Effect of TM-Addition on the Aging Behaviour of Al-Mg-Si Alloys

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Microstructure and aging hardness variation of Al-Mg-Si-TM alloys (TM = Mn, Cr, Fe, Y, and Gd) were investigated to reveal the effect of TMs on the age-hardening behavior of Al-Mg-Si-TM alloys. The peak hardness of Cr- and Fe-added alloys is similar to the base alloy, while the peak hardness of Mn-, Gd-, and Y-added alloys is much lower than the base alloy. It was found different TMs formed the dispersoids with different ratio of TM/Si calculated from the EDS result of the dispersoid. The Si expended for the formation of the dispersoid is the most for Y-added alloy and the least for Fe-added alloy among the five TM-added alloys. It is thought that this will result in the difference of Si in the matrix for the formation of the precipitate. [doi:10.2320/matertrans.M2010370]

(Received October 22, 2010; Accepted November 18, 2010; Published January 13, 2011)

Keywords: aluminum-magnesium-silicon alloys, transition metals, age-hardening, precipitation, transmission electron microscopy

1. Introduction

Transition metals (TMs), such as Cr, Fe and Mn, are usually added to Al-Mg-Si alloys for grain refinement. But these transition elements will easily form some dispersoids as Al(TM)Si. According to Terai and Baba,¹⁾ Cr and Mn affect to the electrical conductivity of Al-Mg-Si alloy for extruded, annealed and even aged samples. It seems that Cr and Mn are more stable to remain in the matrix as solute elements than other elements, in addition to make insoluble intermetallic compounds as Al-Si-TMs. The effect of Cr and Fe addition on the age-hardening behavior of 6000 series alloys is reported by Matsuda *et al.*²⁾ They indicated that the addition of (Cr+Fe) decreased peak hardness. And (Cr+Fe)-bearing alloys included AlSi(CrFe) and AlSiFe dispersoids, which had depleted zones around them, and the number density of precipitates decreased in those alloys. Laughlin *et al.*³⁾ reported an investigation of the effect of Mn content on the aging kinetics of Al alloys based on the 6022 composition and got the conclusion that the Mn level had very little effect on the peak hardness which developed in the 6022 variants. TMs, such as Y and Gd, has been reported to form the dispersoid as Al(TM)Si⁴⁻⁸⁾ in Al alloy, which is similar to Cr, Mn or Fe. It is thought that the addition of Y or Gd in Al-Mg-Si alloy will cause a similar result to the effect of Cr, Mn or Fe on the precipitation.

The aim of this work is to focus on the following issues: (1) the variation of aging hardness for the alloys with different TMs addition, (2) the difference of the dispersoids formed with TMs addition, and (3) the effect of TMs on the microstructure of the alloys. With this purpose in mind, hardness test and transmission electron microscopy (TEM) are used to determine these properties of Al-Mg-Si alloys with different transition metals addition.

2. Experimental

The quasi-binary alloy of Al-1.06Mg₂Si (at%) is usually

called as the base alloy for Al-Mg-Si ternary alloy. In this work, the TM-added alloys (at%) of Al-1.06Mg₂Si-0.2TM (TM-added alloy, TM = Mn, Cr, Fe, Y, and Gd) were prepared by laboratory casting. They were melting in air using 99.99% pure Al, 99.9% pure Mg, 99.9% pure Si, and 99.9% pure TMs. The composition analysis of the obtained alloy is given in Table 1. The samples for Vickers hardness and TEM observation were solution heat treated at 848 K for 3.6 ks in a circulating air furnace, cold water quenched, and followed by the artificial aging treatments at 473 K for different periods of time. The samples for DSC test were solution heat treated at 823 K and quenched into cold water.

Vickers hardness was measured using Akashi MVK-EII hardness tester (load: 0.98 N, holding time: 15 s). The hardness values reported here represent the average of at least ten measurements. TEM observation was performed using Topcon EM-002B equipped with an energy dispersive X-ray spectroscopy (EDS). The accelerating voltage was 120 kV.

3. Results and Discussion

Figure 1 shows the optical micrographs of the alloys with different TMs added. The grain size is calculated as 649, 64, 40, 91, 47 and 55 μm for different alloys, as shown in Table 1. The grain size of TM-added alloys is much smaller than those of the base alloy, which is resulted from the grain refinement effect of TM addition. Figure 2 shows the variation of the micro vickers hardness for the alloys aged at 473 K, which is plotted as a function of aging time. The as-quenched hardness of the TM-added alloys is higher than the base alloy because of the smaller grains formed in TM-added alloys. The peak hardness of Cr- or Fe-added alloy is similar to the base alloy. The peak hardness of Mn, Y-, and Gd-added alloys, however, is much lower than the base alloy. This result is supported by our previous work²⁾ but different with Laughlin *et al.*³⁾ The reason for the difference with Laughlin *et al.* is properly caused by the difference of the chemical composition between the alloys used in this work

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Table 1 Composition analysis result of the alloys used in this work (at%).

