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Effect of Be on Aging Behavior of an Al-Si-Cu-Mg Cast Alloy

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The effect of Be addition on the aging behavior of UNS 03370 (Al11Si3Cu0.3Mg) was investigated by micro-hardness measurement, differential scanning calorimetry (DSC) and transmission electron microscope (TEM) analysis. Age hardening analysis shows Be additions to an Al11Si3Cu0.3Mg alloy accelerates the age hardening rate and increases the peak hardness by 15 HV during aging at 160 °C. DSC shows that Be additions lead to an endothermic peak corresponding to the dissolution of Gunier Preston zones (GP I) disappear with exothermic peaks corresponding to precipitation of GP II zones and the λ′ and/or θ′ phases shift to low temperature. DSC and TEM analyses show that GP II zones are more effective than λ′ and/or θ′ on hardening the alloy, and Be addition increases the homogeneous nucleation density of GP II zones. The possible Be atoms participating in the precipitation process during aging and the high Be-vacancy binding energy can explain the effect of Be on aging behavior of Al11Si3Cu0.3Mg alloy.

Keywords aging behavior, aluminum alloy, effect of Be, nucleation density, precipitates

1. Introduction

Al-Si casting alloys have been widely used in the production of structural components in engineering due to an excellent combination of castability and mechanical properties, as well as good corrosion resistance and weldability. Solution heat treatment and quenching followed by artificial aging are generally needed, whereby nanometer-size dispersoids precipitate from supersaturated solution, hardening the alloy. The main strengthening elements in Al-Si alloys are Mg and Cu, and the age hardening response is significantly influenced by many factors, such as foundry conditions and heat treatment variables.[1-4] Minor alloying is an effective method for increasing the age hardening response in age hardenable aluminum alloys.[5-9] For example, adding Li to Al-Cu-Mg alloy can increase the nuclei density of S′,[7] Be addition to Al-Mg-Si alloy may increase β′ density,[8] and minor additions of Sn, In, and Cd to Al-Cu alloy constrains precipitation of GP zones but increases the nucleation of θ′ phases.[10]

Be has a beneficial effect as a shape modifier of the iron compounds that usually form in the foundry process and weaken alloys properties. Small additions of Be to Al-Si alloys can transform the acicular iron phases which form during solidification into a more favorable rounded shape.[11-13] The present work investigated whether Be additions to Al11Si3Cu0.3Mg alloy affect precipitation behavior during aging. Micro-hardness measurements, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM) analyses are used in this study. The effect of Be additions on precipitation behavior is also discussed.

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2. Experiments

High-purity Al, Mg, Si, and Cu were used in the preparation of Al11Si3Cu0.3Mg (wt%) and Al11Si3Cu0.3Mg0.2Be alloys (wt%). The compositions are shown in Table 1. The alloys were prepared in an electric resistance furnace. The melt was held at 730 °C for about 30 min to ensure complete homogenization. It was then poured into a permanent mold. All samples used in this work are 16 mm in diameter.

An electric resistance furnace with a temperature control of ±3 °C was used for solution heat treatment and artificial aging. Solution heat treatment temperature was 500 ± 3 °C. Samples were held at this temperature for 12 h and then water quenched at room temperature. The artificial aging temperature was 160 ± 3 °C. Hardness test samples were lightly polished. Hardness testing was carried out using HVS-1000 micro Vickers hardness tester with a load of 0.98 N and a dwell time of 10 s. Each Vickers hardness value was the average of at least seven measurements.

