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Chemical composition dependence of atomic oxygen erosion resistance in Cu-rich bulk metallic glasses

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The effect of atomic oxygen (AO) on the surface oxidation of several typical Cu-based bulk metallic glasses (BMGs) was studied in the present work. The AO source using in this study is generated by discharge plasma type ground simulation equipment. The AO erosion/oxidation resistances of the amorphous alloy samples were assessed based on the analysis of mass loss, surface color and microstructure. It is found that these Cu-based BMGs possess good AO erosion/oxidation resistance and their resistance to AO erosion/oxidation strongly depends on the chemical composition. For the samples containing more Ag and/or Cu, the AO erosion/oxidation resistance is weaker. The present result is important for designing new metallic glasses using as space materials.

bulk metallic glass, atomic oxygen erosion, low earth orbit, oxidation

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The presence of atomic oxygen (AO) in low Earth orbit (LEO, altitude from ~200 to ~700 km) is one of important reasons for surface degradation of the aerospace materials. Atomic oxygen, which possesses high chemical activity, is the dominant chemical constituent (80%) in the neutral atmosphere in LEO [1]. When the spacecraft locates in LEO with an orbital velocity of 7–8 km s^{-1}, AO impacts the surface of the spacecraft with a kinetic energy of ~5 eV, thus can react with many elements [2]. Then, it may lead to surface erosion and property degradation of space materials which would further affect the safety/longevity of spacecrafts. Therefore, studies on the AO effects have been widely appreciated. Through testing platforms equipped in spacecrafts and all kinds of ground effect simulation testing devices, a large number of aerospace materials such as polymer [3], inorganic material coating [4,5], silver [6], aluminum [7], titanium [8] and carbon materials [9], etc., have been studied extensively. For most metal materials, AO will react with them to form oxidized film which can prevent further oxidation to erode the material. Except AO sensitive elements such as Os, Ag and Cu, metal materials usually have relatively better AO resistance than those polymers and carbon materials. But the films generated by AO can result in a change in surface roughness and thus leading to degradation of luminous reflectance, frictional wear properties and even welding performance [7]. Therefore it is of great interest to investigate the effect of AO on metallic materials to better understand the oxidation mechanism. So far, the field of AO erosion study is largely focused on crystalline materials. Recent decades, bulk metallic glasses (BMGs), new comers of metallic materials, have attracted lots of attention [10–14] due to excellent mechanical and functional properties [15–21], which are believed to be resulted by their unique structure [22,23]. Since high performance of BMGs make them potential candidates of space materials, their AO erosion resistance is of interest to be investigated.

The main aim of the present work is to explore the influence of Cu or Ag contained on the AO resistance of BMG materials. To our knowledge, those alloys containing elements sensitive to AO, such as Ag and Cu, were worried about whether they are stable in LEO. In addition, as one of the major addition elements, Cu or Ag is often used to improve the glass forming ability or mechanical properties in

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*Corresponding author (email: kfyao@tsinghua.edu.cn) many BMGs [24–27]. Hence, it is of great interest to know whether they adversely affect the AO erosion resistance. We choose a series of Cu-based alloys containing different amounts of Cu/Ag to study the oxidation of such glassy alloys rich in AO sensitive elements. Finally, we will provide some simple empirical rules for designing metallic glasses applied in LEO environment.

1 Experimental

Master alloy ingots with nominal compositions of $Cu_{44.25}Ag_{14.75}Zr_{36}Ti_5$ [27], $Cu_{42}Zr_{42}Ag_8Al_8$ [26,28], $Cu_{45}Zr_{48}Al_7$ [29], and $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1) [30], were prepared by arc melting the mixtures of raw elements with purity better than 99.4% in a Ti-gettered Ar_2 atmosphere. Plates with 2 mm in thickness, 12 mm in width and 60 mm in length were prepared from the ingots by copper mold suction casting method. Thin crosscut pieces of samples were cut down in the middle of the plates and then examined by X-ray diffraction (XRD) using CuKα radiation. Square plate samples with size of 2 mm × 5 mm × 5 mm and 2 mm × 10 mm × 10 mm cut from the as-cast plates, were grinded and polished using fine sandpapers.

