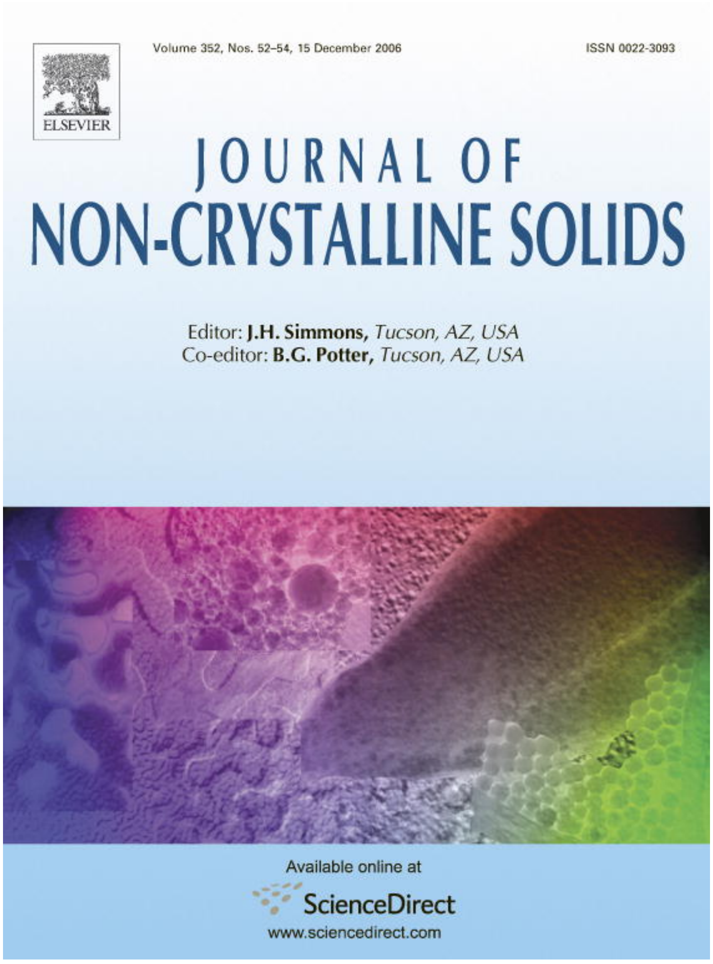
Volume 352, Nos. 52–54, 15 December 2006
ISSN 0022-3093
ELSEVIER
JOURNAL OF
NON-CRYSTALLINE SOLIDS
Editor: J.H. Simmons, Tucson, AZ, USA
Co-editor: B.G. Potter, Tucson, AZ, USA
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ScienceDirect
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LETTER TO THE EDITOR

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Non-Crystalline Solids 352 (2006) 5687–5690
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Letter to the Editor

Metallic plastics based on misch metals

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Received 15 November 2005; received in revised form 6 September 2006

Abstract

We report a family of metallic plastics (MPs) based on misch metals with extremely low glass transition temperature T_g, similar to that of typical polymers such as polyvinyl chloride. In near boiling water, these MPs show superplasticity and can be shaped and imprinted with complex micro- or nano-patterns. Such materials with much low cost compared with that of the MPs based on pure rare-earth metals make them closer to applications. The work might also stimulate more researches for finding new polymerlike metallic alloys.

PACS: 81.05.Kf; 61.43.Fs; 62.65.+k; 81.20.−n

Keywords: Amorphous metals; Metallic glasses

Metals generally show superior mechanical properties but comparably poor workability compared with polymeric plastics with superplasticity in a viscous state [1,2]. Like plastic or glass, however, amorphous metals soften when heated in its supercooled liquid state in the vicinity of T_g. That's what makes it possible, for example, to blow and shape hard metallic glasses [3–5]. Due to this intrinsic viscous state, amorphous metals are called futuristic alloys that could combine the strength and electrical conductivity of ordinary metals with the versatility of plastic [6]. Very recently, cerium-based bulk metallic glasses with exceptionally low T_g close to room temperature have been developed, they can be repeatedly shaped in boiling water, thus be regarded as metallic plastics (MPs) [7]. The MP demonstrates that low-temperature malleability in metals is physically possible. These materials combining the properties of metals and polymers are remarkably significant for industry applications such as finely shaped nano-components [6,7]. Additionally, such glassy alloys with low T_g are useful for understanding glass-forming mechanisms of alloys. Thus, it is of great interest to develop more polymerlike MPs having low cost and high stability.

