Structure and properties of rapidly solidified P/M materials of Al-Mn-Cr alloys

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Abstract

Rapidly solidified P/M materials of Al-Mn-Cr ternary alloys were prepared containing 6~8 mass% Mn and 1~3 mass% Cr. The effect of alloy composition on precipitation hardening was studied with an aim of obtaining precipitation hardened materials having acceptable ductility. The critical composition for observing precipitation hardening was determined to be 8.8 mass% Mn+Cr; above this value hardening increased with increasing the Mn+Cr content. The greatest hardening was observed for Al-7Mn-3Cr alloy. In these alloys, CrAl7 was formed under rapid solidification and precipitation of MnAl6 occurred during hot extrusion in alloys of lower Cr content. Finally, G phase ((Mn,Cr)Al12) was formed during heating of hot-extruded materials, causing hardening when the amount of G phase formation is sufficiently large. For the as-extruded P/M materials, the highest tensile strength at room temperature (480MPa) was obtained for Al-7Mn-3Cr, with 7% elongation. Elongation of the as-extruded P/M materials remained unchanged up to 473K but increased appreciably at 673K. However, precipitation hardened P/M materials showed poor ductility so that the tensile strength decreased with aging time. Increases in the elastic modulus were observed after precipitation heat treatment.

Keywords: Al-Mn-Cr alloy, rapid solidification, powder metallurgy, precipitation hardening, mechanical property

1. Introduction

The equilibrium solid solubility and the diffusivity are lower for transition metals in the aluminum matrix. The strength of aluminum-transition metal alloys at room and elevated temperatures is improved by dispersion of fine aluminate compounds formed under high cooling rate during solidification of the alloy melt, or by precipitation from the super-saturated solid solution. P/M (Powder Metallurgy) alloys of Al-Fe-Ce [1] have been developed by Alcoa, Al-Fe-Mo [2] by P&W and Al-Fe-V-Si [3,4] by Allied Signal by using the rapid solidification technique. Among aluminum alloys containing transition metals, a rapidly solidified Al-Mn-Cr alloy exhibits interesting behavior. Remarkable precipitation hardening occurs during consolidation of rapidly solidified powders of Al-Mn-Cr alloy or after heating of consolidated materials. Hardening is caused by formation of a ternary G phase compound ((Mn,Cr)Al12) [5~8]. In these alloys, precipitation hardening occurs at much higher temperatures than in conventional precipitation hardening aluminum alloys; the amount of hardening is more than 80HV. Accordingly, aluminum alloys having high mechanical strength at high temperatures can be expected [8]. Furthermore, it has been reported that the extent of precipitation hardening increases by plastic deformation prior to precipitation treatment [9], and that both strength and ductility are improved by adding Ni or Zr to Al-Mn-Cr alloys [10]. However, significant precipitation hardening was obtained in alloys containing 10mass% Mn+Cr or more, but no such effect was observed for alloys containing 7mass% Mn+Cr or less [8]. Ductility was reduced for the materials hardened by precipitation heat treatment. No data exist for the rapidly solidified Al-Mn-Cr alloys in the range 7~10mass% Mn+Cr.

In this study the composition ratio of Mn and Cr was changed in the range of 8~10mass% Mn+Cr in order to clarify the critical composition for precipitation hardening in rapidly solidified Al-Mn-Cr alloys. Our aim is to obtain precipitation hardened materials of rapidly solidified Al-Mn-Cr alloy with acceptable ductility.

2. Experimental procedures

The nominal and analyzed composition and designation of tested alloys are listed in Table 1. Alloy ingots were prepared using pure Al(99.99%), pure Mn(99.9%) and pure Cr(99.9%) under an aerial atmosphere. Rapidly solidified flakes (referred to RS flakes hereafter) were produced by argon-gas atomizing the alloy melt and subsequently splat-quenching the atomized droplets on a single copper roll. The apparatus used for rapid solidification has been reported elsewhere [11];
solidification cooling rate greater than $10^4 \text{K/s}$ was attained. Consolidation of the RS flakes was done by cold pressing, vacuum degassing and hot extrusion. Finally, extruded bars 7mm in diameter were obtained as the P/M materials. The changes in hardness of the RS flakes and P/M materials after isochronal annealing at various temperatures for 7.2ks were measured by using a micro-Vickers and Vickers testing machine. Precipitation hardening curves were obtained for RS flakes and P/M materials aged at 573, 673 and 773K without solutionizing. Tensile testing of the P/M materials was carried out at temperatures up to 673K at an initial strain rate of $1.67 \times 10^{-3} \text{s}^{-1}$. The elastic modulus was measured in tensile test at room temperature by using a clip type strain gauge. Microstructures were observed for the RS flakes and P/M materials by optical microscope and TEM. The constituent phases of the RS flakes and the P/M materials were identified by X-ray diffraction with CuKα radiation. The amount of Mn solute was estimated from the lattice parameter calculated from the diffraction angle of (311)Al.

