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New Amorphous Alloys in Al-Ca and Al-Ca-M (M=Mg or Zn) Systems

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Binary Al-Ca alloys were amorphized in the composition range of 9 to 11 at% Ca by melt spinning. The onset temperature of crystallization (T_x), Vickers hardness (H_v), Young's modulus and tensile fracture strength are in the range of 408 to 425 K, 130 to 153, 29 to 31 GPa and 390 to 480 MPa, respectively. The T_x and H_v values tend to increase with increasing Ca content. The crystallization takes place through two stages of $\text{Am} \rightarrow \text{Am} + \text{Al} \rightarrow \text{Al} + \text{Al}_4\text{Ca}$. The addition of Mg, Zn or TM (TM=Fe, Co, Ni, Cu) was also found to be effective for the extension of the glass formation range to the lower and higher Ca concentration sides. The formation of the amorphous phase in the Al-Ca binary alloys consisting of light weight metals is important to the development of Al-based alloys with high specific strength.

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I. Introduction

Since the discovery of Al-based amorphous alloys with good bending ductility in Al-Ni-Si system in 1987⁽¹⁾, a number of Al-based amorphous alloys exhibiting high tensile strength and good ductility have been found to form in Al-Ln⁽²⁾⁽³⁾, Al-Ln-TM⁽⁴⁾⁽⁵⁾ (Ln=lanthanide metal, TM=transition metal), Al-ETM-LTM⁽⁶⁾ (ETM=early transition metal, LTM=late transition metal) and Al-LTM-LTM⁽⁷⁾ systems by a melt spinning technique. Finely mixed crystalline alloys, which were produced by extrusion of the amorphous alloys at temperatures just above the crystallization temperature, have been used⁽⁸⁾ as some machinery parts owing to the advantages⁽⁹⁾⁽¹⁰⁾ of high tensile strength with light weight, high elevated temperature strength, high fatigue strength, high corrosion resistance, high wear resistance and high-strain rate superplasticity etc. Most of the Al-based amorphous alloys found hitherto consist of more than three kinds of constituent elements and the alloys in which an amorphous single phase is obtained in the binary system are limited to the Al-Ln system⁽¹¹⁾. The search of a new binary amorphous alloy is very important to the development of Al-based amorphous alloys. More recently, we have succeeded in finding new amorphous alloys in the Al-Ca binary and Al-Ca-M (M=Mg or Zn) ternary systems. The aim of this paper is to present the composition range in which an amorphous single phase is obtained in the Al-Ca binary system and the thermal stability and mechanical

properties of Al-Ca and Al-Ca-M amorphous alloys and to investigate the reason for the formation of an amorphous phase in the Al-Ca binary system.

II. Experimental Procedure

Binary Al-Ca and ternary Al-Ca-M (M=Mg, Zn, Fe, Co, Ni or Cu) alloys were used. Their ingots were prepared by arc melting a mixture of pure metals in an argon atmosphere. From the master alloy ingots, ribbons with a cross section of about 0.02×1 mm were prepared by melt spinning in an argon atmosphere. The amorphicity of the melt-spun ribbons was examined by X-ray diffractometry and TEM techniques. The thermal stability was measured by DSC at a scanning rate of 0.67 K/s. The hardness and tensile strength of the ribbon specimens were measured by a Vickers microhardness tester with a 0.98 N (100 gf) load and an Instron-type tensile testing machine at a strain rate of $8.33 \times 10^{-3} \text{ s}^{-1}$, respectively. Eight to ten symmetrical indentations and five tensile test data were used to determine the average microhardness value and tensile fracture strength. Tensile specimens were cut from the melt-spun ribbon into strips having a gauge dimension of 10 mm long for fracture strength.

III. Results and Discussion

Figure 1 shows the compositional dependence of as-quenched phase in rapidly solidified Al-Ca alloys, along with the equilibrium phase diagram⁽¹²⁾ in the Al-Ca binary system. The as-quenched phase changes in the order of fcc-Al, Al+amorphous, amorphous, amorphous+Al+Al₄Ca+Al₂Ca and Al+Al₄Ca+Al₂Ca with increas-

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Fig. 1 Compositional dependence of rapidly solidified phase in Al-Ca binary alloys. The data on the equilibrium phase diagram are also shown for reference.

ing Ca content. It is to be noticed that the amorphous single phase is obtained in the Ca concentration range of 9 to 11 at%. The Ca concentration range leading to the formation of the amorphous single phase is considerably higher than the eutectic concentration of 5.3 at% Ca⁽¹²⁾. The deviation of the glass formation range from the eutectic concentration to the higher solute concentration side agrees with that⁽¹¹⁾ for Al-Ln (Ln=lanthanide metal) binary amorphous alloys except the Al-Nd system.