In this work, we report a family of MPs based on misch metal (MM), which is a natural mixture of rare-earth metals of La, Ce, Pr, Nd, and other minute impurities such as Sm, Fe, C, Si and O and so on. The MM is much cheaper than that of the pure rare-earth elements. The blend of MM, conventional Al and Cu metals can be easily cast into fully glassy rods with at least 3 mm in diameter and has the similar glass-forming tendency of previous MM-based alloys [8,9]. These glassy alloys have the lowest T_g down to 347 K and wide supercooled liquid region ($\Delta T_x = T_x - T_g$, where T_x is the onset temperature of crystallization) up to 60 K. These T_g values are even lower than that of polyvinyl-chloride (PVC) (348–378 K) [10]. The strength of these materials is about 10 times larger than those of typical polymers such as nylon [10] and close to those of some high strength commercial Al and Mg alloys. In near boiling water, these materials can be readily imprinted with micrometer depth. Precise grooves with a width of 200 nm can be finely fabricated on the surface of the MPs by focused ion beam (FIB) etching technology. The work demonstrates the possibility of developing more MPs with combined properties of metals and plastics and sheds light on the applications of the materials in industry [11].

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0022-3093/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2006.09.031

Multicomponent ingots of MM, Al, and Cu were prepared by arc melting the mixtures of MM (La 22.4 wt%, Ce 57.1 wt%, Pr 4.2 wt%, Nd 15.6 wt% and impurities), pure Al (99.9 wt%) and Cu (99.9 wt%) under a purified argon atmosphere. The ingots were remelted and suction cast into a Cu mold to obtain bulk forms rods with 1–5 mm in diameter. The structure of the as-cast and processed samples was examined by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu-K_{α} radiation at 40 kV. Differential scanning calorimetry (DSC) was performed under a purified argon atmosphere in a Perkin–Elmer DSC-7, calibrated for temperature and energy with high-purity indium and zinc. The acoustic velocities of the MP were measured using a pulse echo overlap method by a MATEC 6600 model ultrasonic system with a measuring sensitivity of 0.5 ns [12]. The density was determined by the Archimedean technique and the accuracy lies within 0.1%. Elastic constants (e.g., the Yong's modulus E, the shear modulus G, the bulk modulus K, and the Poisson's ratio σ) were derived from the acoustic velocities and the density [12]. Compressive strength of the MP was measured with a MTS880 material testing system. FIB etching experiments were carried out on a DB235 FIB etching system. The electrical resistance of the MP was determined on a physical property measurement system (PPMS6000).

The typical MM–Al–Cu compositions are shown in Table 1. XRD measurement was carried out to examine the glassy state of the as-cast samples as shown in the inset of Fig. 1(a). Except for $MM_{80}Al_{10}Cu_{10}$ and $MM_{80}Al_{15}Cu_{5}$(at.%), all the specimens listed in Table 1 exhibit only two broad maxima diffraction peaks indicating that most parts of these alloys are amorphous. DSC traces for representative $MM_{70}Al_{15}Cu_{15}$, $MM_{65}Al_{10}Cu_{25}$ and $MM_{67.5}Al_{7.5}Cu_{25}$ focusing on the glass transition and crystallization are shown in Fig. 1(a). The samples show distinct glass transition and sharp crystallization confirming the amorphous structure. The heats of crystallization for the $MM_{70}Al_{15}Cu_{15}$ (2 mm-diameter rod), $MM_{65}Al_{10}Cu_{25}$ (1 mm-diameter rod), $MM_{67.5}Al_{7.5}Cu_{25}$ (2 mm-diameter rod) and $MM_{67.5}Al_{10}Cu_{22.5}$ (3 mm-diameter rod) are 4.3 KJ/mol, 3.9 KJ/mol, 4.0 KJ/mol and 3.9 KJ/mol, respectively, which are nearly the same to those (about 4.4 KJ/mol) of MM–Al–Cu–Ni bulk metallic glasses [8]. These results further demonstrate that most parts of these as-cast MM–Al–Cu alloys are amorphous.