The polished samples were tested using the ground-based AO effect simulation facility at Beijing University of Aeronautics and Astronautics (BUAA). By the method of filament discharge plasma, this ground-based AO effect simulation facility can generate a larger amount of AO flux than that in LEO. Therefore, the progress of the experiment can be accelerated so as to shorten experimental period to just a few days. The configuration and characteristics of the facility were detailed in reference [31]. In this case, a Kapton material, which is a commonly used polymer with a constant AO erosion rate of 3.0×10^{-24} cm^3/atom, is chosen as the standard material to estimate the AO flux. In order to avoid forming the autoxidation passive film on the test samples in air and mislead the analysis of test results, all the samples have been carefully grinded with fine sandpaper prior to AO exposure. The experimental materials used in this work with the compositions of $C_{22}H_{10}N_2O_5$ (Kapton), $Cu_{44.25}Ag_{14.75}Zr_{36}Ti_5$, $Cu_{42}Zr_{42}Ag_8Al_8$, $Cu_{45}Zr_{48}Al_7$, and $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ as mentioned above, are named A0, A1, A2, A3 and A4, respectively.

The mass of the samples was measured with a DT-100 balance (Beijing Optical Instrument Factory, China), with a sensitivity of 0.00005 g. The surface morphology was inspected by a scanning electron microscope (SEM) with a field emission gun (LEO 1530).

2 Results

2.1 Changes in the colors of exposure surfaces

The color change of the exposed surface is the most intuitive evidence to determine whether a sample is sensitive to AO environment. Figure 1 shows the color changes on the surfaces of the pre/post exposure samples. Not surprise, the exposure surface colors of those samples with Cu-rich and Ag-rich have changed from a general metallic gray to a more darken color after AO exposure (Figure 1). In the three Cu-Zr-Al alloys with almost the same amount of Cu but different amounts of Ag, a clear trend can be noticed that the more Ag contained, the darken color presented after AO exposure. While, color changes of A4 samples were not that clear (Figure 1(d)).

2.2 Mass loss

Table 1 lists the mass losses of the samples exposed in AO for 40 h together with the color changes. Sample A0, which is the reference material Kapton, has an obvious mass loss of 65.78%, indicating that the experiment complied with the requirements of the AO test. Since the sensitivity of the

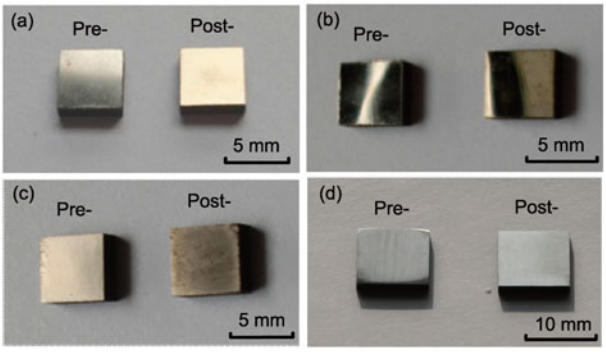

Figure 1 (Color online) The digit images of the pre/post exposure samples for comparing their colors changes on the surfaces. (a) A1; (b) A2; (c) A3; (d) A4.