DSC analysis was performed using a differential scanning calorimeter (NETZSCH DSC 404, Jinan, Shandong Province, P.R. China). Nonmetallic crucibles (Al_2O_3) were used. First, both the empty reference crucible and sample crucible are equilibrated at 25 °C, and then heated to 600 °C with a heating rate of 10 °C min^{-1} under an argon atmosphere with a flow rate of 80 ml min^{-1}. A DSC base curve is thus obtained. Second, a super purity aluminum specimen is placed in the reference crucible and an experimental specimen of equal mass is placed

Table 1 Composition of Test Materials, wt.%

	Si	Mg	Cu	Ni	Fe	Mn	Be
Base Alloy	10.60	0.28	3.2	1.0	0.60	0.4	…
Alloy with Be	11.15	0.27	3.1	1.2	0.55	0.4	0.23

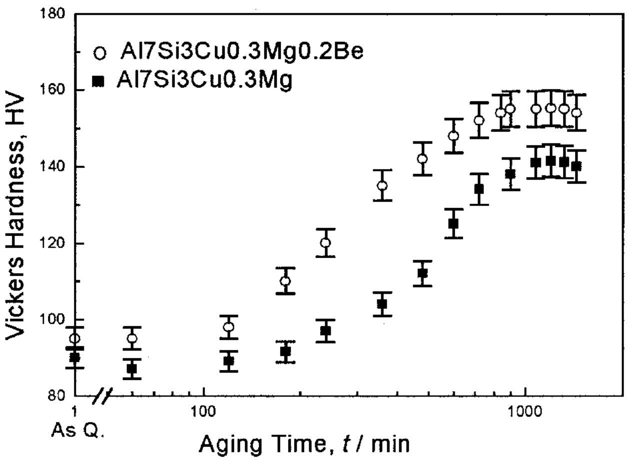

Fig. 1 Micro-hardness versus aging time for quenched samples aging at 160°C

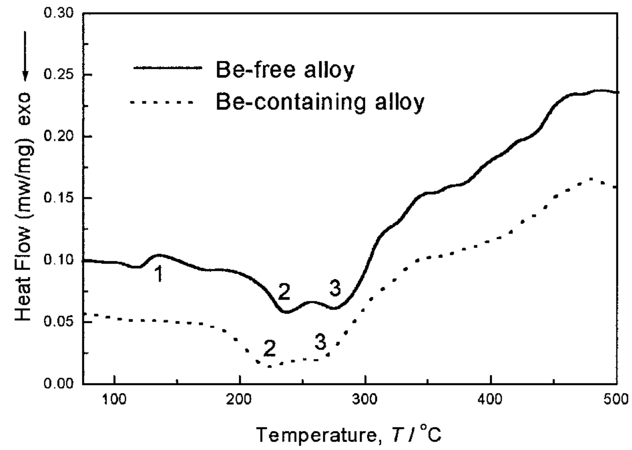

Fig. 2 DSC curves for quenched samples with a heating rate of 10 °C min^{-1}

in the sample crucible. The DSC base curve is now used as a corrective curve for the specimen DSC curve and reflects any transformation effects to the experimental sample during heating.

TEM samples were cut to 0.5 mm thick by a line-cutting machine. Thin samples were mechanically polished to 0.1 mm and then thin foils transparent for electronic beam were obtained using an ion-polishing machine. Microstructures were observed using a H-800 TEM (Hitach Ltd. Company, Tokyo, Japan) operated at 150 kV.

3. Results and Analysis

3.1 Age Hardening Analysis

Figure 1 shows microhardness versus aging time for quenched samples aged at 160 °C for the Be-free alloy and Be-containing alloy, respectively. In the Be-free alloy, there is a decrease in hardness value at the early stage of aging with the peak hardness of 140 HV attained after aging for about 1000 min. In the Be-containing alloy, the hardness increases with increasing aging time, reaching a peak hardness of 155 HV after about 800 min. This result indicates that Be additions to Al11Si3Cu0.3Mg accelerates the age hardening rate and increases the age hardening response. Because Be by itself has little age hardening effect on Al,[10] the effect of Be additions on the age hardening characteristics of Al11Si3Cu0.3Mg may be in combination with Cu, Mg and Si atoms, and this behavior will be analyzed in the following sections.

