Metallic glasses with high strengths and high crystallization temperatures

In the previous communication, we briefly reviewed the results of an alloy research programme that was directed toward synthesizing metallic glasses having high thermal stability, exceptional mechanical properties, as well as maintaining moderate materials cost. Several of these glasses were Mo-based and exhibited outstanding combinations of high crystallization temperatures ($T_c \geqslant 800^\circ$ C) and high hardness ($H_v \geqslant 1600\,\mathrm{kg\,mm^{-2}}$). As is common with the majority of the well-known metal-metalloid glasses [1–3], substantial quantities of the metalloids (i.e. ~ 20 at%) were incorporated in order to produce the glassy state. However, experience has shown that such high metalloid contents combined with large amounts of refractory elements can often give rise to increasing brittleness in the as-quenched glassy state [4–6].

A subsequent development programme was initiated to attempt to modify the alloy compositions such that the desirable properties, noted above, could be retained along with the ease of ribbon fabricability, while improving ductility to levels comparable to those common to the earlier generations of ferrous and non-ferrous glasses [7–12]. This was accomplished by maintaining substantial quantities of Mo (and other potentially effective refractory metal elements) while lowering the metalloid content of the alloys. The following report describes the development of this new class of metallic glass ribbons in the Fe–Mo–B, Ni–Mo–B and Co–Mo–B systems.

Continuous ribbons of Fe–Mo–B, Ni–Mo–B and Co–Mo–B alloys, 30 μm thick by 0.5 mm wide were fabricated from the melt by chill casting and were adjudged to be glassy by X-ray diffraction analysis.

Mechanical properties of the as-quenched ribbons were determined by measurements of hardness and tensile strength. The Vickers diamond pyramid microhardness (H_v) was measured using a Lietz Miniload tester with 100 g load. Tensile strength was measured on an Instron testing machine using specimens with unpolished, parallel-sided edges. Average values were taken from six measurements of hardness and tensile strength, respectively. Crystallization temperatures were determined by differential thermal analysis at a scan rate of 20° C min^{-1} using a Dupont 990 DTA.

The novel metallic glasses in the Fe–Mo–B, Ni–Mo–B and Co–Mo–B systems are characterized by high refractory metal contents between 25 and 45 at% and by low boron contents between 5 and 12 at%. The low metalloid content of these alloys is particularly unique in contrast with the high metalloid contents (15 to 25 at%) characteristic of a vast number of commonly known metal–metalloid type glasses. Notably, the present glassy ribbons were found to have excellent bend ductility unlike the usual brittle type refractory metals-rich glasses with high metalloid contents (~ 20 at%). For example, the new metalloid–lean glassy alloy ribbons can be bent to a radius of curvature ten times the thickness of the ribbon without cracking or fracture.

The ranges of alloy compositions which were synthesized as glassy ribbons with good bend ductility are given in Table I.

The low boron content and the high refractory metal content are interdependent. When the boron content is less than 5 at% and the refractory metal content lies within the limits given in Table I, rapidly quenched ribbons are not totally glassy. Rather, these ribbons contain crystalline phases which may comprise a substantial volume fraction of the material depending on specific composition. Such ribbons are brittle and undergo fracture when bent to a radius of curvature less than 100 times the thickness of the ribbon.

When the boron content is greater than 12 at% and the refractory metal content lies within the limits as specified in Table I, rapidly quenched ribbons, while remaining fully glassy, are brittle and undergo fracture when bent to a radius of curvature less than 100 times the thickness of the ribbon.

Similarly, for refractory metal concentrations less than/or greater than those listed above, compositions containing such low metalloid content do not form glassy ribbons at the usual quench rates.

Table II lists compositions, mechanical properties (hardness and tensile strength) and crystallization temperatures (associated with the first glass-to-crystalline exothermic transition as observed in

TABLE I

System	Composition range (at% of ductile glasses
Fe–Mo–B	$Fe_{48-70}Mo_{25-40}B_{5-12}$
Ni–Mo–B	$Ni_{28-65}Mo_{30-60}B_{5-12}$
Co–Mo–B	$Co_{38-70}Mo_{25-50}B_{5-12}$

0022–2461/80/061599–02$02.20/0 © *1980 Chapman and Hall Ltd.*

TABLE II Mechanical and thermal properties of selected Fe–Mo–B, Ni–Mo–B and Co–Mo–B glasses

