A CALORIMETRIC STUDY OF PRECIPITATION PROCESS IN 2 STEPS AGED Al-Mg-Si ALLOYS

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ABSTRACT

Two steps aging characteristics in Al-Mg-Si alloys was investigated by a calorimetric method. Specific heat-temperature curves (S-T curves) were obtained during re-heating after 2 steps aging mainly for approximate pseudo-binary Al-1.31 mass% Mg_2Si alloys using an adiabatic calorimeter. From comparison with the S-T curves of direct aging (aging without pre-aging), it is found that the formation of G. P.-I zones by pre-aging below 373 K retards the formation of β" phases at final aging of 2 steps aging, mainly contributing to the age-hardening of Al-Mg-Si alloys. It is shown that the deterioration in strength of Al-Mg-Si alloys by 2 steps aging is explained in terms of the decrease in solute concentration available for precipitation of β" phases at final aging and the decrease in the number density of β" phases by the formation of thermally stable G. P.-I zones at pre-aging.

Keywords: *Al-Mg-Si alloys, two step aging, thermal analysis, adiabatic calorimeter, precipitation process and G. P. zones*

1. INTRODUCTION

Al-Mg-Si alloys have recently attracted many researchers and engineers because of the large possibility of application to the body panel for automobiles. The tensile strengths of the Al-Mg-Si alloys are often lowered after 2 step aging, depending on the Mg_2Si content and aging condition: the phenomenon is now practically serious problem. The aging process in Al-Mg-Si alloys is found to be very complicated and various metastable precipitate phases are produced in the alloys: the mechanism of the 2 steps aging has not yet been clarified [1]. Thermal analysis gives very useful information to clarify the complicated precipitation process such as in the Al-Mg-Si alloys. However, the studies of 2 steps aging in Al-Mg-Si alloys by thermal analysis have scarcely been reported. In the present work, the characteristics of 2 steps aging in 1.31 mass% Mg_2Si-0.06 mass% Mg alloys was studied using an adiabatic calorimeter.

2. EXPERIMENTAL PROCEDURE

The Al-Mg-Si alloys were prepared from 99.99 mass% Al, 99.9 mass% Mg and 99.9999 mass% Si. The cast ingots were hot forged and annealed at 723 K for 7 days in order to homogenize the casting structure. According to chemical analysis of the alloys, the composition in mass% is as follows: Alloy A (0.55% Mg, 0.46% Si, 0.87% Mg_2Si, 0.13% excess Si); Alloy B (0.69% Mg, 0.36%Si, 0.99% Mg_2Si, 0.06% excess Mg); Alloy C (0.89% Mg, 0.48% Si, 1.31%Mg_2Si, 0.06% excess Mg). Specimens for the specific heat measurements are closed hollow cylinders, 20 mm in diameter and 25 mm in length. All the specimens were solution heat treated at 823 K for 2 hours and quenched into iced water. The quenched Alloy C was 2 steps aged. The alloy belongs to the composition range in which the deterioration in strength by 2 steps aging generally is observed. Specific heat versus temperature curves (S-T curves) of the as-quenched and the aged alloys during re-heating at a rate of about 1 K min^{-1} were obtained using Nagasaki-Takagi type adiabatic