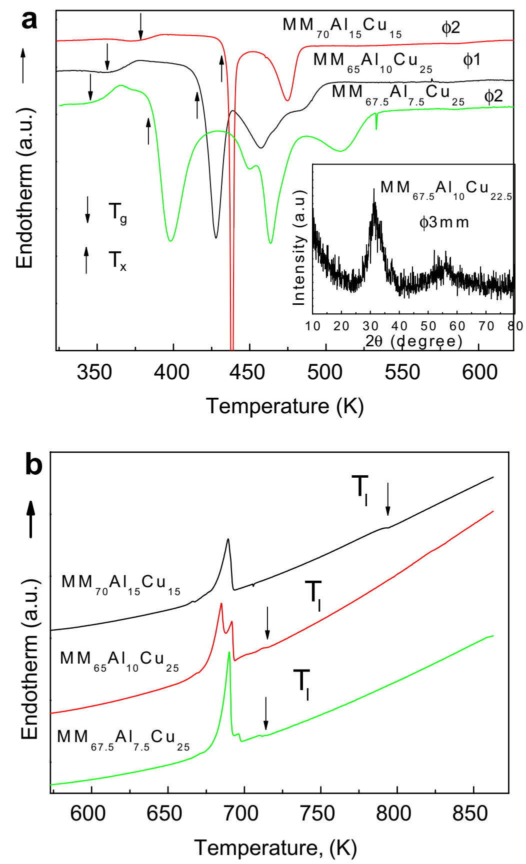

Fig. 1. DSC traces focusing on the glass transition (a) and melting event (b) for the typical as-cast $MM_{70}Al_{115}Cu_{15}$, $MM_{65}Al_{10}Cu_{25}$ and $MM_{67.5}Al_{7.5}Cu_{25}$ rods at a constant scanning rate of 10 K/min. Inset in (a) shows the XRD pattern for the 3 mm diameter as-cast rod of $MM_{67.5}Al_{10}Cu_{22.5}$ MP.

The critical thickness of glassy rods (d_c), thermal parameters (T_g, T_x, ΔT_x, and liquidus temperature T_l) and the

Table 1
Critical diameter d_c, T_g, T_l, ΔT_x, T_g/T_l, $\gamma(=T_x/(T_g+T_l))$, and the normalized supercooled liquid region $S(=\Delta T_x/(T_l-T_g))$ are listed for the $MM_{90-x}Al_{10}Cu_x$, $MM_{85-x}Al_{15}Cu_x$, and $MM_{75-x}Al_xCu_{25}$ ($x = 15$, 10, and 7.5) cast glassy alloys

Compositions (at.%)	d_c (mm)	T_g (K)	T_x (K)	T_l (K)	ΔT_x (K)	T_g/T_l	γ	S
$MM_{80}Al_{15}Cu_{5}$	<1	–	–	858	–	–	–	–
$MM_{70}Al_{15}Cu_{15}$	2	373	436	795	63	0.469	0.373	0.18
$MM_{65}Al_{15}Cu_{25}$	1	390	452	790	62	0.494	0.383	0.18
$MM_{80}Al_{10}Cu_{10}$	<1	–	–	793	–	–	–	–
$MM_{75}Al_{10}Cu_{15}$	1	378	430	751	52	0.503	0.381	0.17
$MM_{70}Al_{10}Cu_{20}$	1	362	388	723	26	0.500	0.358	0.08
$MM_{67.5}Al_{10}Cu_{22.5}$	3	360	412	704	52	0.516	0.386	0.18
$MM_{65}Al_{10}Cu_{25}$	2	359	419	716	60	0.501	0.390	0.21
$MM_{62.5}Al_{10}Cu_{27.5}$	2	372	429	747	57	0.498	0.383	0.18
$MM_{60}Al_{10}Cu_{30}$	1	373	428	759	55	0.491	0.378	0.17
$MM_{67.5}Al_{7.5}Cu_{25}$	2	347	387	714	40	0.486	0.365	l0.13

