass superconductor.

A similar plot is presented in Fig. 3 for the T_c values of the rapidly quenched foils. The T_c values are enclosed by symbols indicating whether the foil was completely amorphous, mostly amorphous, or mostly crystalline to the resolution of X-ray diffraction. Several features of Figs. 2 and 3

can be noted. At the Mo-rich end of the composition range (region A), the rapidly quenched foils have higher T_c values than those for the cast ingot. For mixed structures in this region, it is therefore likely that the amorphous phase has the higher T_c , approximately by a factor of two. As the metalloid concentration increases (region B), the foils continue to have higher T_c values (e.g. Mo-15at% P-10at% B, T_c of the amorphous foil = 8.1 K compared to 5.5 K for the crystalline casting). However, at higher metalloid concentrations (region C), the T_c values become comparable and finally the crystalline castings exhibit somewhat higher values. Thus, for mixed structures in the rapidly quenched foils in this composition range, it becomes difficult to distinguish which phase is responsible for the onset T_c .

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A major difficulty with the study was our

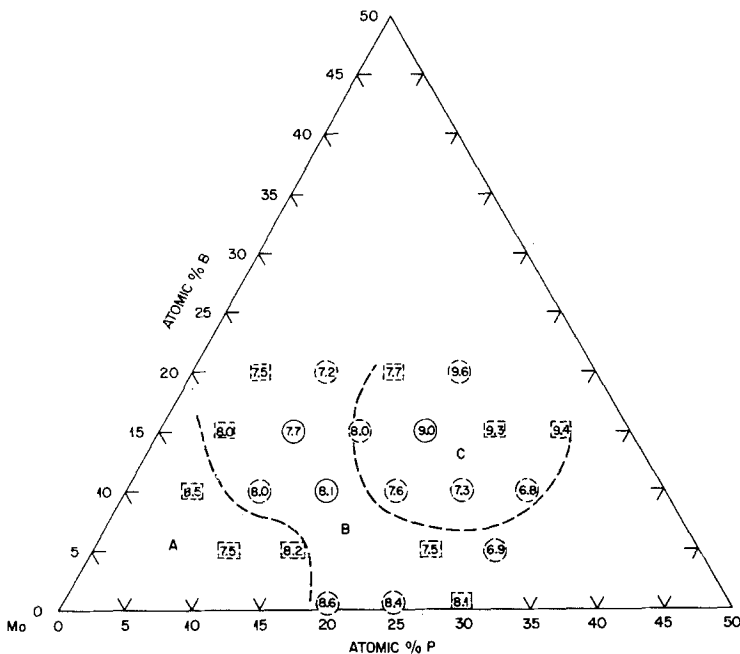


Figure 3 T_c values for rapidly quenched Mo-P-B foils. The structure of the foils is represented by the following symbols: ○ amorphous, ⊙ predominantly amorphous, ⊠ predominantly crystalline.

inability to obtain the completely amorphous structure for many compositions by rapidly quenching with the arc hammer apparatus. As Table I shows, only a few of the Mo-P-B alloys we prepared by rapid solidification were free of crystalline phases, indicating these alloys are not easy glass formers. Thus, even if superior superconducting properties had been observed for an amorphous phase in these alloys, it is unlikely that this system would be practical for superconductors since the commercial rapid solidification technique of melt spinning, with quench rates comparable to those of the arc hammer, probably would not be effective in producing completely amorphous material in this system.

A common feature of easy glass forming alloys is a deep eutectic in the equilibrium phase diagram. The ratio of the eutectic temperature, T_E , to the melting point of the major component, T_M , has been used to compare the glass forming ability of binary systems [17]. The ratio T_E/T_M is approximately 0.6 for easy glass forming alloys while T_E/T_M is about 0.8 for normal eutectic alloys. From the Mo-B phase diagram [18], $T_E/T_M = 2473/2890 = 0.86$ for the Mo-Mo₂B eutectic. This is clearly a much higher T_E/T_M ratio than expected for ready glass formation so it is not surprising that alloys in the Mo-B system are difficult to prepare in the amorphous state by rapid quenching from the liquid. No

phase diagram has been published for the Mo-P system. However, a very low eutectic temperature of 1336 K has been reported at Mo-29.7 at % P [19]. Such a low eutectic should make the Mo-30 at % P alloy an excellent glass former. We obtained some amount of crystalline phase in this alloy, however.