Alloy composition (at%)	Hardness (kg mm^{-2})	Tensile strength (kg mm^{-2})	(10^3 psi)	Crystallization peak (°C)
$Fe_{65}Mo_{25}B_{10}$	1308	334	475	615
$Fe_{60}Mo_{30}B_{10}$	1402	342	486	–
$Ni_{57}Mo_{35}B_8$	1206	345	490	613
$Ni_{55}Mo_{35}B_{10}$	1246	267	380	610
$Ni_{50}Mo_{40}B_{10}$	1240	275	390	825
$Ni_{45}Mo_{45}B_{10}$	1330	373	530	850
$Co_{66}Mo_{26}B_8$	1330	278	395	603
$Co_{58}Mo_{30}B_{12}$	1402	320	455	670
$Co_{55}Mo_{35}B_{10}$	1450	340	483	684
$Co_{50}Mo_{40}B_{10}$	1510	329	467	785

the DTA trace, i.e. T_{c1}) of selected metallic glasses in the Fe–Mo–B, Ni–Mo–B and Co–Mo–B systems.

The glassy alloys within the scope of the present investigation evidence hardness values $\geqslant 1200\,\text{kg mm}^{-2}$, tensile strengths of at least $267\,\text{kg mm}^{-2}$ (380×10^3 psi) and crystallization temperatures of at least 600° C. In all three alloy systems, increasing Mo content in substitution of either Fe, Ni or Co has been found to increase hardness. Compositions with B contents of about 8 to 10 at% have been noticed to be especially ductile. The glasses in the Ni–Mo–B and Co–Mo–B systems which exhibit the best combination of high strength, $\geqslant 280\,\text{kg mm}^{-2}$ (400×10^3 psi) and high crystallization temperature, $\geqslant 750°$ C, are those containing high Mo content between 40 and 45 at% and ~ 10 at% B. Examples include $Ni_{50}Mo_{40}B_{10}$, $Ni_{45}Mo_{45}B_{10}$ and $Co_{50}Mo_{40}B_{10}$.

Among the glasses with moderately high crystallization temperatures around 600° C, the best combinations of cost effectiveness, high strength: $\geqslant 320\,\text{kg mm}^{-2}$ (450×10^3 psi) and high hardness: $\geqslant 1300\,\text{kg mm}^{-2}$ are displayed by Fe-based glasses containing 25 to 30 at% Mo and approximately 10 at% B. Examples include $Fe_{65}Mo_{25}B_{10}$ and $Fe_{60}Mo_{30}B_{10}$.

In summary, a new class of liquid-quenched metallic glasses have been developed in the ternary Fe–Mo–B, Ni–Mo–B and Co–Mo–B systems which are characterized by significantly low metalloid contents between 5 and 12 at%. Some of the glasses in these systems, such as $Ni_{45}Mo_{45}B_{10}$ and $Co_{50}Mo_{40}B_{10}$, have been shown to have the best combination of high tensile strength ($\geqslant 460 \times 10^3$ psi) and high crystallization temperature ($\geqslant 785°$ C).

Acknowledgement

This work was carried out at the Corporate Development Center, Allied Chemical Corporation, Morristown, New Jersey 07960, USA.

References

1. N. J. GRANT and B. C. GIESSEN eds. "Rapidly Quenched Metals", Section I (MIT Press, Cambridge, Mass. 1976).
2. *Idem, ibid,* Section II; *Mat. Sci. Eng.* **23** (1976) 81.
3. J. J. GILMAN and H. J. LEAMY eds. "Metallic Glasses" (ASM, Metals Park, Ohio 1978).
4. R. RAY, US Patent no. 4 133 679 (1979).
5. H. S. CHEN and K. A. JACKSON, in "Metallic Glasses", edited by J. J. Gilman and H. J. Leamy (ASM, Metals Park, Ohio, 1978) p. 74.
6. M. FISCHER, D. E. POLK and B. C. GIESSEN, in "Rapid Solidification Processing", edited by R. Mehrabian, B. H. Kear and M. Cohen (Claitor's, Baton Rouge, 1978) p. 140.
7. J. J. GILMAN, *Met. Prog.* 116 (July 1979) 42.
8. R. RAY, US Patent no. 4 140 525 (1979).
9. *Idem,* US Patent no. 4 067 732 (1978).
10. L. E. TANNER and R. RAY, *Scripta Met.* 11 (1977) 783.
11. T. MASUMOTO and M. NAKA, US Patent no. 3 986 867 (1976).
12. L. A. DAVIS, R. RAY, C.-P. CHOU and R. C. O'HANDLEY, *Scripta Met.* 10 (1976) 541.

Received 23 October
and accepted 14 November 1979

RANJAN RAY
MARKO Materials Inc, 222C Arsenal Street
Watertown, Massachusetts 02172, USA
LEE E. TANNER
ManLabs, Inc, 21 Erie Street, Cambridge,
Massachusetts 02139, USA