often cited parameters for glass-forming ability T_g/T_l and γ [13,14] are listed in Table 1. The T_l for the typical $MM_{70}Al_{15}Cu_{15}$, $MM_{65}Al_{10}Cu_{25}$ and $MM_{67.5}Al_{7.5}Cu_{25}$ glass forming alloys are marked in Fig. 1(b). For $MM_{70}Al_{15}Cu_{15}$ alloy, a small endothermic shoulder is clearly seen at high-temperature above the main melting peak in Fig. 1(b), thus it has a comparably high T_l. The T_g of these alloys changes from 347 K to 390 K depending on the composition, and their values are close to that of polyvinyl-chloride (348–378 K) and nylon(~43 °C/316 K) [10]. The value of T_g is sensitive to Al content and the increase of Al content will increase T_g. The lowest T_g, for the present alloys is 347 K of $MM_{67.5}Al_{7.5}Cu_{25}$, which has the lowest Al percent among these alloys. The results imply that the possibility of further decreasing T_g by appropriately modification of Al content. Interestingly, T_g/T_l, γ, and ΔT_x change in a remarkably different way vs. d_c for the $MM_{90-x}Al_{10}Cu_x$ system as seen in Fig. 2. Although the MM-based alloys can readily form glasses in bulk, their T_g/T_l values are much lower than the expected value of 0.6 for a bulk glass-forming alloy [3,14]. This means that the MM-based alloys may have a different glass forming mechanism from that of conventional systems such as Zr-based alloys [3]. High T_g/T_l value and near eutectic compositions are usually required for the good glass formers such as Zr-based alloys [3,14]. The eutectic principle seems not suitable for the MM-based glass forming alloys having a separate high-temperate primary phase and multiple meting events as shown in Fig. 1(b). The special glass forming ability of these alloys may be related with the scavenging effect of the mixture of rare-earth metals. Previous researchers also have reported that MM-based glass forming system is an exception of T_{rg} and atomic size principles [9] and MM-based bulk metallic glasses even can be readily formed in air atmosphere [8].

Plastic formability in the supercooled liquid region is a crucial property for MP. ΔT_x has been widely used as a parameter to describe the stability and plastic formability of a metallic glass. The normalized parameter $S = \Delta T_x/(T_l - T_g)$ has been successfully used to characterize the formability for different glassy alloys [15]. As listed in Table 1, the S values of $MM_{70}Al_{15}Cu_{15}$, $MM_{65}Al_{15}Cu_{25}$ and $MM_{90-x}Al_{10}Cu_x$ ($x = 22.5$, 25, and 27.5) alloys are between 0.18 and 0.21, and the values are very close to that of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$(0.2), which has excellent plastic formability [16]. When heated in the vicinity of T_g, the MPs show perfect superplasticity and can be repeatedly compressed, stretched, bent and shaped into complicated shapes like polymeric thermoplastics. Fig. 3(a) shows the hand-imprinted articles of the Chinese traditional eight diagrams (left) and our institute badge (right), which are impressed using the metallic plastics in near boiling water. The depth of these impressed patterns is about 0.3 mm. The simple experiments in Fig. 3 demonstrate that the MPs exhibit good micro- and even nano-imprintability. Excellent formability on micrometer scale combined with similar T_g of typical polymers confirms that these materials can be regarded as metallic thermoplastic.

Although these MPs have superplaticity like polymers, they yield much higher mechanical properties than those

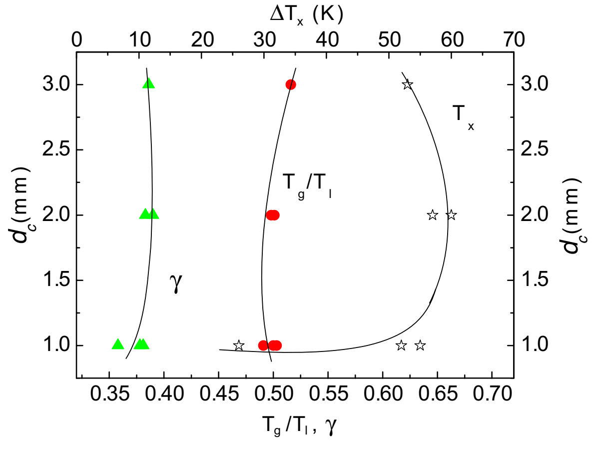

Fig. 2. Critical diameter d_c as a function of T_g/T_l, γ and ΔT_x in the $MM_{90-x}Al_{10}Cu_x$ alloys.

