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EXAFS Studies on Local Atomic Structure in the Amorphous $Mg_{65}Cu_{25}Gd_{10}$ Alloy

LI Guoqiang[1], ZHENG Lijing[2],CAI Quan[3], LI Huanxi[2], WANG Xiaomin[1], SUN Tianyu[4]

(1. Business Development Department, China Perfect Machinery Industry Corp. Ltd, Shanghai 200061, China; 2. School of Materials Science & Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, China; 3. Beijing Synchrotron Radiation Facility, Beijing 100039, China; 4. Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China)

Abstract: Local atomic structures of an amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy and the structural changes by thermal annealing have been studied by extended X-ray absorption fine structure (EXAFS). The correlation between structural changes and mechanical properties for the $Mg_{65}Cu_{25}Gd_{10}$ alloy has also been discussed. Results showed that Cu atoms around Gd in $Mg_{65}Cu_{25}Gd_{10}$ lost rapidly during annealing , resulting in the segregation of Cu atoms. The coordination number $N_{Gd\text{-}Mg}$ of $Mg_{65}Cu_{25}Gd_{10}$ annealed at 373 K first diminished and then augmented with the increase of annealing time. The formation of polyhedral short-range order unit with coordination number of nearly 12 around Gd atoms is in favor of the improvement of mechanical properties. The chemical short-range order, not topological short-range order in the amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy had obvious changes during annealing.

Key words: magnesium alloy; amorphous alloy; short-range; EXAFS; mechanical properties; annealing

1 Introduction

Since the late of 1980s[1-3], bulk Mg-based amorphous alloys with high glass-forming ability(GFA) and good mechanical properties have been well-known for its potential application in the fields of astronavigation, automobile and electronics and so on. Many significative research results on structure analysis for Mg-based amorphous alloys have been reported in the past few decades. Matsubara[4] 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 by anomalous X-ray scattering(AXS) technique; Madge[5] investigated component inhomogeneity in Mg-Ni-Nd system amorphous alloys by energy filtration transmission electron microscope (EFTEM) and concluded that an apparent two-phase cellular microstructure (rich of Ni or Mg and Nd, respectively) is seen in $Mg_{65}Ni_{20}Nd_{15}$ glass; Mizutani[6, 7] studied the electronic structure of amorphous Mg-Ni-La and Mg-Cu-Y alloys by X-ray photoelectron spectroscopy (XPS) and soft X-ray emission spectroscopy 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; Miller surveyed microscopic patterns of Mg-Cu-Y glasses by atomic probe; Matsuura[9] analyzed microscopic structure of $Mg_{97}Zn_3Y_1$ spun-melt ribbon by extended X-ray absorption fine structure (EXAFS) and thought that there is little Zn and Y dissolved in Mg matrix but strong bond between them that results in the forming of clusters and high yield strength of $Mg_{97}Zn_3Y_1$. Recently, $Mg_{65}Cu_{25}Gd_{10}$ amorphous alloy with significantly improved GFA[10] and prominent mechanical properties[11] has been one of research hotspots in Mg-based amorphous alloy scopes, however, intensive studies on its structure are very limited. In the present work, local atomic structures of the amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy and the structural changes by thermal annealing by EXAFS were investigated, furthermore, the relationship between local atomic structures and mechanical properties has been discussed.

2 Experimental

Amorphous $Mg_{65}Cu_{25}Gd_{10}$ rods with the diameter of 3 mm and the length of 8 cm were supplied by The Institute of Metal Research, Chinese Academy of Sciences.

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LI Guoqiang(李国强): Ph D ; E-mail: guoqiangli@chinaperfect.com.cn

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For mechanical testing, cylindrical samples of 3 mm in diameter and 6 mm in 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. All samples were annealed according to the DSC curve[12] and its structure characteristics seen in[12, 13] were examined by X-ray diffractometry(Rigaku D/max 2200PC) with a monochromatic Cu Kα radiation. The room temperature X-ray absorption experiments on Cu K-edge and Gd L_{III}-edge in the usual fluorescence geometry have been 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

The Fourier transform of absorption spectra is shown in Fig.1. It shows that heating at 373 K for 2 h slightly modifies the Cu local environment. Nevertheless, in FT the increase of amplitude intensity and the appreciable decrease of half width for 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[14]. The above change about the Cu atom local environment develops ulteriorly with the increase of annealing time(*e g*, 373 K, 4 h) or temperature(*e g*, 450 K). Though the sample was annealed at 520 K (above the first crystalline temperature) for only 10 min, the nearest neighbor peak becomes sharper and the amplitude is about twice as large as the one of as-cast sample, indicating that great structural changes have taken place after higher annealing temperature which matches to the result of XRD[13]. However, a large amount of structural disorder still remains, as demonstrated by the absence of next neighbor peak. The nearest neighbor interatomic distance for Gd atoms increases slightly while the amplitude intensity decreases after annealing at 373 K for 2 h, as is shown in Fig.1(b). With the increase of annealing time(*e g*, 3 or 4 h) at 373 K, the amplitude intensity of first peak for Gd atoms increases compared to the as-cast sample, especially the annealing sample at 373 K for 4 h, however, the amplitude intensity decreases slightly after annealing at higher temperature. The above situation indicates that the short range order around Gd atoms for $Mg_{65}Cu_{25}Gd_{10}$ first falls then increases and falls again with annealing temperature or time.