The systematics of superconductivity in the transition metals and their alloys have often been discussed in terms of the variation of T_c observed by Collver and Hammond [1] for cryo-quenched vapour deposited films of alloys of neighbouring metals of the 4d and 5d series. A broad maximum in T_c against average group number (AGN) is observed in the 4d series just to the right of molybdenum (i.e. at an AGN of about 6.3). Thus, amorphous molybdenum has nearly the maximum T_c for amorphous transition metals, in contrast to crystalline molybdenum which has a low T_c (0.9 K) and is near the minimum with respect to T_c against AGN for crystalline transition metal alloys. This enhancement of T_c for amorphous molybdenum has been rationalized by considering T_c to be mainly governed by the density of electronic states at the Fermi level, $N(E_F)$. The $N(E_F)$ has a low value for crystalline molybdenum, due to fine structure in the $N(E)$ for the d-bands of crystalline transition metals with E_F for molybdenum lying at a minimum in $N(E)$. The lack of atomic periodicity in the amorphous

structure "washes out" the fine structure in $N(E)$, thus leading to a smoother variation of $N(E_F)$ with AGN and, consequently, of T_c . It has been suggested that the d-band contribution $N_d(E_F)$ is the most important factor controlling T_c in transition metals [20]. Several experiments [3] suggest that $N_d(E)$ loses its structure on going from the crystalline to the amorphous state. Therefore, $N_d(E)$ appears to vary rather smoothly with d-band occupation, exhibiting a maximum for a roughly half filled d-shell, that is, near molybdenum.

"Amorphous molybdenum" has been stabilized by ion implantation [9] and by vapour quenching in the presence of interstitial impurity atoms such as nitrogen [21]. The T_c values obtained for the stabilized amorphous molybdenum can be as high as 8.5 K [21] and 9.2 K [9]. Thin films of disordered molybdenum with implantation of boron or phosphorus exhibit T_c values of 8.7 K and 9.2 K, respectively [9]. These values exceed those found in bulk binary alloys, but approach those observed in the ternary alloys of the present study. The increase in T_c for the amorphous phase of molybdenum has been discussed in terms of atomic disorder enhancing $N(E_F)$ [22] and/or decreasing the phonon density of states. There is evidence that the chemical effects of impurity atoms introduced (by design or due to imperfect vacuum conditions) may also be playing an important role. For example, neon implantation into pure molybdenum films does not increase T_c , but when similar implantations are made in molybdenum containing 1–2% oxygen, T_c can increase up to 5.5 K [23]. Also studies of Mo–N alloys by ion implantation [23] and vapour deposition [24] show metastable crystalline phases (fcc molybdenum) with enhanced T_c values of 6 to 7 K.

In the Mo-rich portions of the Mo–P–B system (region A in Figs. 2 and 3), it is likely that both atomic disorder and chemical effects influence T_c . As for "pure" molybdenum, amorphous (or partly amorphous) Mo–P–B alloys in region A have larger T_c values than their crystalline counterparts. In the more concentrated alloys of region C, however, where T_c values are comparable for the crystalline and amorphous (or partly amorphous) alloys, disorder apparently does not enhance T_c . The similarity of the magnitude of T_c in region C for the amorphous and crystalline phases suggests short range chemical order may be more important

in controlling T_c , and presumably the electronic structure, than the influence of atomic disorder.

Ternary crystalline compounds based on molybdenum have received intense interest in recent years. The ternary molybdenum chalcogenides (Chevrel phases) have been of particular interest because of their unusual superconducting properties (extremely high upper-critical magnetic fields), their magnetic properties, and their simultaneous possession of magnetism and superconductivity [25]. It was established that the molybdenum 4d electrons are mainly responsible for the remarkable superconducting properties of these phases. The present work has described another Mo-base ternary system, Mo–P–B, which shows promise for superconductivity and should be explored in more detail.

4. Summary

The main findings of this study can be summarized in the following list of conclusions.

1. The Mo–P–B alloys studied are not easy glass formers, presumably because of the relatively high eutectic temperatures in this system.

2. The slowly solidified, crystalline Mo–P–B alloys have complex, multi-phase microstructures.

3. Crystalline alloys in the composition range Mo–(20 to 30)at% P–(10 to 20)at% B have relatively high T_c values of 9.6 to 9.9 K. A new series of Mo-base ternary alloys was reported which exhibits higher T_c values than occur in the binary systems.

4. The study of the systematics of T_c in the rapidly quenched amorphous Mo–P–B alloys was made difficult because of the presence of crystalline material in most alloys.

5. The maximum T_c of 9.02 K for an amorphous alloy was consistent with the previous high T_c found in this alloy system for an amorphous phase.

6. All of the rapidly quenched Mo–P–B alloys were brittle, even those which were completely amorphous. It is unlikely that amorphous Mo–P–B alloys will be of practical use for superconductors because of the difficulty in producing them from the liquid state, and because of their brittleness.

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