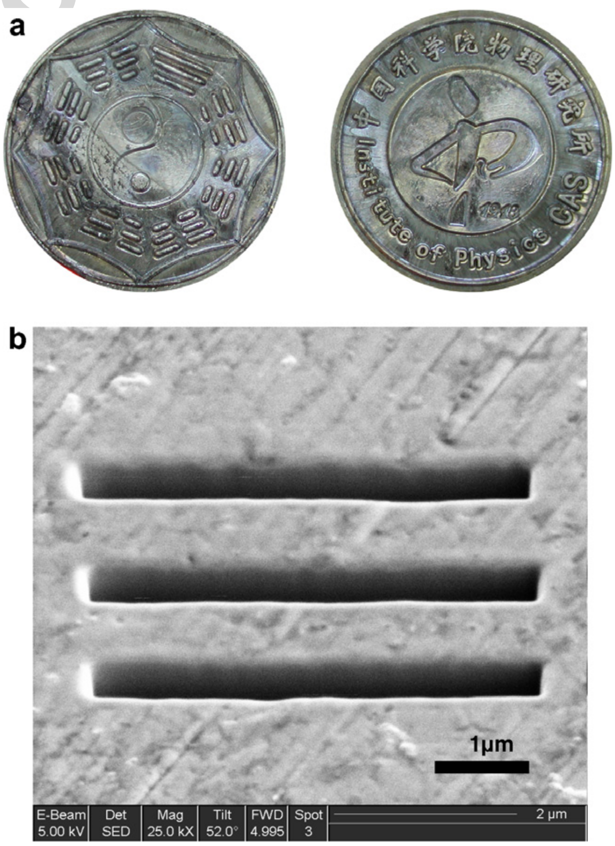

Fig. 3. (a) Articles for the Chinese traditional Eight Diagrams (left), and the badge of the Institute of Physics of Chinese Academy of Sciences (right). These articles with 20 mm in diameter are cheaply imprinted on samples of $MM_{67.5}Al_{10}Cu_{22.5}$ MP in near boiling water. (b) SEM picture of the groove fabricated on the surface of $MM_{67.5}Al_{10}Cu_{22.5}$ MP using the FIB etching technology.

Table 2
Density ρ, elastic constants (E, G, K and σ) obtained by ultrasonic methods, and compressive strength σ_y for the $MM_{67.5}Al_{10}Cu_{22.5}$ MP

Materials	ρ (g/cm^3)	E (GPa)	G (GPa)	K (GPa)	σ	σ_y (MPa)
$MM_{67.5}Al_{10}Cu_{22.5}$	6.564	30.9	11.5	34.1	0.35	615
Nylon 6	1.12–1.16	2–3.6			0.40	69–88
PP	0.9–1.24	0.5–7.6			0.34	18–80
PVC	1.16–1.45	1.2–3.2				17–52
Aluminum 2014-T651	2.8	72	28			483
Magnesium ZE63A-T6	1.87	45	17			448

For comparison, corresponding data for the typical polymers Nylon 6, Polypropylene (PP) and Polyvinyl chloride (PVC),[10] Aluminum 2014-T651 and Magnesium ZE63A-T6 crystalline alloys[10] are also listed.

of typical polymers. As listed in Table 2, for the typical MP of $MM_{67.5}Al_{10}Cu_{22.5}$, compressive strength σ_y (615 MPa), and Yong's modulus E (31 GPa) are about 10 times higher than those of Nylon 6, Polypropylene (PP), and PVC, comparable or even larger than those of some high strength Al and Mg alloys such as 2014-T651, and ZE63A-T6 [10]. In contrast to the light and insulating polymers, the MPs have high density (6.564 g/cm^3) and electric resistivity ($\sim$125 μΩ cm) of a typical metal. The Poisson's ratio σ(0.35) of $MM_{67.5}Al_{7.5}Cu_{25}$ MP is very close to that of typical polymers Nylon 6 (0.40) and PP (0.34). The MPs consisting of misch rare-earth metals alloyed with other multicomponents may have greatly improved oxidation and corrosion resistances [8].

