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Structure Relaxation of $Mg_{65}Cu_{25}Gd_{10}$ Metallic Glass and Its Effect on Strength

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Abstract: To identify the re-arrangement of constituent atoms of an amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy happened with annealing, structure relaxation of the alloy was investigated as a function of annealing time at 373 K through extended X-ray absorption fine structure (EXAFS) analysis procedures. To understand the effect of structure relaxation on strength, compression tests were conducted for both the as-cast and the annealed $Mg_{65}Cu_{25}Gd_{10}$ samples. It is found that short range order around Cu and Gd atoms exhibits different variation trends with increasing annealing time at 373 K, though the structure of the alloy still remains to be amorphous. Based on the fact that the strength of the alloy first exhibits a reduction and then a recovery with annealing time, it is suggested that the enhancement of short range order around Cu should be responsible for the strength reduction, while the enhancement of short range order around Gd should be responsible for the strength recovery.

Key words: Mg-based metallic glass; structure relaxation; strength; annealing

1 Introduction

It is well known that magnesium alloys are the lightest structural materials, however, their applications are so far limited due to their relatively low strength and corrosion resistance. Mg-based metallic glasses have the potential to overcome the deficiencies of traditional magnesium alloys for their higher strength and good corrosion resistance, so they are regarded as a new family of promising structural materials. Regarding Mg-based metallic glasses, Mg-Ln-TM[1-3] (Ln = lanthanide metals, TM = transition metals) system has been focussed on because of its high glass-forming ability and good mechanical properties. Some results on structure of Mg-based bulk amorphous alloys have been reported. Matsubara found that Mg atoms form strong local ordering clusters with the other constituent element Ni and La in amorphous $Mg_{50}Ni_{30}La_{20}$ alloy[4]. Madge showed that an apparent two-phase cellular microstructure is seen in $Mg_{65}Ni_{20}Nd_{15}$ glass[5]. Mizutani studied the electronic structure of amorphous Mg-Ni-La and Mg-Cu-Y alloys and pointed that the Fermi level sits in the La and Y *d*-band and that the density of states at E_F decreases monotonically with increasing Mg content[6]. Recently, it has been reported that $Mg_{65}Cu_{25}Gd_{10}$ alloy[7] exhibits a significantly improved GFA so that metallic glass rods with diameter of 8 mm were obtained by copper mold casting. Moreover, based on $Mg_{65}Cu_{25}Gd_{10}$, a series of new Mg-based amorphous alloys with higher GFA have been developed[8-14]. So $Mg_{65}Cu_{25}Gd_{10}$ has become the foundation for studying other Mg-based metallic glasses, however, the understanding of $Mg_{65}Cu_{25}Gd_{10}$ is very limited. In the present work, we endeavored to study the structural changes in $Mg_{65}Cu_{25}Gd_{10}$ metallic glass resulted from low temperature annealing through extended X-ray absorption fine structure (EXAFS) and evaluate their effects on strength that was in favor of the understanding of the relationship between local atomic structures and properties[15].

2 Experimental

Cu-Gd ingot as intermediate alloy was prepared by arc melting Cu(99.99%) and Gd(99.9%) under a Ti-gettered argon atmosphere in a water-cooled crucible. The alloy was then melted with Mg(99.9%) by induction melting to obtain the master alloy with

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composition of $Mg_{65}Cu_{25}Gd_{10}$. The composition is nominally expressed in atomic percentage. From the master alloy ingot, amorphous rods with the diameter of 3 mm were prepared by the copper mold casting method in an argon atmosphere. The amorphism of rod samples was examined by X-ray diffractometry (Rigaku D/max 2200PC) with a monochromatic Cu K_a radiation. Thermal stability associated with sequential structural changes in glassy solid, glass transition, supercooled liquid and crystallization were measured with a differential scanning calorimeter at a heating rate of 0.33 K/s. The samples were annealed for different time periods at 373 K according to the DSC curve. For mechanical testing, cylindrical samples of 3 mm diameter and 6 mm height were cut from the as-cast rods and polished on both ends. The compression tests were performed using a computer controlled tensile test machine. The room temperature X-ray absorption experiments on Cu K-edge and Gd L_{III}-edge in the usual fluorescence geometry were performed at National Synchrotron Radiation Laboratory (NSRL) in Hefei China running typically at 800 MeV, with an average current of 150 mA, using a double-crystal Si(111) monochromator .