In order to confirm the formation of the amorphous single phase in the Al-Ca binary alloys, Fig. 2 shows a bright-field electron micrograph, a selected-area electron diffraction pattern and an X-ray diffraction pattern of the rapidly solidified Al₉₀Ca₁₀ alloy. No appreciable contrast revealing the existence of a crystalline phase is seen in the bright-field electron micrograph and the electron and X-ray diffraction patterns consist only of broad diffraction peaks. These results indicate clearly that the rapidly solidified Al₉₀Ca₁₀ alloy is composed only of an amorphous phase. Figure 3 shows the DSC curves of the rapidly solidified Al_{100-x}Ca_x (x=9, 10 and 11 at%) alloys, along with the identified result on the structural change caused by each exothermic reaction. One can see two exothermic peaks with maxima at about 430 and 480 K, indicating that these amorphous alloys crystallize through two stages. As is evident from the identified results shown in Fig. 3, the first exothermic reaction at

Fig. 2 Bright-field electron micrograph (a), selected-area electron diffraction pattern (b) and X-ray diffraction pattern (c) of a rapidly solidified Al₉₀Ca₁₀ alloy.

Fig. 3 Differential scanning calorimetric curves of amorphous Al_{100-x}Ca_x (x=9, 10 and 11 at%) alloys.

the lower temperature side is due to the precipitation of Al phase from the amorphous matrix and the second exothermic reaction at the higher temperature side results from the cooperative precipitation of Al and Al₄Ca from

Fig. 4 Changes in the onset temperature of crystallization (T_x) and Vickers hardness (H_v) with Ca content for rapidly solidified Al-Ca binary alloys with the amorphous or amorphous plus crystalline phase.

the remaining amorphous phase. The crystallization process is independent of Ca concentration ranging from 9 to 11 at%. Figure 4 plots the onset temperature of crystallization (T_x) and Vickers hardness (H_v) for amorphous Al-Ca alloys as a function of Ca content. The data of the coexisting amorphous plus crystalline phases are also shown for comparison. As the Ca content increases from 9 to 11 at%, T_x and H_v increase from 408 to 425 K and 130 to 153, respectively. The increases in T_x and H_v are presumably due to the increase in the number of Al-Ca bonding with an attractive bonding nature. The significant decrease in T_x in the higher Ca concentration range of 12 to 13 at% is presumed to result from easy nucleation and growth of a crystalline phase at the interface between amorphous and crystalline phases. Here, it is also noticed that the H_v value for $\text{Al}_{92}\text{Ca}_8$ alloy with a mixed structure of amorphous and Al phases is three times as high as that for the amorphous $\text{Al}_{91}\text{Ca}_9$ alloy. We have confirmed that the Al phase precipitates homogeneously in the amorphous matrix as fine spherical particles with a size of about 10 nm. The extremely high hardness in the coexisting amorphous and nanoscale Al structure agrees with that for rapidly solidified Al-Ni-Ln ternary alloys with high Al concentrations of 88 to 90 at%⁽¹³⁾. The high hardness has been attributed⁽¹⁴⁾ to the nanoscale particle size and the absence of internal defects for the homogeneously dispersed Al particles.

The addition of Mg or Zn to the Al-Ca alloys was also found to be effective for the extension of the glass formation range. The formation of an amorphous phase in the ternary Al-Ca-Mg system consisting only of light weight metals is very attractive as a base alloy for the develop-

Table 1 Thermal stability and mechanical properties of Al-Ca, Al-Ca-Mg, Al-Ca-Zn and Al-Ca-TM (TM=Fe, Co, Ni or Cu) amorphous alloys. T_x : crystallization temperature, H_v : Vickers hardness, σ_f : tensile fracture strength, and E : Young's modulus.

