Formation Range and Thermal Stability of Cu-rich Cu-Mg-Ln (Ln=La, Sm, Eu, Tb, Er or Lu) Amorphous Alloys Tinged with Gold Color

Akihisa Inoue*, Yoshiyuki Shinohara†† and Yoshio Harakawa**

*Institute for Materials Research, Tohoku University, Sendai 980-77, Japan
**Teikoku Pistonring Co. Ltd., Okaya 394, Japan

Cu-rich amorphous alloys with Cu concentrations above 80 at% were formed in melt-spun Cu-Mg-Ln (Ln=La, Sm, Tb, Er or Lu) alloys. The amorphous alloys containing more than 84 at%Cu exhibit a gold-like color with high glossiness of about 45%. The glossiness decreases to about 78% by the precipitation of a crystalline phase in the amorphous phase. The Cu-rich amorphous alloys are formed in wider composition ranges for the alloys containing the Ln (Ln=Ca, Pr, Nd, Sm, Gd, Tb, Dy or Ho) elements with intermediate atomic radii of 0.175 to 0.183 nm. The formation of the Cu-rich amorphous alloys is attributed to the simultaneous dissolution of the three elements with significantly different atomic size ratios and large negative heats of mixing. The crystallization temperature (Tc) is in the range of 490 to 620 K and there is a tendency for Tc to decrease with increasing atomic number, i.e., with decreasing atomic radius of the Ln elements. The finding of the Cu-rich amorphous alloys with the gold-like color and high glossiness is important for future development of Cu-rich amorphous alloys as an engineering material.

(Received January 22, 1996)

Keywords: copper-rich amorphous alloy, gold-like color, high glossiness, copper-magnesium-lanthanide system, rapid solidification, thermal stability

I. Introduction

It is known[1] that Cu is an effective solute element for the formation of an amorphous phase in metal-metal type alloys and a number of alloys containing a large amount of Cu as a solute element are amorphized by a melt spinning technique. However, the alloy systems in which an amorphous phase in Cu-based composition range more than 50 at%Cu is formed by melt spinning have been limited to Cu-Ti[2], Cu-Zr[2], Cu-Ag-P[3], Cu-Ni-P[4] and Cu-Ag-Ln (Ln=lanthanide metal)[5] systems. Little has been reported about Cu-rich amorphous alloys containing more than 80 at%Cu by melt spinning. More recently, it was found that Cu-rich amorphous alloys are formed in Cu-Mg-Ce system[6] and exhibit a peculiar color typical for Cu-rich alloys[7]. This is believed to be the first evidence for the synthesis of an amorphous alloy with a peculiar color tone which is different from ordinary metallic color for conventional amorphous alloys. The search of amorphous alloys with peculiar color tone and high glossiness is important for future development of amorphous alloys as engineering materials as well as for basic science. The appearance of the peculiar color tone has been presumed[7] to be attributed to the formation of Cu-rich amorphous alloys containing more than about 85 at% Cu. Subsequently, we have examined the possibility of forming an amorphous phase in rapidly solidified Cu-Mg-Ln (Ln=lanthanide element) alloys with Cu content above 85 at%Cu. In this paper, we present the glass-forming ranges of the Cu-Mg-Ln alloys containing more than 80 at%Cu by melt spinning and examine the thermal stability and color tone of the amorphous alloys.

II. Experimental Procedure

Ternary Cu-Mg-Ln (Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu) alloys containing 2 to 16 at%Mg and 2 to 10 at%Ln were used in the present study. Ingots were prepared by induction melting a mixture of pure Cu, Mg and Ln metals in a purified argon atmosphere. The compositions are nominally expressed in units of atomic percentage. From the master alloy ingots, ribbons with a cross-section of about 0.02×1.0 mm² were prepared by a single roller melt spinning technique in an argon atmosphere. The amorphous nature of the melt-spun ribbons was examined by X-ray diffractometry and optical and transmission electron microscopy (OM and TEM). The exothermic reaction due to crystallization during continuous heating was examined by differential scanning calorimetry (DSC). The crystallized structure was also examined by X-ray diffractometry and TEM. The TEM samples were prepared by thinning electrolytically the melt-spun ribbons at about 230 K in a solution of 5% phosphoric acid and 95% methanol in volume ratio. The reflectance as a function of wave length was measured by a spectro color meter, in comparison with those of pure Cu and Au metals. The glossiness was also measured by a gloss meter (Nippon Denshoku Kogyo Co., Ltd., PG-3D type) and evaluated as the relative ratio to that for the oxide glass with a refraction ratio

†† On leave from Teikoku Pistonring Co. Ltd., Okaya 394, Japan.
of 1.567°. The incident angle of light was fixed to be 60 degrees.