For the application of micro- or nano-imprintability, there is an advantage in the increased precision possible when the medium has higher moduli [12]. The MPs have high Yong's modulus which is 10 times larger than those of typical polymers, while their low T_g similar to that of polymers means that no more energy is needed for polymerlike imprinting. For example, the MPs can be used as the thermo-mechanical storage medium by forming nanoindentations through Joule heating of scanned nanotips [11]. Fig. 3(b) shows the groove of 200 nm in width and 5 μm in length on $MM_{67.5}Al_{7.5}Cu_{25}$ MP sample fabricated by FIB etching technology. Such a precise groove on nanometer scales demonstrates that the MP has enough strength and modulus to form complicate micro- and nano-shapes. Moreover, in contrast to insulate polymers whose microscopic morphology is quite difficult to investigate by means of scanning electron microscopy (SEM), the conducting MP polymers have merits working under microscopic conditions, and the microscopic patterns on MPs can be easily observed by SEM.

In summary, we have developed a metallic plastics system based on cheap misch metals. The materials combine the typical properties of metallic glasses (higher strength/moduli) and thermoplastics (formability at low-temperatures). The desirable combining properties arise from the exceptionally low value of T_g. The low cost and properties combination might make these materials closer to applications.

Acknowledgement

The support of the Natural Science foundation of China (Nrs. 50371097 and 50321101) and Chinese Academy of Sciences is appreciated.

References

[1] B.H. Billings, R.B. Lindsay, D.E. Gray, et al., American Institute of Physics Handbook, McGraw-Hill, New York, 1972, Chapter 2, pp. 2–1.
[2] W. Fred, J.R. Billmeyer, Textbook of Polymer Science, Wiley, New York, 1984, Chapter 1, p. 3.
[3] W.L. Johnson, MRS Bull. 24 (10) (1999) 42.
[4] A. Inoue, Acta Mater. 48 (2000) 279.
[5] W.H. Wang, C. Dong, C.H. Shek, Mater. Sci. Eng. R 44 (2004) 45.
[6] D. Castelvecchi, Phys. Rev. Focus 15 (6) (2005) 9.
[7] B. Zhang, D.Q. Zhao, M.X. Pan, W.H. Wang, A.L. Greer, Phys. Rev. Lett. 94 (2005) 205502.
[8] J.H. Kim, J.S. Park, H.T. Jeong, W.T. Kim, D.H. Kim, Mat. Sci. Eng. A 386 (2004) 186;
J.H. Kim, J.Y. Lee, J.M. Park, Eric Fleury, W.T. Kim, D.H. Kim, Mater. Trans. JIM 45 (2004) 1395.
[9] R. Li, S. Pang, H. Men, T. Zhang, Mater. Trans. JIM 46 (2005) 2291.
[10] F. Cardarelli, Materials Handbook, Springer Verlag London Limited, 2000.
[11] G. Marsh, Mater. Today 7 (2) (2003) 38.
[12] D. Schreiber, Elastic Constants and Their Measurement, McGraw-Hill, New York, 1973, Chapter 3, p. 35.
[13] D. Turnbull, Contemp. Phys. 10 (1969) 473.
[14] Z.P. Lu, C.T. Liu, Phys. Rev. Lett. 91 (2003) 115505.
[15] S. Mukherjee, Z. Zhou, J. Schroers, W.L. Johnson, W.K. Rhim, Acta Mater. 52 (2004) 3689.
[16] T.A. Waniuk, J. Schroers, W.L. Johnson, Appl. Phys. Lett. 78 (2001) 1213.