3.2 Precipitation Behavior

For AlSiCuMg alloys with a Cu:Mg weight ratio over 2.5, the main precipitates formed during aging are $\lambda(Cu_2Mg_8Si_6Al_5)$ and $\theta(CuAl_2)$ phases.[10] According to the generally accepted sequential representations for precipitation in age hardening aluminum-copper alloys, the following precipitation sequence occurs:

GP I $\rightarrow$ GP II (θ'' and/or λ'') $\rightarrow$ λ' and/or θ' $\rightarrow$ λ and/or θ,

or some such sequence of the above may be associated with the aging curves.

DSC can exactly follow the precipitation sequence during the continuous heating of a sample. Many investigators in studying precipitation reactions in aluminum alloys generally use DSC analysis.[14-17]

Figure 2 shows DSC curves for quenched samples for the Be-free and Be-containing alloys, respectively. An endothermic peak (1) centered at 140 °C, and two overlapping exothermal peaks (2) and (3) at about 235 and 280 °C are detected in DSC curve of the Be-free alloy. According to previous DSC investigations of Al-Mg-Si(-Cu) alloys,[14-17] peak (2) should be caused by GP II zone formation (i.e., either θ'' and/or λ''), and peak (3) should be caused by θ' and/or λ' precipitation. The presence of dissolution peak (1) prior to precipitation peak (2) suggests that the quenched sample contains GP I zones, which are not stable and redissolve if the temperature is over 120 °C. This observation is consistent with the hardness reversion noted in the Be-free alloy during aging at 160 °C, as shown in Fig. 1.

For the Be-containing alloy, it can be seen that peaks (2) and (3) shift to low temperature and the endothermic peak (1), corresponding to the dissolution of GP I zones, is not detected in the DSC curve. This suggests that Be additions to this alloy stabilize the GP I zones, which do not dissolve but may act as nuclei of GP II zones. This appears to accelerate the precipitation of GP II zones. This mechanism will be discussed later in this paper.

DSC analyses were carried out on samples aged at 160 °C for different times for the Be-free and Be-containing alloys to investigate the relationship between precipitation and aging time. Figure 3(a) and 3(b) show the results of DSC curves for the Be-free and Be-containing alloys, respectively.

It can be seen that peaks (2) and (3) decrease in intensity with increasing aging time. In the Be-free alloy, peak (2) disappears and peak (3) becomes small after aging for 18 h. Peak hardness is obtained at this stage just as shown in Fig. 1. After aging 24 h, peak (3) disappears, and at this stage hardness decreases from the data shown in Fig. 1. These results indicate that GPII zones are more effective than the metastable θ' and/