III. Results

Figure 1 shows the X-ray diffraction patterns of the rapidly solidified Cu₄₈Mg₈Ln₈ (Ln = La, Sm, Eu, Tb, Er or Lu) alloys. The X-ray diffraction patterns consist of broad peaks for the Cu₄₈Mg₈Sm₈ and Cu₄₈Mg₈Tb₈ alloys, broad peak and crystalline peaks for the Cu₄₈Mg₈La₈ and Cu₄₈Mg₈Er₈ alloys and crystalline peaks for the Cu₄₈Mg₈Eu₈ and Cu₄₈Mg₈Lu₈ alloys. Thus, an amorphous single phase is formed in the Sm- and Tb-containing alloys. The crystalline phase is identified to be Cu₂Eu, Cu₂La, Cu₂Er or Cu + Cu₂Lu phases. The decrease in Ln content from 8 to 6 at% causes the remarkable extension of the amorphous alloy systems, as shown in Fig. 2. The diffraction pattern consists of broad peaks for the Cu₄₈Mg₈Ln₈ (Ln = La, Sm, Tb, Er or Lu) alloys and coexistent broad and Cu₃Eu peaks only for the Cu₄₈Mg₈Eu₈ alloy. The formation of the amorphous phase is also recognized for the Cu₄₈Mg₈Ln₈ (Ln = La, Sm, Eu, Tb, Er or Lu) alloys and no appreciable change in the glass formation tendency by the decrease in the Ln content from 6 to 4 at% is recognized, as shown in Fig. 3. However, the further decrease in the Ln content from 4 to 2 at% caused the drastic change to crystalline phases for all the ternary Cu₄₈Mg₈Ln₅ alloys. Consequently, it is said that no amorphous phase in Cu-rich compositions above 90 at%Cu is formed in the Cu-Mg-Ln systems and the optimum Ln content for the glass formation is
about 5 at%. In order to confirm the absence of any crystallinity in the amorphous phase, the bright-field electron micrographs and selected-area electron diffraction patterns of the Cu$_{88}$Mg$_8$La$_6$, Cu$_{88}$Mg$_8$Tb$_6$ and Cu$_{88}$Mg$_8$Er$_6$ alloys are shown in Fig. 4. These bright-field images show only a featureless contrast and the diffraction patterns consist only of halo rings. These alloys are composed only of an amorphous phase. Figure 5 summarizes the composition ranges in which an amorphous phase is formed in the rapidly solidified Cu–Mg–Ln (Ln=La, Sm, Tb or Er) alloys. The amorphous phase is formed in the composition ranges of 8 to 10 at% Mg and 4 to 6 at% La for the Cu–Mg–La system, 8 to 12 at%Mg and 4 to 8 at%Sm for the Cu–Mg–Sm system, 8 to 10 at%Mg and 4 to 6 at%Sm for the Cu–Mg–Sm system, 8 to 10 at% Mg and 4 to 6 at% Er for the Cu–Mg–Er system. Figure 6 shows the relation between the glass formation of the Cu$_{88}$Mg$_8$Ln$_6$, Cu$_{88}$Mg$_8$Ln$_6$ and Cu$_{88}$Mg$_8$Ln$_6$ alloys and the atomic radii of the Ln elements. The amorphous phase of the Cu$_{88}$Mg$_8$Ln$_6$ and Cu$_{88}$Mg$_8$Ln$_6$ alloys is obtained in the wide atomic radius range of 0.173 to 0.194 nm, but the formation is limited to the narrow atomic radius range of 0.175 to 0.183 nm for the 8%Ln-containing alloys. This change indicates that the atomic radii of 0.175 to 0.183 nm are optimum atomic sizes for the formation of the Cu–Mg–Ln amorphous alloys. Figure 6 also shows that no amorphous phase is formed over the entire composition range in the Cu–Mg–Eu system and the reason for the low glass-forming ability is presumably because the atomic size is too large to construct an amorphous phase.