3. Results and discussion
3.1. Microstructures and hardness of RS flakes
To confirm that precipitation hardening in Al-Mn-Cr alloys is caused by decomposition of an extended solid solution, we examined changes in hardness of ingots of tested alloys solidified at normal cooling rate after isochronal heating for 7.2ks at various temperatures. Hardness was measured in $\alpha$-Al region, thereby avoiding coarse primary crystals. No change in hardness was observed for all tested alloys. The lattice parameter of the Al matrix was almost equal to that for pure aluminum. Therefore, precipitation hardening did not occur in the ingot solidified at a low cooling rate because of no formation of a super-saturated solid solution. The hardness changes of the RS flakes after isochronal heating for 7.2ks at various temperatures are shown in Fig.1. The hardness of the RS flakes tends to increase with increasing Mn+Cr content. The highest hardness of HV127 was found in the RS flakes of Al-7Mn-3Cr alloy. In alloys other than Al-7Mn-1Cr and Al-6Mn-2Cr alloys, hardness increased with increasing heating temperature up to 773K.

Fig.2 shows age hardening curves of the RS flakes during heating at 673K. The increase in hardness due to precipitation was greater for the alloys containing higher Mn+Cr. Little softening due to over-aging was observed in these alloys, even after heating at 673K for $1.2 \times 10^4$ks. The highest hardness (217HV) was obtained in precipitation hardened flakes of Al-7Mn-3Cr alloy. In the alloy containing 9% Mn+Cr, increases in hardness due to precipitation were highest for Al-7Mn-2Cr alloy. Al-7Mn-1Cr and Al-6Mn-2Cr alloys showed little hardening with heating time. Contrastively, hardness of alloys containing higher amount of Mn+Cr was still increasing after heating at 573K for $1.2 \times 10^4$ks. In precipitation hardening curves at 773K, softening was observed due to over-aging, and the peak hardness was obtained by heating for 400-600ks. However, the peak hardness values were lower than these at 673K.

Fig.3 shows TEM micrographs of the RS flakes of Al-7Mn-1Cr and Al-7Mn-3Cr alloys after heating at 673K for 7.2ks. Formation of primary crystals was suppressed by high solidification cooling rate. In both micrographs the amount of the second phase particles was increased.
remarkably larger compared with the as-RS flakes, due to decomposition of the super-saturated solid solution after heating at 673K. The size of the particles precipitated was almost the same in both alloys. However, there was a remarkable difference in the number and distribution of particles precipitated. Precipitates were uniformly distributed at high density in Al-7Mn-3Cr alloy, whereas they were distributed only near the cell boundaries in Al-7Mn-1Cr alloy. This structural difference corresponds well with the hardening caused by heating at 673K for 7.2ks, as shown in Fig.1.

3-2 Structure and hardness of P/M materials

The hardness of P/M materials is shown in Fig.4 before and after heating for 7.2ks at various temperatures. Hardness of the as-extruded P/M materials tends to increase with increasing Mn+Cr, and the highest value (HV143) was obtained in Al-7Mn-3Cr alloy. No hardening was observed in both Al-7Mn-1Cr and Al-6Mn-2Cr alloys containing 8% Mn+Cr; moreover, softening occurred upon heating at 773K. In the other alloys, hardness increased after heating at 673 and 773K. and the hardness of Al-7Mn-3Cr alloy reached 242HV by heating at 773K. Hardness after heating at 873K for 7.2ks was less than that of as-RS flakes.

Age hardening curves at 673K are shown in Fig.5 for the P/M materials without solution heat treatment. The amount of precipitation hardening increased with increasing Mn+Cr, and Al-7Mn-3Cr alloy showed the highest hardness (247HV) after heating at 673K for 1.2x10^3ks. Little precipitation hardening was observed in Al-7Mn-1Cr and Al-6Mn-2Cr alloys. The hardening curves of all P/M materials showed no softening due to overaging.

The hardening curves of three alloys (Al-7Mn-2Cr, Al-6Mn-3Cr and Al-8Mn-1Cr) containing 9% Mn+Cr are almost identical. At an aging temperature of 573K, hardness of the P/M materials containing 9 and 10% Mn+Cr was still increasing after heating for 1.2x10^7ks. These alloys reached almost peak hardness after heating at 773K for 20~50ks. The peak hardness values were 10~20HV lower than at 673K.