3 Results and Discussion

3.1 DSC analysis

In order to check the thermal stability of $Mg_{65}Cu_{25}Gd_{10}$ metallic glass, differential scanning calorimetry (DSC) was conducted. Fig.1 shows the DSC curve of $Mg_{65}Cu_{25}Gd_{10}$ amorphous rod with a heating rate of 0.33 K/s. From the DSC curve, a glass transition temperature of $T_g = 419$ K and a crystallization temperature of $T_x = 481$ K were determined, resulting in an under cooled liquid region of ?T_x(? $T_x = T_x - T_g$) =62 K .

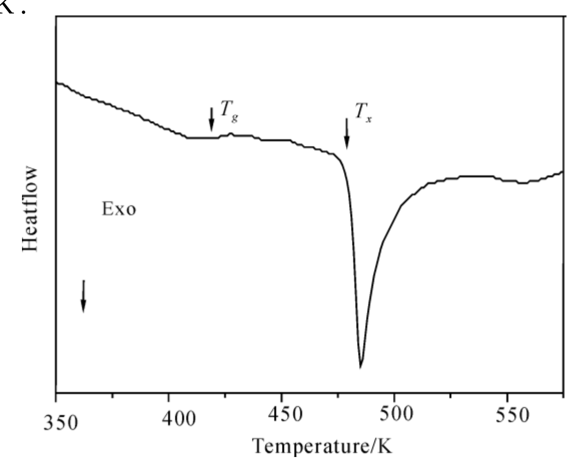

Fig.1 The DSC trace of as-cast $Mg_{65}Cu_{25}Gd_{10}$ rod at a heating rate of 0.33 K/s

3.2 XRD analysis

According to the DSC result, the samples were annealed at 373 K (below T_g) for 2 h and 4 h, respectively. Fig.2 shows the X-ray diffraction patterns of the $Mg_{65}Cu_{25}Gd_{10}$ rods heat treated at 373 K along with the X-ray diffraction pattern of the as-cast rod. The XRD pattern of as-cast rod exhibits a broad diffraction peak instead of a sharp diffraction peak, indicating that a dominantly single amorphous phase is formed. The magnitude of broad diffraction peak decreases after annealing while no obvious sharp diffraction peaks are observed, indicating that some changes for the samples heat treated at 373 K have taken place but no observable crystalline phases appear.

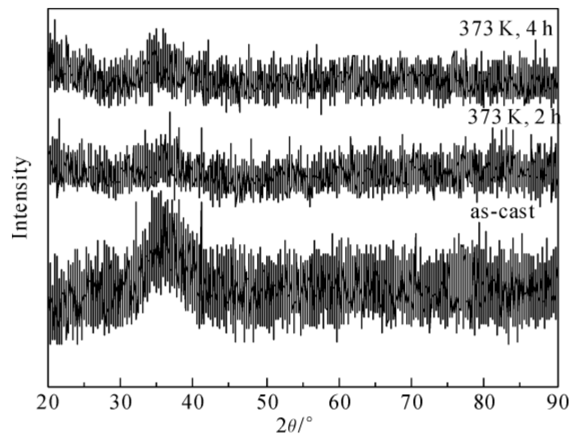

Fig.2 XRD patterns of as-cast $Mg_{65}Cu_{25}Gd_{10}$ rods heat treated at different conditions

3.3 Compression test

Fig.3 shows compressive stress-strain curves of the as-cast and heat treated bulk glassy $Mg_{65}Cu_{25}Gd_{10}$ rods with a diameter of 3 mm. The fracture strength (σ_{cf}) for the as-cast $Mg_{65}Cu_{25}Gd_{10}$ rod decreased while the brittleness increased after annealing at 373 K for 2 h, however, with further increase of annealing time, the fracture strength (σ_{cf}) increased while the brittleness decreased compared with the sample heat treated at 373 K for 2 h. The change in mechanical properties for $Mg_{65}Cu_{25}Gd_{10}$ metallic glass is suggested to have most probably resulted from structural changes during annealing.