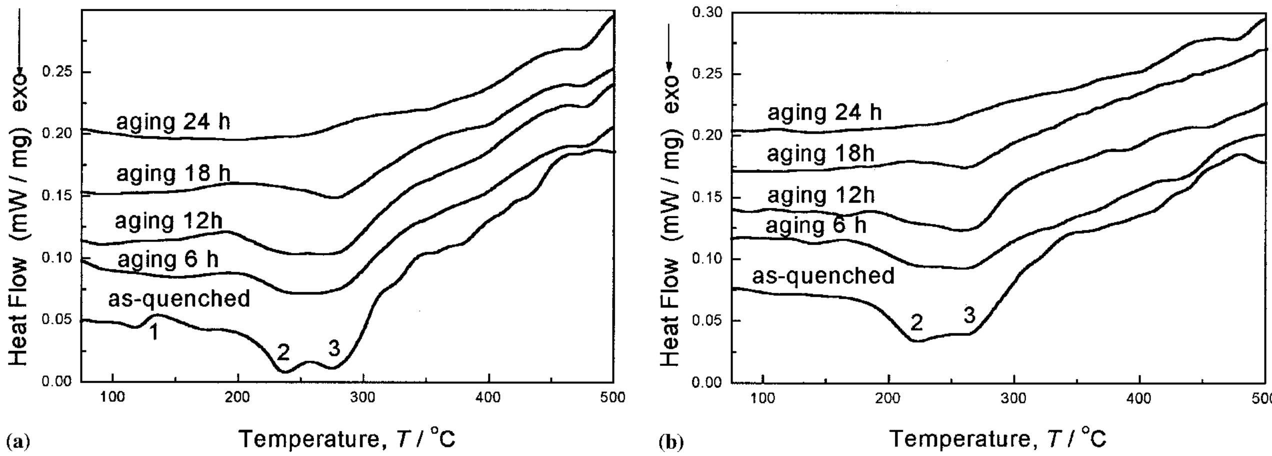

Fig. 3 DSC curves with a heating rate of 10 °C min^{-1} for **(a)** Be-free alloy and **(b)** Be-containing alloy

or λ′ phases on hardening the alloy, and peak hardness is obtained just after the density of GPII zones reaches the maximum.

Comparing Fig. 3(a) with Fig. 3(b), peaks (2) and (3) decrease quickly in size with increasing aging time in the Be-containing alloy. After aging 12 h, peak (2) almost disappears. This suggests that Be additions to Al11Si3Cu0.3Mg accelerate the precipitation of GP II zones so as to increase the age hardening rate.

3.3 TEM Analysis

Figure 4 and 5 show TEM micrographs of quenched samples after aging at 160 °C to produce peak hardness for the Be-free and Be-containing alloys, respectively. The wave-like precipitates indicate that they formed on dislocations. These dislocations in the α(Al) relieve the thermal stresses that are generated during quenching due to the difference in the thermal expansion coefficient between the α(Al) and the eutectic Si. According to the corresponding selected area diffraction patterns, most precipitates are GP II zones that are coherent with α(Al), with hexagonal λ′ phases and tetragonal θ′ phases that are semi-coherent with α(Al) also detected.

Comparing Fig. 5 with Fig. 4, there are more homogeneous nm-sized phases precipitated in the Be-containing alloy, and the density of precipitates is obviously higher than that in the Be-free alloy. This suggests that Be additions to Al11Si3Cu0.3Mg increase the net nucleation density of GP II zones.

4. Discussion

From the experiment results, the beneficial effects of Be additions on the aging response of Al11Si3Cu0.3Mg is attributed to the effect of Be on precipitation behavior. Figure 6 shows DSC curves for the as-cast samples of both alloys in the upper temperature regimen. It reflects the effect of Be on precipitation of polynary eutectic phases. According to Ref.10, peaks 1,2,3 in the DSC curve of Al11Si3Cu0.3Mg correspond with following reactions, respectively:

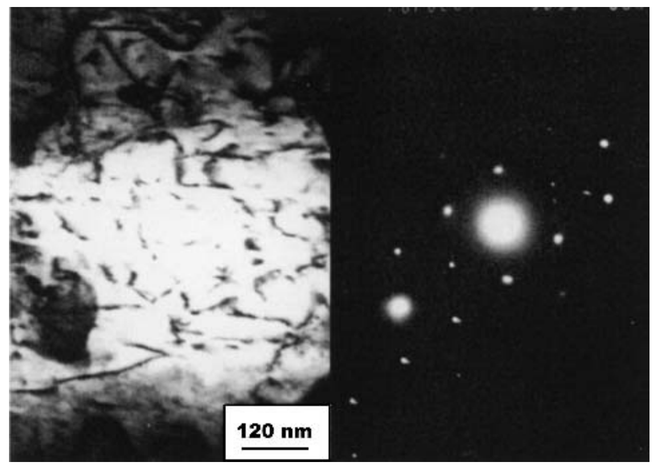

Fig. 4 TEM micrograph and correspondent selected area diffraction pattern [110] for Be-free alloy aging at 160 °C with peak hardness

Reaction of peak 1: α (A1) + Si (+$A1_5SiFe$ + · · ·) → Liq.
Reaction of peak 2: α (A1) + $CuAl_2$ + Si → Liq.
Reaction of peak 3: α (A1) + $CuAl_2$ + Si + $Cu_2Mg_8Si_6Al_5$ → Liq.