In brief, the short range order around the Cu atoms in $Mg_{65}Cu_{25}Gd_{10}$ amorphous alloy increases gradually during annealing while the one around the Gd atoms decreases slightly except for the annealing conditions(*e g*, 3 or 4 h at 373 K). Integrating with the effect of heat treatment on mechanical prosperities of $Mg_{65}Cu_{25}Gd_{10}$ amorphous alloy[12, 13], the enhancement of short range order around Cu and the abatement around Gd during annealing should be responsible for the strength reduction, however, the enhancement of short range order around Gd atoms after annealing for 3 or 4 h at 373 K has stronger effect on the strength than that around Cu atoms, which is the reason of compressive strength recovery for $Mg_{65}Cu_{25}Gd_{10}$ alloy after longer annealing at 373 K.

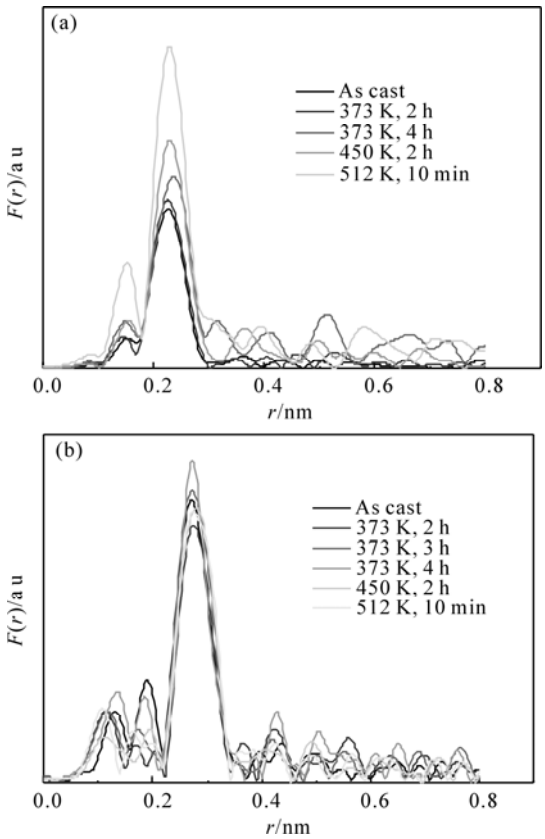

Fig.1 The Fourier transforms of absorption spectra for amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy annealed at different conditions (a) Cu-K edge; (b) Gd-L_{III} edge

In order to confirm the above analysis and determine structure parameters (coordination numbers and interatomic distances) for the first neighbors, experimental curves have been fitted. The inverse Fourier transformation of $F(r)$ was employed to the isolated first peak to obtain a filtered EXAFS function in k space. Fig.2 shows the results of the Cu K-edge and Gd-L_{III} edge for $Mg_{65}Cu_{25}Gd_{10}$ at different conditions in terms of $\chi(k) \cdot k^3$ *versus* k. The nearest neighbor distances and coordination numbers around Cu and Gd atoms(as shown in Table 1 and 2) were determined from the filtered EXAFS function by a curve-fitting method.

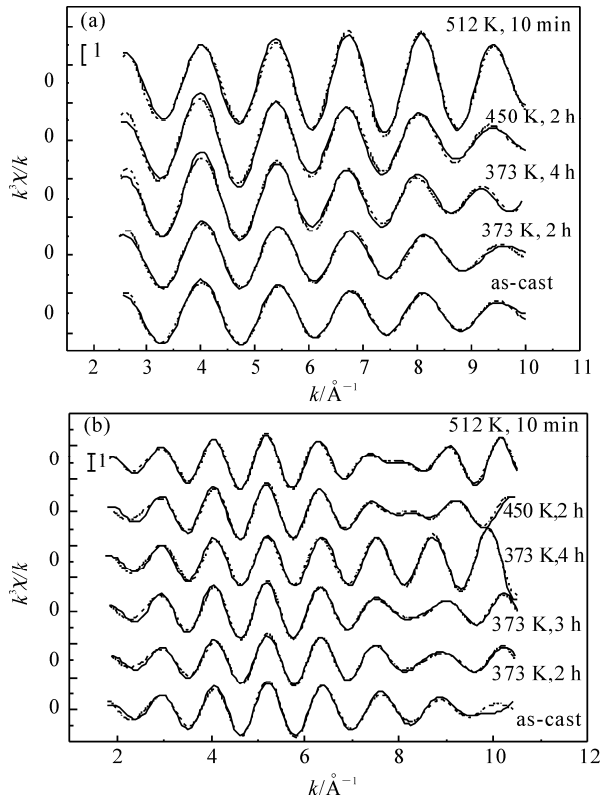

Fig.2 Comparison between EXAFS experimental data (solid)and curve-fitting result (dash) for the amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy before and after annealing(a) Cu-K edge; (b) Gd-L_{III} edge