Alloys	Mg	Si	Fe	Cu	Mn	Cr	Zn	Y	Gd	Al	Grain size (μm)
Base alloy	0.71	0.37	<0.01	<0.01	<0.01	0.00	<0.01	0.00	0.00	bal.	649
Cr-addition alloy	0.72	0.36	<0.01	<0.01	<0.01	0.19	<0.01	0.00	0.00	bal.	64
Fe-addition alloy	0.67	0.32	0.16	<0.01	<0.01	0.00	<0.01	0.00	0.00	bal.	91
Mn-addition alloy	0.75	0.31	<0.01	<0.01	0.24	<0.01	<0.01	0.00	0.00	bal.	40
Y-addition alloy	0.61	0.36	<0.01	<0.01	<0.01	<0.01	<0.01	0.17	0.00	bal.	47
Gd-addition alloy	0.73	0.35	0.02	<0.01	<0.00	0.00	<0.01	0.00	0.19	bal.	55

Fig. 1 Optical micrographs of the alloys with different TMs addition: (a) base, (b) Mn-, (c) Cr-, (d) Fe-, (e) Y-, and (f) Gd-added alloys.

Fig. 3 TEM bright-field images of the alloys with different TMs addition: (a) base, (b) Mn-, (c) Cr-, (d) Fe-, (e) Y-, and (f) Gd-added alloys.

Fig. 2 Micro Vickers hardness curves of six alloys aged at 473 K.

and the previous work,³⁾ in which the existence of 1.0 mass% ex.Si for the alloy including Cu is enough to form the precipitates that affect the age hardening behavior of the alloy.

The six alloys peak-aged at 473 K are taken to examine the difference of the precipitation distribution in this work. The TEM bright-field images are shown in Fig. 3. There are only needle-shaped precipitates aligning with $\langle 100 \rangle_{Al}$ direction for the six alloys. The number density of these precipitates can be calculated as 146, 157, 150, 37, 36 and 31 μm^{-2} for the base, Fe-, Cr-, Mn-, Y-, and Gd added alloys, respectively. The number density of the precipitates for Mn, Y-, and Gd-added alloys is much lower than the other alloys, which is attributed to one of the reason why their peak hardness is much lower than the other alloys. The difference between the peak hardness and the as-quenched hardness is described as ΔHV . The variation of ΔHV according to the number density of the precipitates (N) is shown in Fig. 4(a). The square root of number density of the precipitates, $N^{1/2}$, for every alloy was calculated and it was normalized to divide the value $N^{1/2}$ of Fe-added alloy, as L^{-1} , which is assumed as the inverse of

Fig. 4 Variation of ΔHV according to (a) the number density and (b) L^{-1} .

the normalized distance between precipitates. The variation of ΔHV against L^{-1} is shown in Fig. 4(b). There is a linear relationship between two parameters, which is thought as the mechanism for the effect of the precipitates on the motion of dislocation, $\tau \propto L^{-1}$, where τ is the applied stress and L is the average distance between the particles.⁹⁾

HRTEM observation is taken for Fe-, Mn-, Gd-, and Y-added alloys peak-aged at 473 K. Figure 5 shows the HRTEM images of the typical precipitates observed in Fe-added alloy as an example. Figure 5(a) shows the precipitate with the parallelogram networks of the bright dots. Its interior angle (θ) is not fixed to a certain degree but spans the range of $60^\circ < \theta < 90^\circ$. It can be attributed to the parallelogram-type precipitate,¹⁰⁾ which is the transition phase between GP-zone and the β' phase. Figure 5(b) also shows the precipitate with the parallelogram networks of the bright dots. And its interior angle is fixed to 75° . This can be attributed to the β'' phase,¹¹⁾ which is a special case of the parallelogram-type precipitate. The hexagonal networks of the bright dots of the precipitate in Mn-added alloy are observed in Fig. 5(c) with the spacing about 0.7 nm, and the direction of the precipitate (indicated as P) is inclined by 10° to the $\langle 100 \rangle_{Al}$ direction of the matrix which is similar to the data shown in Refs. 12, 13) for the β' phase. The random-type precipitate,¹⁴⁾ which is the predominant precipitate at the early aging stage and a precursor of the parallelogram-type precipitate appearing after GP-zone, cannot be observed as the main precipitate in this alloy. The precipitate distribution of the alloys is shown in Fig. 6 with the decreasing order of the peak hardness from the top to the