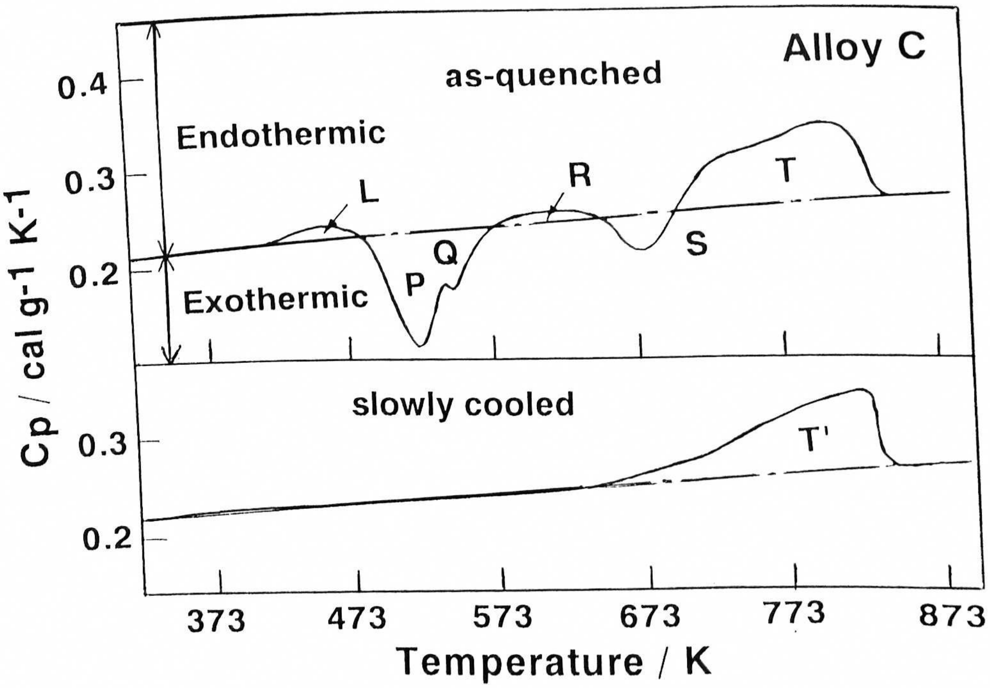

Fig. 1 Specific heat vs. temperature curves of as-quenched and slowly cooled Al-1.31 mass% Mg_2Si-0.06 mass% Mg alloys, showing three precipitation formation peaks and three dissolution peaks.

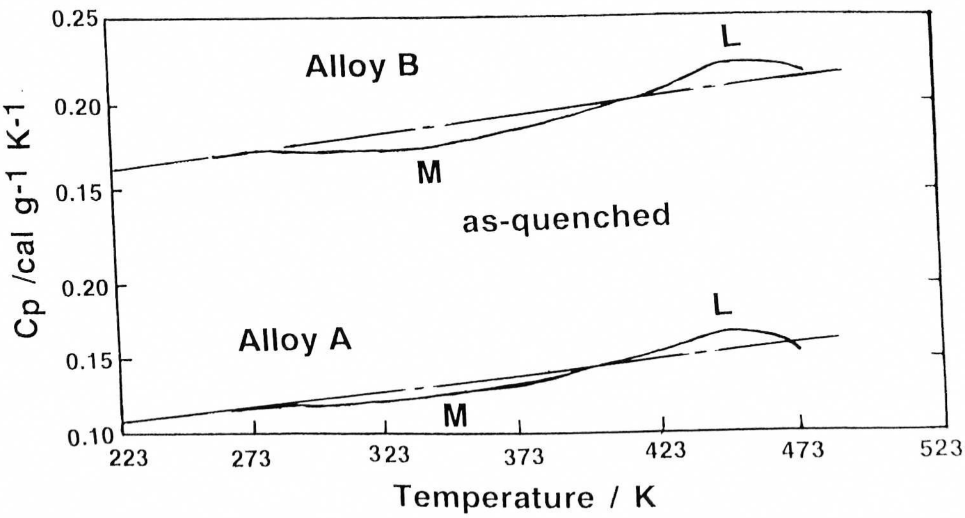

Fig. 2 Specific heat vs. temperature curves of as-quenched Al-0.87 and 0.99 mass% Mg_2Si alloys measured by low temperature adiabatic calorimeter, showing the formation and dissolution of G. P.-I zones.

calorimeter (AGNE, Ltd). To check the G. P.-I. formation, the specially designed low-temperature adiabatic calorimeter was used. All the measurements were carried out in pure Ar gas atmosphere to avoid evaporation of Mg from the specimens.

3. RESULTS and DISCUSSION

Based on many recent and old works [2-10] about the precipitation process in Al-Mg-Si alloys, the possible precipitation sequence is as follows: supersaturated solid solution →Si clusters and Mg clusters→G. P.-I zones having both Mg and Si atoms, disordered structure and unresolved shapes→intermediate needle-like β" phases having both Mg and Si atoms and ordered structure (they are frequently called G. P.-II zones)→intermediate rod-like β' phases→stable plate-shaped β-