Table 1 shows that the coordination number of Cu atom around Cu (N_{Cu-Cu}) increases obviously with annealing temperature and time while N_{Cu-Mg} has no inerratic change, indicating that the increase of amplitude intensity for the first peak in Fig.1(a) is owe to Cu-Cu pairs. The nearest interatomic distances between Cu-Cu and Cu-Mg under heat treatment are similar with the as-cast one, so there is a chemical not topological short range order change during annealing. From the foregoing analysis, it is suggested that the enhancement of short range order around Cu atoms damages the strength of $Mg_{65}Cu_{25}Gd_{10}$, meanwhile, the fitting results indicate further that the decrease of strength during annealing results from the partial aggregation of Cu-Cu pairs. It can be seen from Table 2 that Cu atoms around Gd lose rapidly during annealing and form the partial aggregation of Cu atoms, indicating Gd-Cu bonds are weaker and break easily under heat conditions. It is interesting the N_{Gd-Mg} of $Mg_{65}Cu_{25}Gd_{10}$ after annealing for 2 h at 373 K decreases from 8.6(as-cast) to 5.7 and has a recovery with annealing time(3 or 4 h) at 373 K(*e g,* 8.0 and 11.3, respectively), though it decreases again after annealing at higher temperature. It is remarkable that the change of N_{Gd-Mg} has a homologous trend with the one of compression strength and the strength of $Mg_{65}Cu_{25}Gd_{10}$ annealed at 373 K seems to been submitted to the change of N_{Gd-Mg}. The larger N_{Gd-Mg} is, the more favorable it is to the compression strength. The total coordination number around Gd for as-cast and annealed $Mg_{65}Cu_{25}Gd_{10}$ at 373 K for 4 h is about 12 which may be corresponding with some polyhedral structure in favor of mechanical properties of the alloy. The nearest interatomic distance for Gd has no apparent change under annealing, indicating the topological short range order has little change.

Table 1 Structural parameters in the neighbourhood of Cu atoms for the amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy before and after annealing

	Cu-Cu			Cu-Mg		
	N	*R*	σ^2	*N*	*R*	σ^2
As-cast	2.3	2.47	0.009	2.5	2.50	0.005
Annealing for 2 h at 373 K	2.9	2.47	0.013	3.0	2.51	0.009
Annealing for 4 h at 373 K	3.4	2.49	0.009	2.7	2.51	0.004
Annealing for 2 h at 450 K	3.4	2.49	0.01	3.2	2.52	0.003
Annealing for 10 min at 520 K	3.9	2.46	0.008	2.5	2.48	0.001

Table 2 Structural parameters in the neighbourhood of Gd atoms for the amorphous $Mg_{65}Cu_{25}Gd_{10}$ alloy before and after annealing

	Gd-Cu			Gd-Mg		
	N	*R*	σ^2	*N*	*R*	σ^2
As-cast	3.2	2.94	0.016	8.6	3.35	0.025
Annealing for 2 h at 373 K	0.5	2.91	0.017	5.7	3.34	0.013
Annealing for 3 h at 373 K	0.6	2.90	0.002	8.0	3.35	0.016
Annealing for 4 h at 373 K	0.7	2.98	0.001	11.3	3.35	0.029
Annealing for 2 h at 450 K	0.5	2.87	0.003	7.2	3.35	0.013
Annealing for 10 min at 520 K	0.5	2.91	0.001	7.2	3.39	0.013

4 Conclusions

a) The enhancement of short range order around Cu and the abatement around Gd during annealing damage the mechanical properties of $Mg_{65}Cu_{25}Gd_{10}$;

b) The amount of Cu around Gd in $Mg_{65}Cu_{25}Gd_{10}$ obviously decreases during annealing and the lost Cu atoms form partial aggregation of Cu.

c) The enhancement of short range order around Gd has more effect on mechanical properties of

$Mg_{65}Cu_{25}Gd_{10}$ than the change of local atomic structure for Cu and benefits the improvement of mechanical properties for $Mg_{65}Cu_{25}Gd_{10}$. The improvement of mechanical properties for annealing $Mg_{65}Cu_{25}Gd_{10}$ (*e g*, 4 h at 373 K) is essentially attributed to polyhedral short range order structure unit with nearly 12 coordination number around Gd atoms.

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