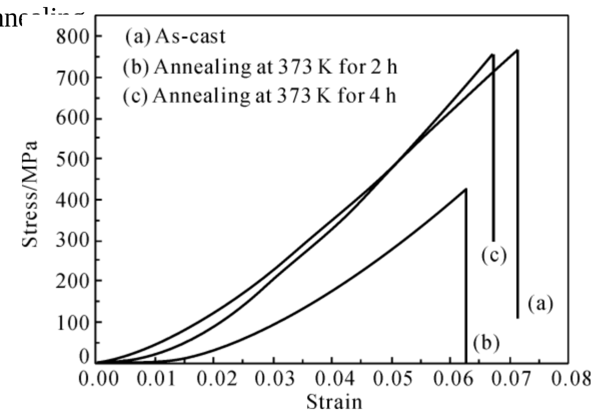

Fig.3 Compressive stress-strain curves of the as-cast and heat

treated $Mg_{65}Cu_{25}Gd_{10}$ glassy rods with a diameter of 3 mm

3.4 EXAFS analysis

Raw X-ray absorption data are background-subtracted, normalized and transformed from energy to momentum space, resulting in the experimental function $c(k)$. This $c(k)$ function is weighed by k^3 and k for Cu and Gd respectively to correct for the decaying amplitude at high k, and is subsequently Fourier transformed into real space, producing FT[$k^3c(k)$] and FT[$k\ c(k)$].

Fig.4 shows the EXAFS spectra of Cu K and Gd L_{III} edge of the as-cast and heat treated $Mg_{65}Cu_{25}Gd_{10}$ alloys. From Fig.4(a), the amplitude of oscillations increased slightly as the annealing time increased, however, in Fig.4(b), the amplitude of oscillations first decreased and then increased slightly with the annealing time increasing as distinctly seen from the radial distribution functions (RDFs) results.

Even by restricting our attention only to the qualitative features emerging from the Fourier transforms (FT) data, some important observations can be made. Form Fig.5, it can beseen that the FT of the as-cast $Mg_{65}Cu_{25}Gd_{10}$ rod is typical of a highly disordered (amorphous) structure with a single broad peak around 0.23 nm for the absorbing atom Cu and for the absorbing atom Gd around 0.27 nm corresponding to the nearest neighbor distribution. Fig.5(a) shows that heating at 373 K for 2 h slightly modifies the Cu local environment. Nevertheless, in FT the increase of amplitude intensity of the first peak can be observed. This indicates that the short range order around the Cu atoms increases slightly and some atoms transfer towards the Cu atoms resulting in an increase of coordination number as can be seen from the increase of amplitude intensity. The nearest neighbor peak becomes sharper and higher and moves to higher ‘*r*’ after treatment at 373 K for 4 h, indicating the above situation about the Cu atom local environment develops ulteriorly while the bonds between absorbing Cu atoms and their first neighbor atoms become weaker. Fig.5(b) shows that changes in the Gd atom local environment differ from the Cu atoms as the annealing time increases. The short range order around the Gd atoms initially decreases and then increases with increase of annealing time at 373 K.