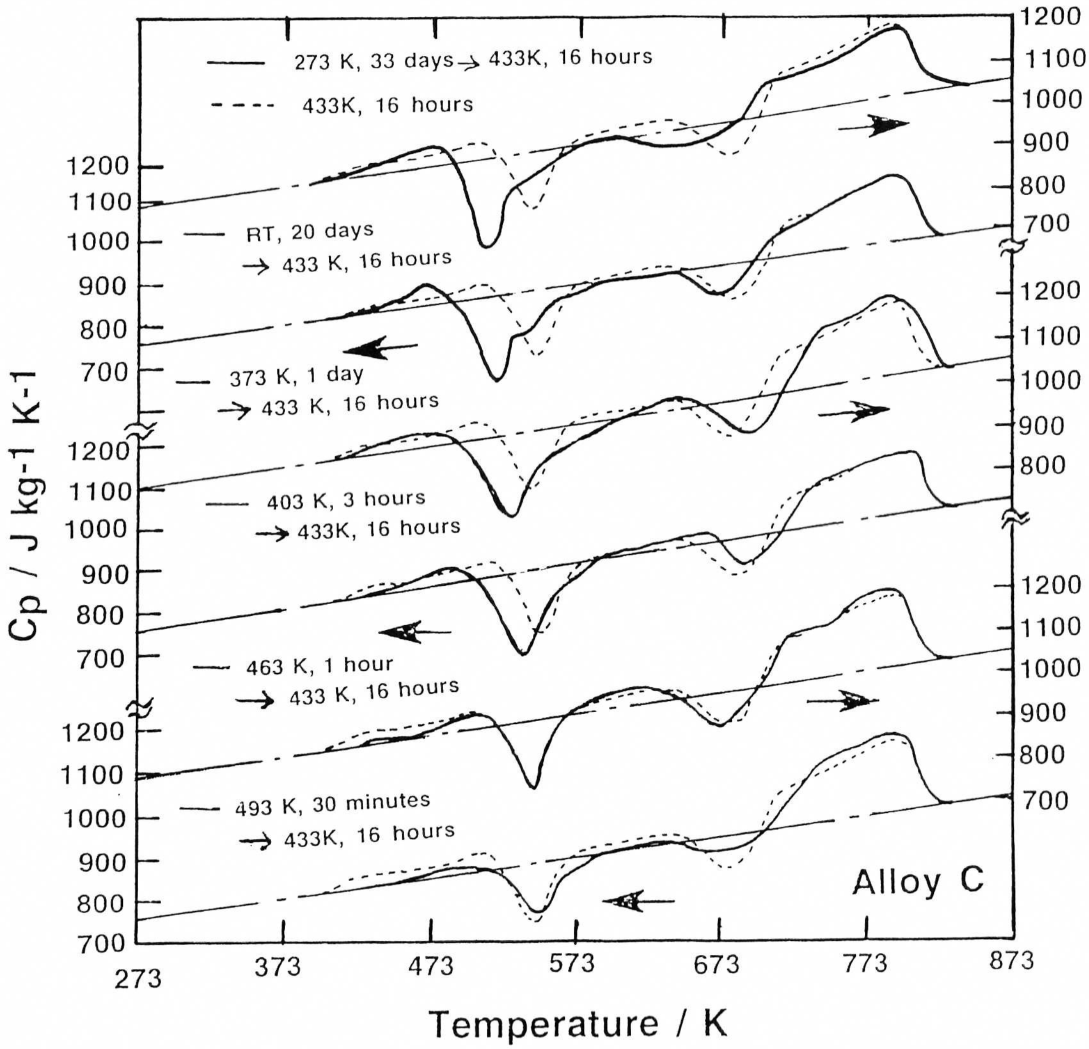

Fig. 3 Effects of pre-aging conditions on specific heat vs. temperature curves of Al-1.31 mass% Mg_2Si-0.06 mass% Mg alloys finally aged 433 K for 16 hours.

Mg_2Si. The strength of Al-Mg-Si alloy is clearly related to the number density of β" phases [4]. In order to analyze the S-T curves of the aged specimens, the S-T curves of the as-quenched and slowly cooled specimens were measured at first. Fig. 1 shows the S-T curves of the Alloy C obtained during re-heating immediately after quenching and slow cooling. The time for slow cooling from 823 K to room temperature was 30 days. The chained line was obtained according to the Kopp-Neumann rule and represents the S-T curve of a homogeneous solid solution consisting of Al, Mg and Si when no phase change takes place during the measurement. This line will be referred to as the base line. Three exothermic formation peaks, including two partially overlapping peaks close to 523 K (P) and 548 K (Q) and one at 673 K are apparent. Three endothermic peaks, including L, R and T are observed. From the above described precipitation process and the other thermal analysis [5], L, P, Q, R, S and T correspond to the reversion of G. P.-I zones, the formation of β" phases, the formation of β' phases, the formation of β phases and the dissolution of β phases, respectively. Fig. 2 shows the S-T curves measured by the low-temperature adiabatic calorimeter of as-quenched Alloy A and Alloy B. The exothermic formation peak (M) in the temperature range from about 283 K to about 413 K and the endothermic peak (L) were detected. The exothermic quantity of M peak increased with the Mg_2Si content. Dutta et al. [2] have found the similar exothermic peak in the DSC thermogram in 6061 alloy and attributed to the formation of Si clusters. However, considering the low Si content, the high thermal stability of L peak and the resistivity measurements [7], it is suggested reasonably that the peaks M and L are mainly associated with the formation and reversion