Fig. 5 HRTEM images of the precipitates formed in Fe-added alloy peak-aged at 473 K.

bottom. The distribution of the precipitates for the base alloy has been reported in our previous work.¹⁰⁾ The random-type and parallelogram-type precipitates are observed as the main precipitates in the base alloy. The precipitation sequence for four TM-added alloys is shifted to more stable phases than the base alloy because the random-type precipitates are formed between GP zone and parallelogram-type precipitate, β'' or β' phase according to our previous report.¹⁵⁾

It has been well known that Mn, Cr or Fe will form the dispersoids of Al(TM)Si with the inhomogeneous distribution. The dispersoids are observed in five TM-added alloys in this work, as shown in Fig. 7(a), which is taken

from Cr-added alloy as an example. The size of the dispersoid is much larger than the precipitates. And there is a precipitate free zone around the dispersoid. Figure 7(b)–(f) show the EDS spectrum of the dispersoids formed in different TM-added alloys. Al, Si, and TMs (Mn, Cr, Fe, Gd, and Y) peaks were detected for all TM-added alloys. The

relative ratio of TM:Si is determined using the Cliff-Lorimer method shown in Fig. 8 with respect to Al (i.e. matrix).¹⁶⁾ The TM:Si ratio is estimated as 2.1, 1.7, 1.5, 1.3 and 0.5 for the dispersoids formed in Fe-, Cr-, Mn-, Gd-, and Y-added alloys, respectively. The dispersoids with the TMs used in this work are reported before, as shown in Table 2. The dispersoids observed in TM-added alloys are thought to attribute to $\text{Al}_8\text{Fe}_2\text{Si}$,^{24,25)} $\text{Al}_{8.9}\text{Cr}_4\text{Si}_{2.1}$,²⁹⁾ $\text{Al}_{12}\text{Mn}_3\text{Si}_2$ ^{34,35)} ($\text{Al}_{15}\text{Mn}_3\text{Si}_2$ ³⁶⁾), AlGd_4Si_3 ,⁷⁾ and Al_2YSi_2 ⁸⁾ for Fe-, Cr-, Mn-, Gd-, and Y-added alloys, respectively. Amount of Si for the formation of homogeneous precipitates becomes small and the formation of the precipitates will decrease in TM-added alloy because of the existence of the dispersoids formed with Si. As the interface between the dispersoid and the matrix acts as the sink of the quenched-in vacancy, vacancy in the matrix decreases and it causes the decrease of the diffusion rate of the solute atom in the matrix and the number density of nucleation sites as vacancy-solute atom. On the other hand, β' phase is observed as the main precipitate in Mn-, Y-, and Gd-added alloys in which much Si is expensed to form the dispersoid. The absence of supersaturation of solute atoms for the nucleation furthermore results in the decrease of the precipitates in TM-added alloy. The relationship between the peak hardness and the

Fig. 6 Relative frequency of the precipitates in the five alloys.

Fig. 7 (a) TEM image of the dispersoid formed in Cr-added alloy, (b)–(e) EDS spectrum of the dispersoids formed in different TM-added alloys.

Fig. 8 Determination of the relative ratio of TM/Si for the dispersoids obtained in (a) Mn-, (b) Cr- and (c) Fe-, (d) Y-, and (e) Gd-added alloys using Cliff-Lorimer method.

Fig. 9 Relationship of TM/Si ratio, peak hardness and number density of the precipitates.

TM/Si ratio, as well as the number density of the precipitates and the TM/Si ratio is shown in Fig. 9. It can be seen that the lower the TM/Si ratio is, the lower the number density of the precipitates is, and the lower the peak hardness is.

The bond overlap population (BOP) value by discrete-variational (DV)- $X\alpha$ method using the BONDODR program³⁷⁾ was calculated for the cluster indicated in Fig. 10 which include some TM elements and summarized Fig. 11 as the relationship with the ratio of TM/Si in the dispersoid reported before. It is the easiest to form the dispersoid of AlYSi because the value of BOP is the highest for Y-added alloy. On the other hand, the value of BOP calculated in this work is larger than Al-Mg-Si-Co or Al-Mg-Si-Ni alloy with BOP about 0.3, in which the dispersoid Al(TM) is formed without Si.

Table 2 Dispersoids in Al alloys reported before.