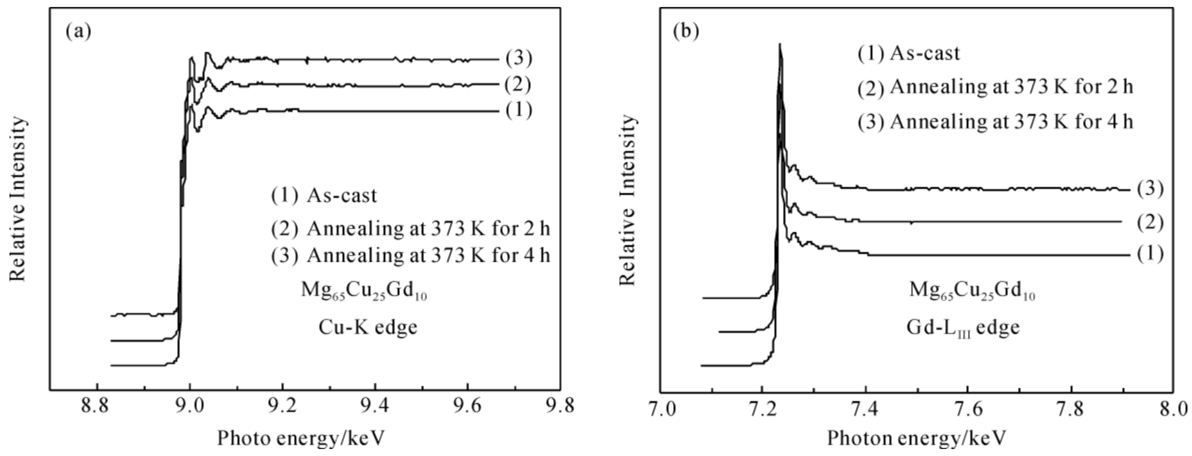

Fig.4 (a) Cu-K edge absorption spectra and (b) Gd-L_{III} edge absorption spectra for $Mg_{65}Cu_{25}Gd_{10}$ at different conditions

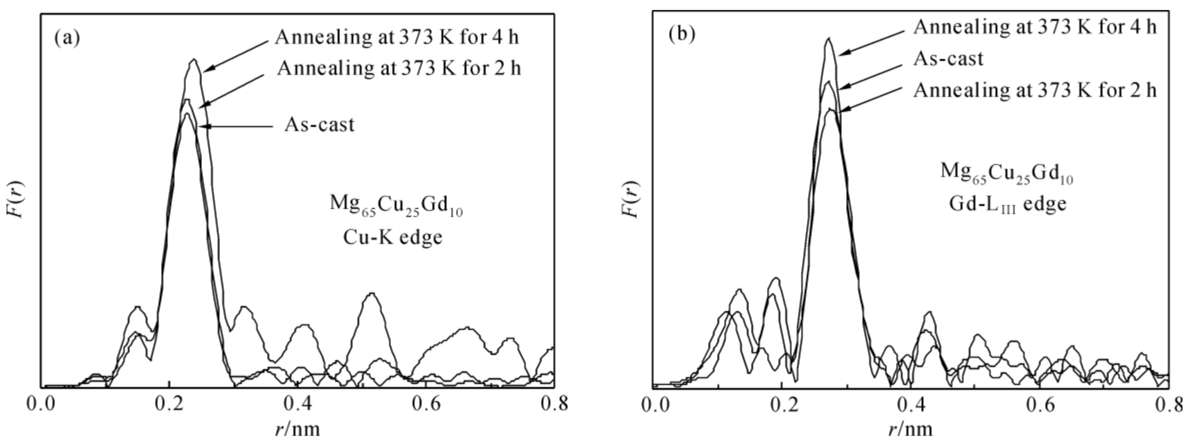

Fig.5 (a) The Fourier transforms at the K-edge of Cu and (b) the Fourier transforms at the L_{III}-edge of Gd in the sample rods

The above analysis results suggests that the changes of strength for $Mg_{65}Cu_{25}Gd_{10}$ samples after annealing at 373 K for different time are closely related to the changes of absorbing Cu and Gd atom local environment resulting from annealing. Integrating with the previous work (having been discussed in other where), we think that the increase of short range order around the Cu atoms and the decrease of short range order around the Gd atoms induced by annealing have a negative effect on the strength of $Mg_{65}Cu_{25}Gd_{10}$ alloy, and the decline of strength is also related to the weaker bonds between the absorbing atoms (*ie*, Cu and Gd) and their first neighbor atoms. It is noticeable that an increase of the short range order around Gd atoms is accompanied with an improvement of the strength for $Mg_{65}Cu_{25}Gd_{10}$ metallic glass annealed at 373 K for 4 h though the short range order around Cu atoms also has an increase at the same time. It seems to be suggested that the increase of the short range order around Gd atoms has a stronger effect on the strength for $Mg_{65}Cu_{25}Gd_{10}$ metallic glass than that around Cu atoms. The mechanism about above phenomenon will be specially discussed in other where.

4 Conclusions

a) The compressive strength of $Mg_{65}Cu_{25}Gd_{10}$ alloy after annealing at 373 K for different time exhibits sharper decrease then pronounces recovery.

b) The decline of strength for $Mg_{65}Cu_{25}Gd_{10}$ metallic glass annealed at 373 K for 2 h can be mainly attributed to an increase of short range order around Cu atoms and a decrease of short range order around Gd atoms.) The increase of the short range order around Gd atoms that occurred after annealing at 373 K for 4 h has resulted in the improvement of strength.

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