Table 1 The summarized results of the experiment including color change, microstructure change and mass loss with Cu and Ag contained

Sample	Composition (in at.)	Cu (at %)	Ag (at %)	Change in color	Change in microstructure	Mass (g)		Mass loss (%)
						Pre-exposure	Post-exposure	
A0	$C_{22}H_{10}N_2O_5$(Kapton)	–	–	obvious	obvious	0.00564	0.00193	65.78
A1	$Cu_{44.25}Ag_{14.75}Zr_{36}Ti_5$	44	15	obvious	obvious	0.43460	0.43455	0.01
A2	$Cu_{42}Zr_{42}Ag_8Al_8$	42	8	none	slight	0.49565	0.49560	0.01
A3	$Cu_{45}Zr_{48}Al_7$	45	0	slight	slight	0.51585	0.51585	0
A4	$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1)	13	0	none	none	1.05880	1.05880	0

balance is 0.00005 g, the values obtained in this case are of an instrumental error of ±0.00005 g. In other words, it is then somewhat negligible with the mass value smaller than 0.0001 g. Although the surface color changes reveal the effectiveness of the role of atomic oxygen, all the test BMG samples have no obvious mass loss more than 0.01% as listed in Table 1, indicating that glass alloy possesses very good property in AO erosion/oxidation resistance.

2.3 Surface microstructure morphology

Figure 2 shows some typical surface microstructure morphology images of the samples. For sample A1, an obvious change between the pre-exposure and post-exposure surface can be found. It has been transformed from a smooth surface morphology except some scratches (Figure 2(a)) to a quite rough surface morphology with obvious AO erosion features (Figure 2(b)). On the exposed surface of A1, not only oxidation product but also some voids and cracks can be clearly observed in a relative low magnification which is a clear evidence that the interaction of AO with the sample. For sample A2, it is found that the oxidation product particles with a smaller size of ~50 nm, uniformly distributed on the surface (Figure 2(c)). While for sample A3, the morphology is similar with A2, except particle size which ranges from ~30 to ~200 nm (Figure 2(d)). However, for A4 (Figure 3(e), (f)), no changes could be observed before and after AO exposure, except scratches on the surface, suggesting a good AO erosion/oxidation resistance.

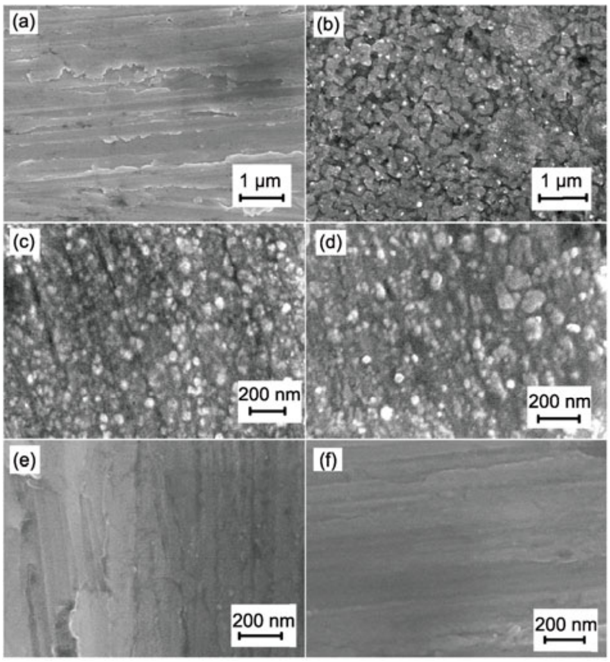

Figure 2 Typical morphologies of the pre/post exposure surface in AO for 40 h. (a) A representative morphology of the pre-exposure sample A1; (b) A1 for post-exposure; (c) A2 for post-exposure; (d) A3 for post-exposure; (e) A4 for pre-exposure; (f) A4 for post-exposure.

3 Discussions

Based on the results reported above, Cu and Ag are key constitute elements that control the AO erosion resistance of the BMGs. Table 1 also summarizes a qualitative analysis results showing that the AO erosion resistance of the tested BMG samples depended on the Cu and/or Ag contains. Taking samples A1–A3 into account, with clearly increasing Ag in content, the effect of Ag on AO erosion in Cu-based BMGs can be measured. Comparing sample A2 with A3, a similar change can be found that they had similar changes in surface color and microstructure. The result demonstrates that samples A2 and A3 have similar oxidation behavior in AO environmental which suggested the Ag containing in sample A2 has no obvious effect on the AO erosion resistance. But when Ag content reaches 15% (sample A1), the AO oxidation is quite different. For example, the color has been transformed into a pale yellow and its microstructure has become more complex which composed of particles, clusters, voids and cracks, etc. It is suggested that in Cu-based metallic glasses the surface oxidation depends on the Ag content. But if it is below 8%, Ag may not significantly affect the AO erosion resistance. From samples A1–A4 of Zr-Cu alloy system with a significant Cu composition variation compare to other elements, the role of Cu can be roughly estimated. When the Cu content is below ~13% (such as sample A4), no change in exposed surface color or microstructure has been noticed. The result suggests that sample A4 possesses a better ability in anti-erosion/oxidation of AO.