TEM micrographs of the P/M materials of Al-7Mn-1Cr and Al-7Mn-3Cr alloys are shown in Fig.6 and Fig.7 respectively. Rod-shaped particles about 1µm in length were observed in the micrographs of the as-extruded P/M materials shown in Fig.6(a) and Fig.7(a). Al-7Mn-3Cr alloy showed microstructures with a higher volume fraction of dispersed particles than for Al-7Mn-1Cr alloy. Fine particles approximately 0.1µm in diameter were
distributed in both P/M materials heated at 673K for 7.2ks. Relatively coarse particles approximately 1µm in size were also observed densely in the heated P/M materials of Al-7Mn-3Cr alloy. In Al-7Mn-1Cr alloy, the coarse rod-shaped particles about 1µm which were observed in the as-extruded P/M materials (Fig.6(a)) disappeared after heating at 673K for 7.2ks. These rod-shaped particles were thought to be CrAl7 and MnAl6 based on X-ray diffraction analysis as set out in the next section. However, fine particles identified as G phase were precipitated in Al-7Mn-1Cr alloy after heating at 673K. Both fine and coarse particles observed in the P/M materials of Al-7Mn-3Cr alloy after heating at 673K were thought to be G phase. The fine G phase particles were formed in the as-extruded P/M materials and grew into coarse particles after heating at 673K for 7.2ks. Remarkable age hardening in Al-7Mn-3Cr alloy occurred due to precipitation of G phase in a high density.

Precipitation hardening of rapidly solidified Al-Mn-Cr alloys is caused by the formation of a large volume fraction of hard equilibrium G phase precipitates. The size and inter-particle distance of the G phase precipitates are larger than in conventional age-hardened aluminum alloys. It follows that softening due to overaging scarcely occurred as shown in the age hardening curves of these Al-Mn-Cr alloys. Precipitation hardening was not observed in the Al-7Mn-1Cr alloy because the volume fraction of G phase was insufficient to contribute to hardening.

3-3 X-ray diffraction of RS flakes and P/M materials

Fig.8 shows the lattice parameter of α-Al for the RS-flakes and P/M materials before and after heating. The lattice parameter was calculated from the diffraction angle of (311)Al. For the three stages (RS flakes heated at 673K for 600ks, as-extruded P/M materials and P/M materials heated at 673K for 7.2ks) the lattice parameter were almost equal to that of pure aluminum for all tested alloys. This implies that nearly all Mn and Cr atoms in the RS flakes and P/M materials formed precipitates. Therefore, precipitation hardening of Al-Mn-Cr alloys occurred without change in lattice parameter of α-Al. On the other hand, the lattice parameter of the as-RS flakes is smaller than that of pure aluminum. The change in the lattice parameter of α-Al is 3.5x10⁻¹³ m and 4.0x10⁻¹³ m due to solute as addition of 1mass% Mn and Cr, respectively [12]. Only CrAl7 compound was crystallized in the as-RS flakes described later. It follows that all added Mn in the Al-Mn-Cr tested alloys formed super-saturated solid solution at the stage of the as-RS flakes. In rapidly solidified Al-Mn-Cr alloys containing higher Cr, CrAl7 tended to form during solidification, and hence strength tended to decrease [6,7]. These results imply that alloys containing higher Cr are not desirable.

Fig.9 and Fig.10 show X-ray diffraction patterns at various stages of Al-7Mn-1Cr and Al-7Mn-3Cr alloys, respectively. Diffraction lines from CrAl7 were observed in the as-RS flakes of both alloys (Fig.9(a), Fig.10(a)). In addition, all added Mn of 7mass% was dissolved as super-saturated solute in these flakes. Diffraction lines from G phase were evident in the RS flakes heated at 673K for 600ks (Fig.9(b), Fig.10(b)). Weak diffraction lines from MnAl6 in Al-7Mn-1Cr alloy and CrAl7 in Al-7Mn-3Cr alloy were also observed after heating of the as-RS flakes (Fig.9(b), Fig.10(b)). For the as-extruded P/M materials, diffraction lines were observed from MnAl6 and CrAl7 in Al-7Mn-1Cr alloy, and from G phase and CrAl7 in Al-7Mn-3Cr alloy. Strong diffraction lines from G phase can be seen in both P/M materials heated at 673K for 600ks. Diffraction lines from MnAl6 and CrAl7 were identified in the heated P/M materials of Al-7Mn-1Cr and Al-7Mn-3Cr alloys. From these experimental results, it follows that CrAl7 crystallizes in the as-RS flakes of all tested alloys. During heating of the RS flakes of the alloys with high ratios of Mn to Cr, MnAl6 precipitated from an extended solid solution. Also, G phase precipitates were formed by further heating of the RS flakes and P/M materials of all tested alloys. Precipitation hardening of the Al-Mn-Cr alloy did not necessarily take place by precipitation of G phase, as we suggested that extensive G phase precipitation is necessary to observe precipitation hardening. Further research is needed on the quantitative relationship between the amount of G phase precipitation and the amount of hardening.
3-4 Tensile properties of P/M materials

Tensile strength of the as-extruded P/M materials at room and elevated temperatures is shown in Fig.11. At room temperature tensile strength of the P/M materials increased with increasing Mn+Cr content; the highest strength (480MPa) was obtained in Al-7Mn-3Cr alloy. This value is almost equal to 470MPa for the rapidly solidified P/M material of Al-8Mn-2Cr alloy reported in our previous paper [9]. Tensile strength of all tested alloys decreased with increasing testing temperature, falling below 250MPa at 573K and below 100MPa at 673K. The difference in tensile strength between these alloys diminished at higher testing temperature. Elongation at room temperature was 7~16% in all tested alloys.