TM	Dispersoid	Crystal Structure	Alloy (mass%)	Ref.
Fe	Al ₂ FeSi	orthorhombic	Al-Si	17)
	Al ₃ FeSi ₂	hexagonal	Al-Si	18)
	Al ₄ Fe ₂ Si	hexagonal	Al-Si	19)
	Al ₇ Fe ₂ Si	hexagonal	Al-Si	20)
	Al ₁₂ Fe ₇₅ Si ₁₃	cubic	Al-Si	21)
	Al ₅ FeSi	monoclinic	Al-0.54Mg-0.28Si-0.24Fe-0.014Mn-0.005Cu-0.009Ti	22)
	Al ₄ FeSi ₂	tetragonal	Al-25Si-5Fe-3Cu	23)
	Al ₈ Fe ₂ Si	cubic	Al-0.58Mg-0.58Si-0.29Fe-0.003Mn-0.007Ti-0.004B-0.002Cu-0.004Pb-0.006Zn	24)
	Al ₈ Fe ₂ Si	hexagonal	—	25)
	AlCr ₆ Si	cubic	Al-Si	26)
Cr	Al ₁₀ Cr ₂₂ Si	teragonal	Al-Si	27)
	Al ₁₃ Cr ₄ Si ₄	cubic	Al-Si	28)
	Al ₉ Cr ₆₃ Si ₂₈	teragonal	Al-Si	26)
	Al ₁₄ Cr ₃₂ Si ₅₄	hexagonal	Al-Si	26)
	Al _{8,9} Cr ₄ Si _{2,1}	hexagonal	Al-24Cr-10Si	29)
	Al ₃ Mn ₃ Si ₄	hexagonal	Al-Si	30)
	Al ₃ Mn ₄ Si ₂	cubic	Al-Si	31)
	Al ₅ Mn ₂ Si ₅	hexagonal	Al-Si	18)
	Al ₉ Mn ₂ Si	cubic	Al-Si	32)
	Al ₉ Mn ₃ Si	hexagonal	Al-Si	30)
Mn	Al ₉ Mn ₄ Si ₃	hexagonal	Al-Si	31)
	Al ₁₃ Mn ₁₀ Si ₇	monoclinic	Al-Si	33)
	Al ₁₂ Mn ₃ Si ₂	cubic	Al-0.87Si-1.17Si-0.37Mn-0.29Cr	34)
	Al ₁₂ Mn ₃ Si ₂	cubic	Al-0.91Mg-1.11Si-0.4Mn	35)
	Al ₁₅ Mn ₃ Si ₂	cubic	Al-(0.3-0.45)Mg-0.35Mn-(6.5-7.5)Si-0.6Fe-0.25Ti	36)
	AlGdSi	hexagonal	Al-Si	4)
	Al ₂ GdSi ₂	hexagonal	Al-Si	5)
	Al ₃ Gd ₆ Si	hexagonal	Al-Si	6)
	Al ₅₈ Gd ₃₃ Si ₉	cubic	Al-Si	4)
	AlGd ₄ S ₃	orthorhombic	Al-Si	7)
Y	Al ₃ Y ₆ Si	hexagonal	Al-Si	6)
	Al ₁₄ Y ₅ Si	hexagonal	Al-Si	8)
	Al ₂ YSi ₂	cubic	Al-Si	8)

4. Conclusions

The grain refinement effect of TMs causes the grain size of the TM-added alloys smaller than the base alloy, which results in the increase of the hardness for as-quenched TM-added alloys.

The precipitates in four alloys peak-aged at 473 K are observed by HRTEM and classified as the random-type precipitate, parallelogram-type precipitate, β'' phase and β' phase. The precipitation sequence for TM-added alloys is shifted to more stable phases, parallelogram-type precipitate,

Fig. 10 Cluster model for the calculation of BOP.

Fig. 11 Variation of BOP according to ratio of TM/Si for the alloys.

β'' phase and β' phase, than the base alloy in which the random-type precipitate is observed as the main precipitate.

The dispersoids of Al(TM)Si are formed in TM-added alloys. The ratio of TM/Si calculated from the EDS result of the dispersoid is the highest for Fe-added alloy and lowest for Y-added alloy. The peak hardness of Fe- and Co-added alloys is similar to the base, while the Mn-, Gd-, and Y-added alloys much lower than the base alloy.

It is the easiest to form the dispersoid with Si in Y-added alloy according to its highest value of BOP. The BOP result obtained in this work indicates that Al(TM)Si dispersoid is formed easier in Cr-, Mn-, Fe-, Y-, and Gd-added alloys than Co- and Ni-added alloys.

Acknowledgement

A part of this work was supported by BILAT project of Norwegian Research Council. Authors thank Mr. J. Nakamura, University of Toyama for his help of BOP calculation.

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