Figure 7 shows the DSC curves of the Cu$_{88}$Mg$_8$Ln$_6$ (Ln=Nd, Sm, Tb or Er) amorphous alloys. Only one exothermic peak is seen on the DSC curve, indicating that these amorphous alloys crystallize through a single stage. As exemplified for the Cu$_{88}$Mg$_8$Nd$_6$ alloy in Fig. 8, the crystallized structure consists of Cu, Cu$_2$Nd and unknown phases. The crystallization takes place through the simultaneous precipitation of these phases. Figure 7 also shows that the onset temperature of crystallization...
(Tₙ) tends to decrease gradually with increasing atomic number of the Ln elements. Figure 9 also shows the relation between Tᵣ of the Cu₆₈M₆₈₈Ln₆ amorphous alloys and the atomic radii of the Ln elements. There is a tendency for Tᵣ to decrease with decreasing atomic radius. This tendency is in agreement with that for the Mg₆₈Ln₃₀Cu₂₀ amorphous alloys. This tendency suggests that Tᵣ decreases with filling of the 4f electrons through the decrease in the bonding nature of the Cu–Ln and Mg–Ln atomic pairs.

Figure 10 shows the color on the freely solidified surface of the Cu–Mg–Ln amorphous alloy ribbons. It is seen that these ribbons exhibit gold-like color, in spite of the Cu-rich alloy compositions. In order to investigate the reason for the appearance of the gold color, we examined the relation between the reflectance and wave length for the Cu-based amorphous alloys. Figure 11 shows the change in the reflectance for the amorphous Cu₆₈M₆₈₈Ln₆ (Ln=La, Tb or Er) alloy ribbons, together with the data of pure Cu and Au metals. The reflectance of the amorphous alloys increases gradually in the wave length range of 400 to 500 nm, distinctly in the vicinity of 540 nm and then gradually in the range above 600 nm. When the feature of the change is compared with those for pure Cu and Au metals, one can notice that the feature of the amorphous alloys is analogous to that for Au and completely different from that for Cu. The similarity of the feature seems to be the origin for the appearance of the gold-like color for the Cu-based amorphous alloys. However, the reason why the Cu-based amorphous alloys exhibit the similar relation as that for Au remains unclear in the present study.

Table 1 summarizes the as-quenched structure and glossiness for the Cu–Mg–Ln (Ln=La, Tb, Er or Lu) amorphous alloys. The glossiness is as high as 448 to 455% for the amorphous alloys and no distinct change in the glossiness with Ln elements is seen. However, the glossiness decreases significantly to 78% for the coexis-
The high glossiness of 448% has featureless and smooth surface, while the coexistent amorphous and crystalline phase ribbon with the low glossiness of 78% has a distinct ruggedness resulting from the dispersion of the crystalline phases with a size of about 10 μm. Considering that the rugged regions correspond to the crystalline precipitates, the decrease in the glossiness is concluded to result from the precipitation of the crystalline phase. It is therefore concluded that the appearance of the gold-like color with the high glossiness of about 450% for the Cu-Mg-Ln amorphous alloy ribbons is due to the formation of the amorphous phase containing the three elements.

IV. Discussion

We discuss the reason for the formation of an amorphous phase in the Cu-rich Cu–Mg–Ln ternary alloys by rapid solidification. No amorphous phase is formed in Cu-rich Cu–Mg and Cu–Ln binary alloys containing more than 70 at%Cu. Consequently, it is essential for the formation of the Cu-rich amorphous phase to dissolve simultaneously the three elements. It has previously been reported\(^{9-12}\) that the mixing of the three elements with significantly different atomic size ratios and large negative heats of mixing causes the formation of an amorphous phase with large glass-forming ability and a wide supercooled liquid region before crystallization. Based on the structural analyses of the Ln–Al–TM\(^{13}\), Mg–Ln–TM\(^{14}\) and Zr–Al–TM\(^{15}\) amorphous alloys consisting of the aboved described three elements, the effectiveness of the simultaneous dissolution of the three elements has been interpreted\(^{9-12,16}\) to result from the formation of a highly dense random packed structure in which the liquid/solid interface energy is large and the atomic rearrangement on a long range scale is difficult. Considering that the atomic radius is 0.128 nm for Cu, 0.160 nm for Mg and 0.173 to 0.188 nm for Ln\(^{17}\) and the heat of mixing is calculated to be \(-23\) kJ/mol for Cu\(_2\)Mg phase, \(-18\) kJ/mol for Cu\(_3\)La phase and \(-13\) kJ/mol for
Mg$_2$La$_3$ phase, the combination of the three elements is concluded to satisfy with the above-described criteria for the achievement of easy glass formation. The importance of the atomic size is also supported from the experimental result (shown in Fig. 6) that the composition range of the amorphous phase is wider for the Cu–Mg–Ln alloys containing the Ln (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy or Ho) elements with intermediate atomic radii of 0.175 to 0.183 nm.

