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Novel W-based metallic glass with high hardness and wear resistance

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ABSTRACT

An attempt has been made to develop a new metallic glass (MG) that combines high hardness with wear resistance. Refractory metallic films of $W_{33}Ni_{32}B_{35}$ (at.%) have been deposited on stainless steel and Si substrates by dc magnetron sputtering. The alloy films are glassy, have a high crystallization temperature of 873 °C and rank among the very hard metallic materials (~24 GPa). Importantly, this MG also shows excellent wear resistance, approaching that of standard tribological materials like TiN and hence it represents one of the most wear-resistant known metallic materials. Based on its unique combination of high strength and low elastic modulus, other potential applications are also discussed.

1. Introduction

Metallic glasses (MGs) possess certain attributes like a high hardness, low modulus and some compositions show good wear resistance [1], making them candidates for use in hard coatings. Frictional forces on metals arise from their resistance to plastic deformation during sliding contact and are related to material hardness [2]. While the wear resistance of MGs also scales with hardness [1,3], it can depend on the initial relaxation state [4] and on material transfer [5]. For example, dynamic relaxation during sliding contact can explain the velocity dependence of friction in metallic glasses and the low wear of some metallic glasses has been attributed to crystallization in the transfer layer [6]. The tribological properties of bulk metallic glasses (BMGs) can be affected by heat generation leading to glass transition or crystallization within the sliding contact layer [7,8]. Surface oxidation of MGs may also enhance wear resistance as reported for Zr-based BMGs [9] and a Ni-based MG [10]. In general, a useful strategy in developing more wear-resistant MGs is to enhance their hardness and thermal stability, i.e. the glass transition temperature T_g. Since the hardness (or strength) of metallic glasses directly scales with T_g [11], high wear resistance can be expected in MGs based on refractory metals, since they are most likely to have a high T_g. The present work is an attempt to develop a new wear-resistant W-based metallic glass. Some of the early work on refractory glasses dealt with systems like W–Ru–B or Mo–Ru–B [12], where the maximum hardness is limited to ~17 GPa. Subsequently, a $W_{45.6}Re_{30.4}B_{24}$ glass with a hardness of 23.5 GPa [13] was developed, which showed wear resistance superior to a high C steel. Later work focused on newer W–Ru–B and Re-based amorphous alloys, although the hardness in these systems is limited to ~16–17 GPa [14]. Harder glasses (26–31 GPa) are found in the W–Si–N system [15–19], but the Si and N levels can be high, with the metal (W) content between 26 and 64 at.%. This may not be desirable, because with some glassy alloys, a large metalloid content can reduce toughness and hence wear resistance, which derives from both hardness and toughness [20]. Also, in W–Si–N alloys, Si and N bond preferentially [15], leading to a more covalent nature, which is usually less tough than metallic bonding. In fact, only when one of Si and N has been consumed, does the remaining content of the other bond with W [16]. Hence, phase separation also occurs, with W-based phases dispersed in a Si–N ceramic glass [15], making some of these alloys technically metal-ceramic composites (cermets), quite distinct from the glassy alloys like W–Re/Ru–B with a more metallic character. In any case, we are unaware of reports comparing wear behaviour of either W–Si–N or W–Re/Ru–B alloys with similarly hard materials used

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industrially. Besides, alloying elements like Re/Ru/Ir are very expensive.

In this work, W–Ni–B is identified as a potential glass-forming system, based on the following factors known [21] to be conducive to glass-formation: (1) the binary phase diagrams show deep eutectics and (2) there is a range of atomic sizes, with W being the largest atom and B the smallest. From typical MG compositions, the B content was fixed at 25 at.%, to arrive at $W_{50}Ni_{25}B_{25}$. We report the successful synthesis and properties of this new refractory glassy alloy and show that a metallic glass can approach the wear resistance of classic tribological materials like TiN. Likely applications are also discussed, based on the strength-modulus combination.

2. Experimental techniques

Fine powders (325 mesh) of W, Ni and B, with a purity of 99.9 wt.% were thoroughly mixed in the ratio $W_{50}Ni_{25}B_{25}$ (at.%) using a roller mill. Sputtering targets, 50 mm in diameter, were prepared by compacting the powder mixture using spark plasma sintering (SPS) at 1400 °C. Films (3–4 μm thick) were deposited using a dc magnetron sputtering unit (Hind-Hivac Bangalore) with the following parameters: base pressure – 3×10^{-6} mbar; sputtering pressure – 0.03 mbar; voltage – 0.3 kV; current – 0.5 mA. Films were deposited on AISI 304 stainless steel and Si substrates, at both room temperature and 400 °C. Thicker films (>5 μm) deposited on Si substrates tend to crack and the peeled-off films were used for thermal analysis using a Seiko high-temperature differential scanning calorimeter (DSC) at a heating rate of 40 °C/min. The amorphicity of films was verified by using a Bruker X-ray diffractometer (CuKα radiation) and compositions checked with an electron microprobe analyzer (EPMA; SEMQ 51, ARL) utilizing wavelength-dispersive X-ray analysis (WDX). Hardness and modulus measurements were performed using an MTS Nanoindenter XP in the continuous stiffness mode (CSM) at a loading rate of 0.05 s^{-1}. The data presented are an average of 10 indents. The Young's modulus was calculated from the reduced modulus using standard relations [22], after assuming a reasonable Poisson's ratio of 0.3. A Bruker Dektak XT stylus profilometer was used for film thickness and residual stress measurements. The latter was done using an in-built Vision software that is based on the standardized approach of curvature evaluation for coated and uncoated substrates and the use of Stoney's equation. TiN films were also deposited by the same DC sputtering unit at 1×10^{-2} mbar pressure and at 400 °C substrate temperature in a gaseous Ar + N_2 mixture. The Ti–Si–B–C films are a nanocomposite of TiB_2, Ti_3B_4 and a glassy phase, obtained by sputtering of a composite target, as reported elsewhere [23].