Fig.12 shows changes in tensile strength and elongation of the precipitation hardened P/M materials at room temperature with aging time at 673K. Tensile strength decreased with increasing aging time, whereas hardness increased as shown in Fig.5. Tensile fracture of the precipitation hardened materials occurred in a brittle manner because of extremely poor ductility of G phase. Elongation decreased to almost 0% accompanied with precipitation of the G phase for Al-7Mn-1Cr and Al-6Mn-2Cr alloys, which
showed only slight precipitation hardening. Precipitation of G phase clearly causes a large decrease in ductility with or without precipitation hardening. The elastic modulus of P/M materials at room temperature increased with increasing precipitation of G phase. The highest elastic modulus (85.7 GPa) was obtained in the as-extruded P/M material of Al-7Mn-3Cr alloy. The elastic modulus of this alloy increased to 94.7 GPa after heating at 673 K for 600 ks. Precipitation of G phase therefore caused an increase in the elastic modulus of the rapidly solidified Al-Mn-Cr alloys.

In tensile test at 673 K for the precipitation hardened P/M materials, tensile strength increased with increasing aging time because tensile fracture occurred in a ductile manner. Optimum combination between strength and ductility for rapidly solidified P/M materials of Al-Mn-Cr alloys is probably obtained before full hardening by precipitation of G phase.

4. Conclusions
(1) The amount of precipitation hardening was about 100 HV for Al-7Mn-3Cr alloy, and about 50 HV for Al-7Mn-2Cr and Al-6Mn-3Cr alloys. However, precipitation hardening was scarcely observed in Al-7Mn-1Cr and Al-6Mn-2Cr alloys. Thus, the critical composition of Mn+Cr is determined to be 8.8 mass% for exhibiting precipitation hardening.
(2) Of all the as-extruded P/M materials we tested, Al-7Mn-3Cr alloy showed the highest tensile strength of 480 MPa at room temperature, together with a tensile elongation of 7%.
(3) Tensile fracture of precipitation hardened materials occurred in a brittle manner because of extremely poor ductility of G phase. Tensile strength corresponding to hardness was not obtained in the precipitation hardened materials.
(4) Precipitation of G phase clearly caused an increase in the elastic modulus of the rapidly solidified Al-Mn-Cr alloys.
(5) CrAl7 was crystallized, and all Mn was dissolved in a super-saturated solid solution in the as-RS flakes of all tested alloys. MnAl6 precipitated during heating of the P/M materials before precipitation of G phase.

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References
Table 1 Nominal and analyzed compositions and designation of tested alloy.

Fig.1 Process flow chart of the tested materials.

Fig.1 Hardness changes of cast materials after heating at various temperatures for 7.2ks.

Fig.1 Hardness changes of rapidly solidified flakes after heating at various temperatures for 7.2ks.

Fig.2 Age hardening curves of rapidly solidified flakes at 673K.

Fig.3 TEM micrograph of as rapidly solidified flake of Al-7Mn-1Cr alloy.

Fig.3 TEM micrographs of as rapidly solidified flakes heated at 673K for 7.2ks, (a) Al-7Mn-1Cr alloy and (b) Al-7Mn-3Cr alloy.

Fig.4 Hardness changes of extruded P/M materials after heating at various temperatures for 7.2ks.

Fig.5 Age hardening curves of extruded P/M materials at 673K

Fig.6 TEM micrographs of extruded P/M materials of Al-7Mn-1Cr alloy, (a) as-extruded and (b) heated at 673K for 7.2ks.

Fig.7 TEM micrographs of extruded P/M materials of Al-7Mn-3Cr alloy, (a) as-extruded and (b) heated at 673K for 7.2ks.

Fig.8 Changes of lattice parameter of α−Al at various stages.

Fig.9 X-ray diffraction patterns of Al-7Mn-1Cr alloy at various stages.

Fig.10 X-ray diffraction patterns of Al-7Mn-3Cr alloy at various stages.

Fig.11 Tensile strength of as-extruded P/M materials at various temperatures.

Fig.12 Changes of tensile strength and elongation of extruded P/M materials with heating time at 673K.

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