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Molybdenum-based metallic glasses

Metallic glasses, a unique class of materials which can be fabricated inexpensively in useful shapes (e.g. wire, ribbon and strip) directly from the melt by rapid liquid quenching (RLQ) techniques, are being recognized as having high technological potential [1, 2]. As a consequence, there is a growing awareness of these products in the scientific community [3–5]. While ferrous metallic glasses are emerging as frontrunners for various commercial applications [6–8], efforts are also being made to synthesize a broad spectrum of new glass-forming alloys with competitive properties [9–11].

The majority of the current ferrous and non-ferrous metallic glasses, i.e. those predominantly based on Fe, Ni, Co and Ti, will be restricted to applications at low temperatures because of their low thermal stabilities [12, 13]. These glasses usually have crystallization temperatures (T_c) between 400 and 550° C. High-temperature mechanical applications are feasible for metallic glasses provided the glasses are properly designed and fabricated to possess high thermal stability in combination with desirable mechanical properties. For example, high-strength glassy ribbons with high $T_c \geq 700°$ C, or preferably $\geq 800°$ C, may be utilized to reinforce a metal matrix, e.g. aluminium whose melting point is 660° C.

Several refractory metal-containing metal–metal type glasses [14, 15] are known to possess high values of T_c in the range of 700° C to 900° C. Examples include $Ni_{60}Nb_{40}$, $Ta_{50}Ni_{50}$, $Nb_{60}Rh_{40}$, $Nb_{55}Ir_{45}$, $Ta_{55}Rh_{45}$ and $Ta_{55.5}Ir_{44.5}$ (subscripts in at%). Nevertheless, the above mentioned high T_c glasses will have limited practical uses because of: (a) high cost and/or high density, and (b) relatively low hardness (≤ 950 kg mm^{-2}) and consequently low yield strength. During the past few years, an intensive programme has been undertaken to develop moderate-cost metallic glasses with high thermal stabilities and desirable mechanical properties.

Experience has shown that devitrification of metallic glasses usually proceeds at 0.4 to 0.6 T_e, the eutectic temperature [3–5]. The search for high T_c glass-forming compositions was necessarily concentrated on alloys having high contents of the high melting-point refractory metals, with primary focus given to molybdenum because of its cost and density advantages. Some of the accomplishments of this programme are briefly reported here. A detailed description of this investigation will be published later [16].

RLQ techniques of arc-splat quenching [17] and chill-casting on a rotating substrate [18] were variously employed to explore the new glass-forming compositions. Chill wheels composed of either molybdenum or a precipitation-hardened

TABLE I

Composition (at%)	Crystallization temperature, T_{c1} (°C)	Hardness (kg mm^{-2})
$Mo_{48}Cr_{32}P_{12}B_8$	878	–
$Mo_{48}Fe_{32}P_{12}B_8$	828	–
$Mo_{48}Ni_{32}P_{12}B_8$	805	–
$Mo_{50}Fe_{10}Al_{20}P_{10}B_7Si_3$	837	1026
$Mo_{52}Cr_{14}Fe_{14}P_{12}B_8$	863	1260
$Mo_{52}Cr_{10}Fe_{10}Ni_8P_{12}B_8$	831	1234
$Mo_{40}Cr_{25}Fe_{15}B_8C_7Si_5$	913	–

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copper–beryllium alloy were used to fabricate rapidly quenched ribbons. The arc-splat quenched foils (~ 50 μm thick) and the chill-cast ribbons (40 to 60 μm thick and 1 to 2 mm wide) were examined for glassy structure by X-ray diffraction analysis. The mechanical properties of fully glassy materials were determined by measurements of Vickers diamond pyramid microhardness (H_v) using a Leitz Miniload tester with a 100 g load. The average value of hardness was obtained from at least six measurements. The crystallization temperatures of selected glassy compositions were determined by differential thermal analysis at a scan rate of 20° C min^{-1} using a Dupont 990 DTA.

The alloy compositions investigated were predominantly based on molybdenum, containing approximately 20 at% of one or more of the metalloids P,B,C and Si. In addition, the candidate alloys also included one or more of the elements Fe, Ni, Co, Cr and Al in various proportions. In the initial phase of the programme, alloy compositions were rapidly screened by arc-splat quenching for glass-forming ability. Subsequently, the promising alloy systems were further developed by composition variation, and glasses were fabricated by melt-spinning on a rotating chill-wheel culminating in the optimization of mechanical behaviour, thermal behaviour and ease of ribbon fabricability.

The compositions in the alloy systems with a multiple number of metalloid elements were found to form glasses within the ranges as follows:

$$Mo_{40-60}T_{20-40}X_{20},$$

where T is one or more of the elements Fe, Ni, Co, Cr and Al, and X is two or more of the elements P, B, C and Si. Typical examples include

$$Mo_{48}Fe_{32}P_{12}B_8,\ Mo_{50}Fe_{10}Al_{20}P_{10}B_7Si_3,$$
$$Mo_{52}Cr_{10}Fe_{10}Ni_8P_{12}B_8 \text{ and } Mo_{40}Cr_{25}Fe_{15}B_8C_7Si_5.$$

The above Mo-based glasses exhibit very high T_{c1} (temperature of the first glass-to-crystalline exothermic reaction) in the range 800 to 900° C. The hardness values of these glasses were found to be between 1000 and 1250 kg mm^{-2}. Table I lists compositions, hardness values and T_{c1} values of selected Mo–T–X alloys described above.