It is obvious that peaks (1) and (2) have merged to one peak in the Be containing alloy. This suggests that Be atoms are involved in the precipitation of polynary eutectic phases α(Al) + $CuAl_2$ + Si + $Cu_2Mg_8Si_6Al_5$ and shifts its melting point to a higher temperature. During solution heat treatment and quenching, both of the polynary eutectic phases and the bulk $CuAl_2$ phase dissolve, and the α (Al) is supersaturated with Mg, Cu, Si, and Be atoms. While the quenched sample is heated to the aging temperature, precursor phases of λ($Cu_2Mg_8Si_6Al_5$) and θ ($CuAl_2$) precipitate. From the preceding analysis, we can speculate that Be atoms are involved in the formation of precursors of θ ($CuAl_2$) and λ ($Cu_2Mg_8Si_6Al_5$) precipitates during aging. Because Be has a relatively high vacancy binding energy (0.26 eV),[9] more vacancies will be involved in Be containing GP I zones so as to accommodate its larger size. According to the critical radius theory, the Be containing GP I zones may be stable enough so that they would not

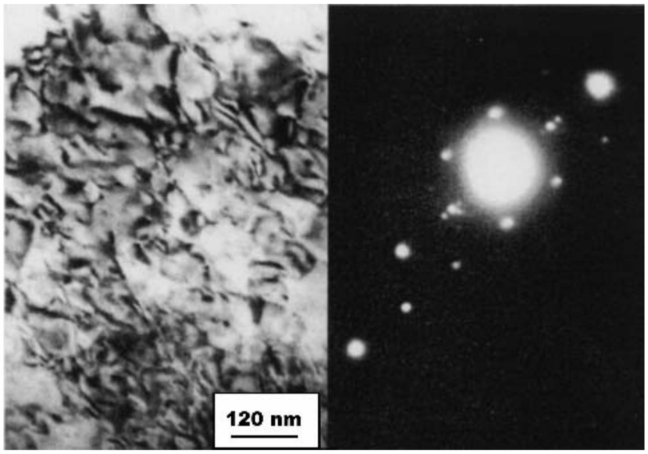

Fig. 5 TEM micrograph and correspondent selected area diffraction pattern [110] for Be-containing alloy aging at 160 °C with peak hardness

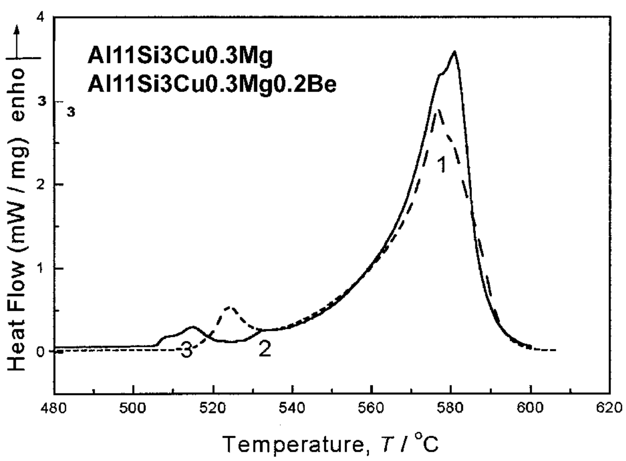

Fig. 6 DSC curves for as-cast samples at a heating rate of 10 °C min^{-1}

dissolve during aging at 160 °C, and thus may act as the nuclei of GP II zones, increasing the precipitation rate.

5. Conclusions

Be addition to Al11Si3Cu0.3Mg accelerates the age hardening rate and increases the age hardening response during aging at 160 °C.

During aging at 160 °C, GP II zones are more effective than λ' and/or θ' phases on hardening the alloy. The addition of Be to this alloy stabilizes GP I zones and increases the homogeneous nucleation density of GP II zones.

The large Be-vacancy binding energy and possible Be atoms participating the precipitation during aging may explain the effect of Be on aging behavior of the Al11Si3Cu0.3Mg alloy.

Acknowledgments

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