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Cu-Rich Colored Amorphous Alloys in Cu-Mg-Ce System

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Cu-based amorphous alloys containing above 80 at%Cu are found to form in the Cu-Mg-Ce ternary system by rapid solidification. The composition range extends from 8 to 14 at%Mg and 4 to 8%Ce. No amorphous phase is formed in the Cu-rich Cu-Mg and Cu-Ce binary systems and hence the simultaneous dissolution of the three elements with significantly different atomic size ratios is essential for the glass formation. The increase of the glass-forming ability in the ternary system has been interpreted to be due to the difficulty of nucleation and growth reactions of crystalline phases through the formation of a higher degree of dense random packed structure. The crystallization for the Cu-Mg-Ce amorphous alloys takes place through two stages of $\text{Am} \rightarrow \text{Am}' + \text{Cu} + \text{Cu}_6\text{Ce} \rightarrow \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ in the range above about 84 at% Cu and $\text{Am} \rightarrow \text{Am}' + \text{Mg}_2\text{Ce} \rightarrow \text{Mg}_2\text{Ce} + \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ in the range below 80 and 83 at% Cu. The Cu-based amorphous alloys exhibit a color tone typical for crystalline Cu metal and are expected to develop as an amorphous alloy with the distinguishable color.

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I. Introduction

It has recently been reported⁽¹⁾⁻⁽³⁾ that the appropriate multiplication of alloy components with larger, intermediate and smaller atomic sizes causes the formation of new amorphous alloys by rapid solidification as well as the significant increase in glass-forming ability accompanying a remarkable extension of the supercooled liquid region defined by the temperature difference between glass transition temperature (T_g) and the crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$. As examples of the notable results on new amorphous alloys, one can list the formation of an amorphous phase in the Cu-Ag-Ln⁽⁴⁾⁽⁵⁾ and Al-Mg-Ln⁽⁶⁾ (Ln=lanthanide metal) ternary systems. On the other hand, the large glass-forming ability and the large ΔT_x value have been obtained in a number of alloy systems such as Ln-Al-TM⁽⁷⁾⁽⁸⁾, Mg-Ln-TM⁽⁹⁾⁽¹⁰⁾, Zr-Al-TM⁽¹¹⁾⁽¹²⁾, Hf-Al-TM⁽¹²⁾ and Ti-Zr-TM⁽¹³⁾ (TM=transition metal) and the largest values of the sample thickness for glass formation and ΔT_x are about 20 mm⁽¹⁴⁾⁽¹⁵⁾ and 130 K⁽¹⁶⁾, respectively. It is known that the Cu-based ternary amorphous alloys containing more than 50 at%Cu are formed in the Cu-Ag-P⁽¹⁷⁾, Cu-Ni-P⁽¹⁸⁾ and Cu-Ag-Ln⁽⁴⁾⁽⁵⁾ systems by rapid solidification. However, the Cu concentrations in these amorphous alloys lie in the range of 50 to 75 at% and the resulting amorphous alloys have a silver-like metallic luster because of the rather low Cu contents. No Cu-based amor-

phous alloys with a color tone typical of the crystalline Cu metal have been prepared up to date. More recently Cu-based amorphous alloys have attracted increasing interest because of the possibility to various kinds of coating materials as colored and antifouling pigments⁽¹⁸⁾. Furthermore, if we can produce Cu-rich amorphous alloys exhibiting a Cu-like color tone, the colored amorphous powders are also expected to develop as a new type of coating material. However, little is known about the formation, properties and surface color of Cu-rich amorphous alloys containing more than 80 at%Cu. Based on the effectiveness of the alloying of the elements with significantly different atomic sizes for the formation of an amorphous phase, we have searched a new amorphous alloy in the Cu-rich alloy system in which the atomic size rule is satisfied. As a result, we have succeeded in finding Cu-rich amorphous alloys containing Cu element as much as 80 to 88 at% in the Cu-Mg-Ce system by using the rapid solidification technique. This paper is intended to present the composition range in which an amorphous phase is formed in the rapidly solidified Cu-Mg-Ce alloys and the thermal stability and surface color of the Cu-Mg-Ce amorphous alloys containing more than 80 at%Cu.

II. Experimental Procedure

Ternary Cu-Mg-Ce alloys containing 4 to 14 at%Mg and 2 to 12%Ce were used in the present study. Ingots were prepared by induction melting a mixture of pure Cu, Mg and Ce metals in a purified argon atmosphere.