Alloy (at%)	T_x (K)	H_v	σ_f (MPa)	E (GPa)
$\text{Al}_{91}\text{Ca}_9$	408	130	480	31
$\text{Al}_{90}\text{Ca}_{10}$	419	148	410	29
$\text{Al}_{89}\text{Ca}_{11}$	425	153	390	30
$\text{Al}_{85}\text{Ca}_{10}\text{Mg}_5$	424	123	480	28
$\text{Al}_{85}\text{Ca}_{10}\text{Zn}_5$	407	139	410	32
$\text{Al}_{85}\text{Ca}_{10}\text{Fe}_5$	548	137	480	46
$\text{Al}_{85}\text{Ca}_{10}\text{Co}_5$	465	245	—	—
$\text{Al}_{85}\text{Ca}_{10}\text{Ni}_5$	489	150	660	45
$\text{Al}_{85}\text{Ca}_{10}\text{Cu}_5$	385	135	340	29

ment of a high-strength material with light weight. In a series of studies on the search of a new amorphous Al-based alloy, we have also found that an amorphous phase forms in rapidly solidified Al-Ca-TM (TM=Fe, Co, Ni or Cu) ternary alloys. However, the detailed result on the glass formation of the Al-Ca-TM amorphous alloys is omitted because the data on the glass formation in the Al-Ca-TM (TM=Co or Ni) ternary alloys were presented⁽¹⁵⁾ during the present study.

Table 1 summarizes the T_x , H_v , tensile fracture strength (σ_f) and Young's modulus (E) for the Al-Ca, Al-Ca-Mg, Al-Ca-Zn and Al-Ca-M (M=Fe, Co, Ni or Cu) amorphous alloys. The new amorphous alloys in the Al-Ca and Al-Ca-M (M=Mg or Zn) systems have T_x values of 407 to 425 K, H_v of 123 to 153, σ_f of 390 to 480 MPa and E of 28 to 32 GPa. Although the T_x and H_v values increase with increasing Ca content, σ_f has an inverse tendency, i.e., the decrease in σ_f with increasing Ca content. The contrast result is presumably because of the decrease in the degree of ductility with increasing Ca content. The replacement of Mg or Zn by Fe, Co or Ni causes distinct increases in T_x , H_v , σ_f and E , though these values are much smaller than those⁽¹¹⁾ for Al-TM-Ln, Al-ETM-LTM and Al-LTM-LTM amorphous alloys. Furthermore, the T_x , H_v , σ_f and E values for the Al-Ca binary amorphous alloys are also much smaller than those⁽²⁾⁽³⁾⁽¹⁶⁾ for Al-Ln binary amorphous alloys. It is therefore presumed that the low values of T_x , H_v , σ_f and E for the Al-Ca base amorphous alloys are due to the weaker bonding nature for the Al-Ca atomic pair as compared with that for the Al-Ln atomic pair. The weaker bonding nature for the Al-Ca pair is also supported from the fact⁽¹²⁾ that the decomposition temperature of the Al-rich Al_4Ca compound is much lower than that for the $\text{Al}_{11}\text{Ln}_3$ compound.

Finally, we shall consider the reason for the formation of the amorphous phase in the Al-Ca binary alloys. The glass-formation range is located at Ca concentrations between 9 and 11 at% and the melting temperature (T_m) is in the range of about 950 to 990 K⁽¹²⁾. No appreciable glass transition is observed for the present amorphous alloys and the reduced glass transition temperature (T_g/T_m) remains unknown. Consequently, we roughly estimate the ratio of T_x to T_m instead of T_g/T_m . The T_x/T_m

value is in the range of 0.426 to 0.428. The small T_x/T_m values suggest that the glass formation is not due to the lowering of T_m through the increase in the metastability of the liquidus phase. Considering that Al and Ca elements have a large atomic size ratio and a large negative heat of mixing, the viscosity of the supercooled liquid seems to increase rapidly through the rapid decrease in diffusivity of the two constituent elements, leading to the formation of the amorphous phase. This result also suggests that the Al-Ca amorphous alloys have rather high T_g values, even though no glass transition temperature is detected because of the easy crystallization before the glass transition. The concept that T_g is considerably higher than T_x for amorphous alloys having easy progress of crystallization⁽¹⁷⁾ is generally known for amorphous metallic alloys.

In conclusion, it was found that an amorphous single phase formed in the Al-Ca binary and Al-Ca-M (M=Mg or Zn) ternary systems by melt spinning. Considering that the formation of an amorphous single phase in a binary system has previously been limited to the Al-Ln system⁽¹¹⁾, the formation of the amorphous phase in the Al-Ca binary system is very important to the development of Al-based amorphous alloys.

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