It has previously been reported$^{9-13}$ that the multicomponent amorphous alloys consisting of the three elements, which satisfy the above-described criteria, usually exhibit the glass transition, followed by the appearance of a wide supercooled liquid region before crystallization. In fact, the glass transition and its subsequent wide supercooled liquid region have been observed around Mg$_{50}$Cu$_{20}$Ln$_{30}$ in Mg–Cu–Ln amorphous alloys. However, no glass transition phenomenon is observed in the present Cu-rich Cu–Mg–Ln alloys, in spite of the same constituent elements. The absence of the glass transition is presumably due to the existence of Cu–Cu atomic pairs with weak bonding nature resulting from the high Cu concentrations of the present Cu–Mg–Ln amorphous alloys. The weak bonding nature in the Cu-rich phase is also understood from the result$^{10}$ that the fcc-Cu phase can dissolve Mg up to about 7 at% and a binary Cu-rich Cu–Mg compound is formed at the high Mg concentration of 33.3 at%. That is, the existence of a large number of Cu–Cu atomic pairs in the Cu-rich Cu–Mg–Ln amorphous alloys causes the easy precipitation of fcc-Cu (Mg) phase from the amorphous phase in the low temperature range before the glass transition to the supercooled liquid region, leading to the disappearance of the glass transition and supercooled liquid region before crystallization.

Furthermore, it is seen in Figs. 7 and 9 that the crystallization temperature increases almost linearly with increasing atomic radius, i.e., with decreasing atomic number. Figure 8 also indicates that the crystallized structure of the amorphous Cu$_{50}$Mg$_{30}$Nd$_{20}$ alloy consists of Cu, Cu$_3$Nd and unknown phases and hence the atomic rearrangement of the Ln elements is required for the progress of crystallization. The atomic rearrangement is thought to be more difficult for the Ln elements with larger atomic sizes, leading to the increase in crystallization temperature. Besides, the increase in atomic number implies the increase in the number of the 4f electrons, indicating that the filling of the 4f electrons causes the decrease in crystallization temperature through the reduction of the bonding nature of Cu–Ln and Mg–Ln pairs. We do not have any information about a more important factor in the two factors of atomic size and bonding nature. However, the simultaneous satisfaction of the two factors seems to play a dominant role in the achievement of high thermal stability of the amorphous alloys.

V. Summary

The formation of Cu-rich amorphous alloys containing more than 80 at%Cu by melt spinning was searched in Cu–Mg–Ln (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu) systems. The results obtained are summarized as follows:
(1) An amorphous phase is formed in the rapidly solidified Cu$_{60}$Mg$_{30}$Ln$_{4}$ (Ln = La, Sm or Tb), Cu$_{60}$Mg$_{30}$Ln$_{6}$ (Ln = La, Sm, Tb, Er or Lu) and Cu$_{60}$Mg$_{30}$Ln$_{8}$ (Ln = Sm and Tb) alloys. The optimum Ln content for the glass formation of the 8 at% Mg-containing alloys is about 5 at% Ln.

(2) The glass formation range tends to be extended for the Cu–Mg–Ln alloys containing the Ln elements with intermediate atomic radii of 0.175 to 0.183 nm. The formation of the Cu-rich Cu–Mg–Ln amorphous alloys is presumably due to the simultaneous dissolution of the three elements with significantly different atomic size ratios and large negative heats of mixing.

(3) The onset temperature of crystallization is in the range of 490 to 602 K and there is a tendency for $T_c$ to decrease with increasing atomic number, i.e., with decreasing atomic radius. The crystallization of the Cu$_{60}$Mg$_{30}$Ln$_{6}$ alloys takes place through a single stage resulting from the simultaneous precipitation of more than three kinds of phases.

(4) The Cu-rich amorphous alloy ribbons exhibit a gold-like color combined with high glossiness values of about 450%. The relation between the reflectance and wave length is analogous to that for pure gold metal and hence the similarity in the relation seems to be the origin for the appearance of the gold-like color for the Cu-rich Cu–Mg–Ln amorphous alloy ribbons.

The appearance of the gold-like color with the high glossiness for the Cu–Mg–Ln amorphous alloys is promising for future development as a new type of engineering amorphous alloys.

REFERENCES


(2) R. Ray, B. C. Giessen and N. J. Grant: *Scripta Met.*, 7 (1968), 357.