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The compositions are nominally expressed in units of atomic percent. From the master alloy ingots, ribbons with a cross section of about $0.02 \times 1.5 \text{ mm}^2$ 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 transmission electron microscopy (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.

III. Results and Discussion

Figure 1 shows the composition range in which an amorphous phase in Cu-Mg-Ce alloys containing above 78 at%Cu is formed by melt spinning. It is seen that an amorphous phase is formed in a composition range of 8 to 14 at%Mg and 4 to 8 at%Ce. It is to be noticed that an amorphous phase is formed in the Cu-rich alloys containing above 82 at% Cu. It has previously been reported that Cu-based amorphous alloys more than 50%Cu are formed in the Cu-Ti⁽¹⁹⁾, Cu-Zr⁽¹⁹⁾ and Cu-Hf⁽²⁰⁾ binary and Cu-Ag-P⁽¹⁷⁾, Cu-Ni-P⁽¹⁸⁾ and Cu-Ag-Ln⁽⁴⁾ (Ln=lanthanide metal) ternary systems. However, the highest Cu concentration in these alloy systems is about 75 at% for the Cu-Ni-P and Cu-Ag-Ln systems. Consequently, the present alloys are believed to be the first evidence on the formation of Cu-rich amorphous alloys containing above 80 at%Cu. Furthermore, it is seen that no amorphous single phase is formed in the rapidly solidified Cu-rich Cu-Mg and Cu-Ce binary alloys and the simultaneous dissolution of Cu, Mg and Ce elements is essential for the formation of the amorphous phase. In order to

Fig. 1 Composition range in which an amorphous single phase is formed in rapidly solidified Cu-Mg-Ce alloys and the onset temperature of crystallization (T_x) of the amorphous alloys.

Fig. 2 X-ray diffraction patterns of rapidly solidified $\text{Cu}_{92-x}\text{Mg}_x\text{Ce}_8$ ($x=6, 8$ and 10 at%) alloys. The arrows represent the peak positions of the (104), (311) and (213) diffraction peaks with high intensity for the Cu_6Ce phase.

Fig. 3 Bright-field electron micrograph (a) and selected-area electron diffraction pattern (b) of a rapidly solidified $\text{Cu}_{84}\text{Mg}_8\text{Ce}_8$ alloy.

confirm the formation of the amorphous phase, the X-ray diffraction patterns of the rapidly solidified $\text{Cu}_{92-x}\text{Mg}_x\text{Ce}_8$ ($x=6, 8$ and 10) alloys are shown in Fig. 2. The patterns consist only of a broad peak typical for an amorphous phase for the 8%Mg and 10%Mg alloys, while it for the 6%Mg alloy includes an additional weak peak in the 2θ range of 35 to 40 degrees, in addition to the broad amorphous peak. The diffraction angle of the additional broad peak agrees with those for the high intensity peaks (104), (311) and (213) of the orthorhombic Cu_6Ce phase as marked with arrows, indicating that the as-quenched phase of the $\text{Cu}_{86}\text{Mg}_6\text{Ce}_8$ alloy consists of an amorphous phase containing a small amount of Cu_6Ce phase. Furthermore, as shown for the $\text{Cu}_{84}\text{Mg}_8\text{Ce}_8$ alloy in Fig. 3, no any contrast revealing the precipitation of a crystalline phase is seen in the bright-field electron micrograph and the electron diffraction pattern also consists of a halo ring. These results obtained by X-ray diffractometry and TEM indicate clearly that the Cu-Mg-Ce ternary alloys containing 8 and 10%Mg are composed of an amorphous phase.

Fig. 4 Differential scanning calorimetric curves of amorphous $\text{Cu}_{92-x}\text{Mg}_x\text{Ce}_8$ ($x=6, 8$ and 10 at%) alloys.