It is known that, in many BMGs, Cu or Ag is often added in the alloys for improving the GFA or turning the mechanical properties. If the BMGs were designed to use in AO environment, it is then necessary to avoid adding such elements, or at least, to control the amount of them in the total composition. Interestingly in this case, it seems that adding these two elements with some specific amounts do not change the oxidation behavior of these alloys in AO. But the concentration of Ag and Cu must be limited to certain amount which needs lots of experiments to explore. Our work have provided some simple clues that, if Ag is added no more than about 8% or Cu is no more than about 13%, the AO effect on the BMGs is acceptable. Of course, a more detailed study is needed to be carried out in the future to confirm the maximum amount of Cu or Ag to be added without obvious change of their AO resistance.

4 Conclusion

In the present work, a group of Cu-based BMGs were exposed in the AO environment simulated on the ground. It was found that these Cu-based BMGs possess good property of anti-erosion/oxidation of AO, despite that in the three Cu-based BMGs a clear oxidation trace could be identified, which was confirmed to be strongly related to the chemical composition of the BMGs. The oxidation of BMGs in AO is obvious when the Cu component excess than about 40% and Ag excess than 15% in atomic percent. While Cu content is lower than about 13% the oxidation can be negligible. The study of the AO effect on different MGs provides a clue to select and design new metallic glasses especially for using as space materials. The present result is also of significance for extending the application of this new class of materials in the aerospace field.

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1 Packirisamy S, Schwam D, Litt M H. Atomic oxygen resistant coatings for low earth orbit space structures. J Mater Sci, 1995, 30: 308–320

2 Reddy M R. Effect of low Earth orbit atomic oxygen on spacecraft materials. J Mater Sci, 1995, 30: 281–307

3 Miyazaki E, Tagawa M, Yokota K, et al. Investigation into tolerance of polysiloxane-block-polyimide film against atomic oxygen. Acta Astronaut, 2010, 66: 922–928

4 Hu L, Li M, Xu C, et al. Perhydropolysilazane derived silica coating protecting kapton from atomic oxygen attack. Thin Solid Films, 2011, 520: 1063–1068

5 Huang Y, Tian X, Lv S, et al. An undercutting model of atomic oxygen for multilayer silica/alumina films fabricated by plasma immersion implantation and deposition on polyimide. Appl Surf Sci, 2011, 257: 9158–9163

6 Li L, Yang J C, Minton T K. Morphological changes at a silver surface resulting from exposure to hyperthermal atomic oxygen. J Phys Chem C, 2007, 111: 6763–6771

7 Aoki Y, Fujii H, Nogi K. Effect of atomic oxygen exposure on bubble formation in aluminum alloy. J Mater Sci, 2004, 39: 1779–1783

8 Raspopov S A, Gusakov A G, Voropayev A G, et al. Interaction of titanium with atomic and molecular oxygen. J Chem Soc, Faraday Trans, 1996, 92: 2775–2778

9 Srinivasan S G, van Duin A C T. Molecular-dynamics-based study of the collisions of hyperthermal atomic oxygen with graphene using the reaxff reactive force field. J Phys Chem A, 2011, 115: 13269–13280

10 Zhang T, Yang Q, Ji Y, et al. Centimeter-scale-diameter Co-based bulk metallic glasses with fracture strength exceeding 5000 MPa. Chin Sci Bull, 2011, 56: 3972–3977