Partial substitution of Mo with W in the Mo–T–X glasses further enchances thermal stability. Alloys containing 8 to 20 at% W have crystallization temperatures in the range 900 to 950° C; for example, T_{c1} of a glassy alloy having the composition $Mo_{35}W_{20}Cr_{18}Fe_7P_6B_6C_5Si_3$ was found to be 950° C.

When boron was present as the only metalloid up to about 20 at%, Mo-based glassy alloys were found to have extraordinarily high hardness values in the range of about 1450 to 1950 kg mm^{-2}. The composition ranges of Mo/B-based glassy alloys which were fabricated as melt-spun ribbons are defined by the formula given by:

$$Mo_{40-65}T_{15-40}B_{20},$$

where T is one or more of the elements Fe, Ni and

TABLE II

Composition (at%)	Crystallization temperature, T_{c1} (°C)	Hardness (kg mm^{-2})
$Mo_{40}Fe_{40}B_{20}$	852	1950
$Mo_{50}Fe_{30}B_{20}$	860	1750
$Mo_{60}Fe_{20}B_{20}$	906	1750
$Mo_{65}Fe_{15}B_{20}$	–	1750
$Mo_{40}Co_{40}B_{20}$	790	1700
$Mo_{50}Co_{30}B_{20}$	851	1650
$Mo_{60}Co_{20}B_{20}$	877	1650
$Mo_{65}Co_{15}B_{20}$	856	1700
$Mo_{40}Ni_{40}B_{20}$	–	1500
$Mo_{50}Ni_{30}B_{20}$	–	1450
$Mo_{60}Ni_{20}B_{20}$	–	1500
$Mo_{40}Co_{20}Fe_{20}B_{20}$	835	1750
$Mo_{50}Co_{15}Fe_{15}B_{20}$	870	1780
$Mo_{50}Fe_{20}Co_{10}B_{20}$	–	1770
$Mo_{60}Fe_{10}Co_{10}B_{20}$	–	1780
$Mo_{50}Co_{15}Ni_{15}B_{20}$	–	1650

Co. Examples of glassy alloys belonging to this category include $Mo_{40}Fe_{40}B_{20}$, $Mo_{65}Fe_{15}B_{20}$, $Mo_{50}Ni_{30}B_{20}$, $M_{60}Co_{20}B_{20}$ and $Mo_{50}Ni_{15}Co_{15}B_{20}$. The Mo/B-based glasses here also exhibit very high crystallzation temperatures (T_{c1}) in the range between about 800 and 900° C. Table II lists compositions, crystallization temperatures and hardness values of selected Mo/B-based metallic glasses. It is seen that the Mo/B-based glasses containing Fe and Co (individually or combined) exhibit especially high hardness (1650 to 1950 kg mm^{-2}). In fact the glass having the composition $Mo_{40}Fe_{40}B_{20}$ has a hardness value of 1950 kg mm^{-2}, which to our knowledge is the highest value of H_v of any metallic glass reported to date. Comparisons of Tables I and II indicate that crystallization temperatures vary rather modestly (within the range 800 to 900° C) for these Mo-rich glasses, irrespective of the type of metalloid incorporated in the alloys. On the contrary, however, changing the metalloid content from $(P, B, C, Si)_{20}$ to B_{20} leads to a marked enhancement of hardness values. Similar effects were observed in Fe-rich metallic glasses and have been attributed to possible metal–metalloid bonding effects resulting from charge transfer between the metal and metalloid atoms [19]. It is worth noting that the binary Mo–B and Mo–P systems are potentially glass-forming (considering melting point reduction and size criteria); however, $Mo_{80}B_{20}$ and $Mo_{80}P_{20}$, and other binary compositions, were found to be fully crystalline upon arc-splat quenching. Thus, in terms of current RLQ technology, the Mo-based glasses can only be fabricated from ternary or higher order alloys.

In summary, we have reported that Mo-based metallic glass alloys with high thermal stabilities (i.e. high T_{c1}) and high hardnesses have been synthesized. Selected alloys have been fabricated in the form of continuous ribbons possessing extraordinarily high hardnesses. A $Mo_{40}Fe_{40}B_{20}$ glassy alloy ribbon shows a high T_{c1} (~ 850° C) and remarkably a high hardness (~ 1950 kg mm^{-2}), the highest such H_v value reported thus far. Large increases in hardness were achieved when the metalloid contents of the alloys were changed from $(P, B, C, Si)_{20}$ to B_{20}. The high thermal stabilities, high hardnesses, ease of ribbon fabricability and the availability and moderate cost effectiveness of the constituent elements suggest that the present alloys may serve as the basis for the development of technologically useful Mo-based metallic glasses.

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