Wear testing on the films was performed with a Hysitron TI 950 TriboIndenter. Two types of tests were conducted. First, scratch tests (1 cycle) were done over a 10 μm length at loads ranging from 4 to 12 mN to record the wear depth and friction coefficient. Tests were also performed at a fixed load of 8 mN, with the number of cycles varying from 1 to 20. In all cases, a constant sliding speed of 500 nm/s was maintained and the tests were repeated twice.

3. Results and discussion

Fig. 1(a) shows an X-ray diffraction (XRD) pattern of a 3.5 μm thick film deposited on a steel substrate. Broad peaks, typical of amorphous materials [24], can be seen; in addition to the primary peak, a secondary peak is also visible, with its intensity essentially related to short-range ordering in the material [24]. Similar XRD traces are also seen for other amorphous alloys, e.g. W–Re–B [13]. Similarly amorphous films were also obtained on a Si substrate (not shown) as well as on heated substrates (400 °C). Substrate heating only lowers the deposition rate from about 1.2 μm/h to 0.7 μm/h. Microprobe analysis (WDX) revealed the film composition to be $W_{33}Ni_{32}B_{35}$ (±1.5 at.%), rather different from the target, likely due to higher sputtering yield for light elements (B) compared to the heavier W.

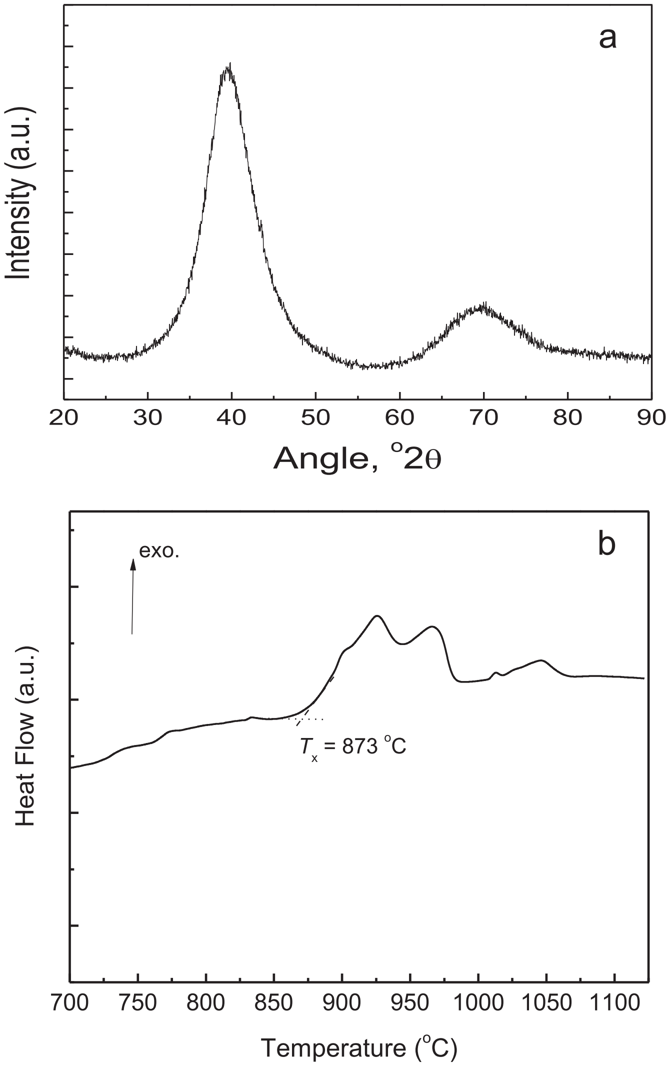

Fig. 1. (a) An X-ray diffraction pattern (CuK$_\alpha$ radiation) showing the amorphous nature of a $W_{33}Ni_{32}B_{35}$ film deposited on a stainless steel substrate. (b) A differential scanning calorimetry (DSC) trace showing its high crystallization temperature (873 °C).

Fig. 1(b) is a DSC thermogram showing the high crystallization temperature (T_x) of ~873 °C, much higher than other metallic glasses, e.g. 560–600 °C for many Fe-based MGs [24], but similar to other W-based glasses, where T_x varies from 776 °C for W–Ru–Rh–B to 1025 °C for W–Os–B glasses [14]. The high T_x is desirable for potential applications involving a temperature increase, e.g. cutting tools. The crystallization reaction is complex, with 2–3 overlapping peaks in the DSC trace.

Fig. 2 shows the hardness and modulus values as a function of indentation depth, obtained using the CSM method in nanoindentation. The average hardness is 24 ± 1.6 GPa and modulus is 350 ± 10 GPa, values similar to the W–Re–B glass (23.5 GPa hardness) but much higher than the W–Ru–B glasses (16 GPa) reported earlier. As noted by Ye et al. [25], thin film metallic glasses (TFMGs) can show tensile residual stress that may lower the hardness compared to that of the corresponding bulk material. For the present films deposited on Si substrates, a tensile residual stress of 0.9 GPa