11 Schuh C A, Hufnagel T C, Ramamurty U. Overview no.144-mechanical behavior of amorphous alloys. Acta Mater, 2007, 55: 4067–4109

12 Wang W H, Dong C, Shek C H. Bulk metallic glasses. Mater Sci Eng R-Rep, 2004, 44: 45–89

13 Qiu S B, Yao K F, Gong P. Effects of crystallization fractions on mechanical properties of Zr-based metallic glass matrix composites. Sci China Phys Mech Astron, 2010, 53: 424–429

14 Qiu S B, Yao K F, Gong P. Work toughening effect in $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass. Chin Sci Bull, 2011, 56: 3942–3947

15 Li G, Huang L, Dong Y, et al. Corrosion behavior of bulk metallic glasses in different aqueous solutions. Sci China Phys Mech Astron, 2010, 53: 435–439

16 Xie K F, Yao K F, Huang T Y. A Ti-based bulk glassy alloy with high strength and good glass forming ability. Intermetallics, 2010, 18: 1837–1841

17 Yao K F, Ruan F, Yang Y Q, et al. Superductile bulk metallic glass. Appl Phys Lett, 2006, 88: 1221106

18 He Q, Cheng Y Q, Ma E, et al. Locating bulk metallic glasses with high fracture toughness chemical effects and composition optimization. Acta Mater, 2011, 59: 202–215

19 Hofmann D C, Suh J Y, Wiest A, et al. Designing metallic glass matrix composites with high toughness and tensile ductility. Nature, 2008, 451: 1083–1085

20 Wang A, Zhang M, Zhang J, et al. Effect of Ni addition on the glass-forming ability and soft-magnetic properties of FeNiBPNb metallic glasses. Chin Sci Bull, 2011, 56: 3932–3936

21 Hui X, Xu Z, Wu Y, et al. Magnetocaloric effect in Er-Al-Co bulk metallic glasses. Chin Sci Bull, 2011, 56: 3978–3983

22 Li Q, Li M. Rethinking atomic packing and cluster formation in metallic liquids and glasses. Chin Sci Bull, 2011, 56: 3897–3901

23 Li F, Qiang J, Wang Y, et al. Revisiting Al-Ni-Zr bulk metallic glasses using the “cluster-resonance” model. Chin Sci Bull, 2011, 56: 3902–3907

24 Lue X, Bian X, Xiang N, et al. Correlation between liquid structure and glass forming ability in glassy Ag-based binary alloys. Sci China Phys Mech Astron, 2010, 53: 399–404

25 Zhou W, Lu B, Kong L, et al. Rolling-induced microstructure change in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glass. Chin Sci Bull, 2011, 56: 3948–3951

26 Zhang W, Zhang Q S, Inoue A. Fabrication of Cu-Zr-Ag-Al glassy alloy samples with a diameter of 20 mm by water quenching. J Mater Res, 2008, 23: 1452–1456

27 Dai C L, Guo H, Shen Y, et al. A new centimeter-diameter Cu-based bulk metallic glass. Scripta Mater, 2006, 54: 1403–1408

28 Zhang W, Zhang Q S, Inoue A. Synthesis and mechanical properties of new Cu-Zr-based glassy alloys with high glass-forming ability. Adv Eng Mater, 2008, 10: 1034–1038

29 Wang D, Tan H, Li Y. Multiple maxima of GFA in three adjacent eutectics in Zr-Cu-Al alloy system—A metallographic way to pinpoint the best glass forming alloys. Acta Mater, 2005, 53: 2969–2979

30 Peker A, Johnson W L. A highly processable metallic glass: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$. Appl Phys Lett, 1993, 63: 2342–2344

31 Zhao X H, Shen Z G, Xing Y S, et al. A study of the reaction characteristics and mechanism of kapton in a plasma-type groundased atomic oxygen effects simulation facility. J Phys D Appl Phys, 2001, 34: 2308–2314