Here, it is important to discuss the reason why the simultaneous dissolution of the three elements causes the formation of the amorphous phase even in the Cu-rich composition range. We have recently succeeded⁽¹⁾⁻⁽³⁾ in finding a number of new amorphous alloys in ternary alloy systems consisting of the three elements with significantly different atomic sizes which are classified into larger, intermediate and smaller groups. As similar to the ternary amorphous alloys which are exemplified for Al-TM-Ln, Zr-Al-TM and Mg-Ln-TM systems, the present Cu-Mg-Ce system is also composed of larger (Ce), intermediate (Mg) and smaller (Cu) elements. As described in the previous papers, the effectiveness of the simultaneous dissolution of the three kinds of elements on the increase in the glass-forming ability is thought as follows; the amorphous alloy consisting of their elements has a higher degree of dense random packed structure which causes the difficulty of the nucleation of a crystalline phase through the increase in the liquid/solid interfacial energy as well as the suppression of the growth reaction which requires atomic rearrangements. The first formation of the Cu-rich amorphous alloy in the Cu-Mg-Ce system which satisfies with the above-described atomic size rule also supports the effectiveness of the concept on the atomic size rule for the glass formation in multicomponent alloy systems. Appropriate alloy designs on the basis of this concept are expected to give rise to the finding of new amorphous alloys in other alloy systems.

Figure 4 shows the DSC curves of the amorphous $\text{Cu}_{92-x}\text{Mg}_x\text{Ce}_8$ ($x=6, 8$ and 10 at%) alloys. The three alloys show two exothermic peaks, indicating that the

Fig. 5 Surface appearance and color tone on the freely solidified side of amorphous $\text{Cu}_{86}\text{Mg}_6\text{Ce}_8$ (a), $\text{Cu}_{84}\text{Mg}_8\text{Ce}_8$ (b) and $\text{Cu}_{82}\text{Mg}_{10}\text{Ce}_8$ (c) ribbons produced by single roller melt spinning.

crystallization takes place through two stages. However, no appreciable endothermic reaction corresponding to the glass transition is seen in the temperature range before crystallization. From X-ray diffraction analyses and TEM observations, the exothermic peaks marked with A, B and C in Fig. 4 are due to the precipitation of $\text{Cu} + \text{Cu}_6\text{Ce}$, Cu_2Mg and Mg_2Ce , respectively. It is therefore concluded that the crystallization process consists of two stages of $\text{Am} \rightarrow \text{Am}' + \text{Cu} + \text{Cu}_6\text{Ce} \rightarrow \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ for the $\text{Cu}_{92-x}\text{Mg}_x\text{Ce}_8$ alloys containing 6 and 8% Mg and $\text{Am} \rightarrow \text{Am}' + \text{Mg}_2\text{Ce} \rightarrow \text{Mg}_2\text{Ce} + \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ for the $\text{Cu}_{82}\text{Mg}_{10}\text{Ce}_8$ alloy. Thus, each exothermic peak corresponds to the precipitation of their intermetallic compounds and the three constituent elements in the amorphous phase seem to have an attractive bonding state with each other.

Finally, it is important to point out that the Cu-based amorphous alloys have a color tone typical for conventional Cu-based crystalline alloys even in the as-quenched state, as shown in Fig. 5. All the amorphous alloys reported up to date exhibit silver-like metallic luster and no amorphous alloys exhibiting a distinguishable color typical of a crystalline metal itself have been found. Consequently, the present amorphous alloy is also believed to be the first example of the formation of the amorphous alloy exhibiting a color tone typical of crystalline Cu metal. The appearance of the color is presumed to come from the high Cu content above 80 at%. The success of forming a colored amorphous alloy is important for the future development of amorphous alloys in practical applications.

IV. Summary

The formation of new Cu-based amorphous alloys con-

taining more than 80 at%Cu by rapid solidification was examined in the Cu-Mg-Ce system where their constituent elements have significantly different atomic sizes and large negative heats of mixing. As a result, an amorphous phase was found to form in a composition range of 8 to 14%Mg and 4 to 8%Ce. Furthermore, the amorphous alloys have a color tone typical of the crystalline Cu metal. The crystallization takes place through two stages and the crystallization process changes from $\text{Am} \rightarrow \text{Am}' + \text{Cu} + \text{Cu}_6\text{Ce} \rightarrow \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ to $\text{Am} \rightarrow \text{Am}' + \text{Mg}_2\text{Ce} \rightarrow \text{Mg}_2\text{Ce} + \text{Cu} + \text{Cu}_6\text{Ce} + \text{Cu}_2\text{Mg}$ with increasing Mg content. The success of forming the colored Cu-rich amorphous alloys is expected to open up a new application field in amorphous alloys.

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