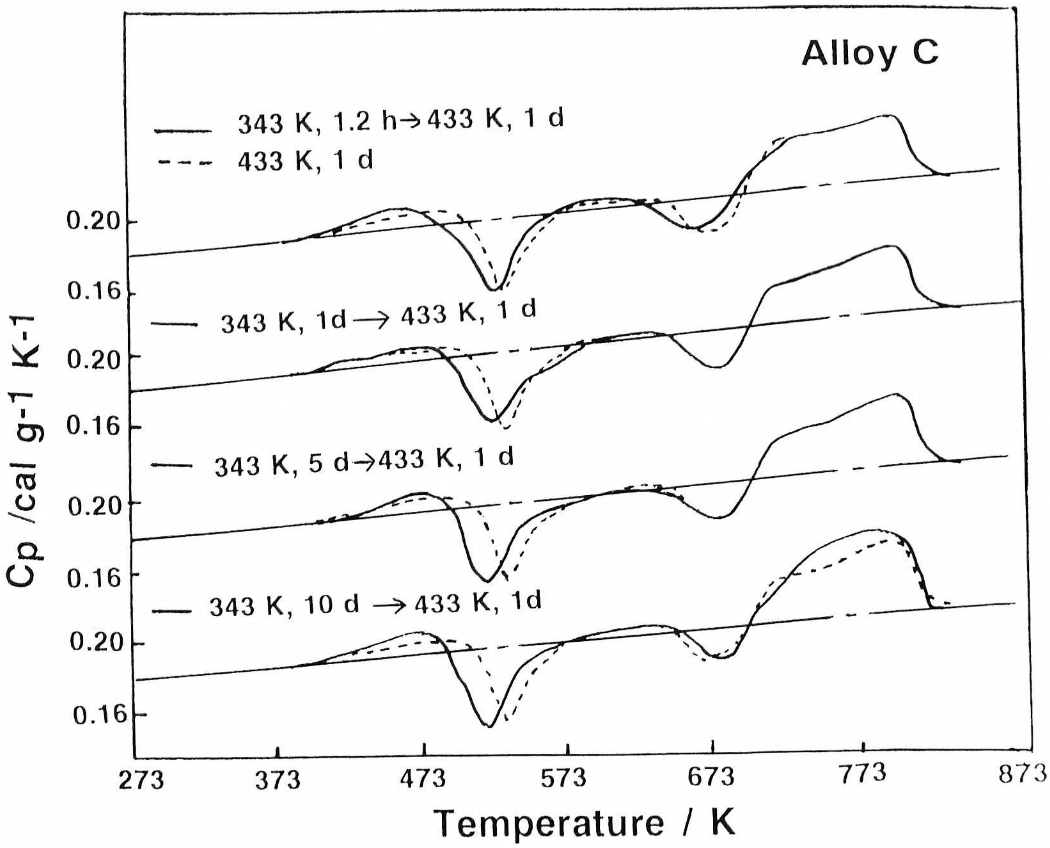

Fig. 4 Effects of pre-aging time at 343 K on specific heat vs. temperature curves of Al-1.31 mass% Mg_2Si-0.06 mass% Mg alloys finally aged at 433 K for 1 day.

of G. P.-I zone although the contribution of Si clusters can not be completely ruled out. Fig. 3 shows the S-T curves of the Alloy C aged at 433 K after pre-aging at different temperatures. According to the results [6], the final aging at 433 K after pre-aging at 273 K, room temperature, 343 K or 373 K produced the deterioration in strength. The absence of P peak in the S-T curve after direct aging (aging without pre-aging) at 433 K for 16 hours represents that β" phase formation is completed. On the other hand, the S-T curves of the 2 steps aged after pre-aging at 273 K or room temperature show that large P peak and small Q peak were detected: hence, this 2 steps aging extremely retarded β" phase formation and accelerated β' phase formation. Then, the L peak was apparently smaller than the real peak owing to the overlapped L and P peaks. It is suggested that the real L peak was larger than that after the direct aging because of large quantity of G. P.-I zones formed at the pre-aging. The similar tendency was observed in the other pre-aging temperatures (373 and 403 K). Fig. 3 shows that in the case of higher pre-aging temperature than final aging temperature, 2 steps aging decreased L peak without changing P and Q peaks. The results represent that the quantities of G. P.-I zones decreased after this aging treatement, compared with the direct aging treatment. Fig. 4 shows the S-T curves of Alloy C aged at 433 K for 1 day after pre-aging at 343 K for different times. The absence of P peak in the S-T curve of the direct aged Alloy C at 433 K for 1 day suggests that the β" phase formation is completed. After pre-aging at 343 K, L and P peaks increased with increasing pre-aging time. The similar behavior was observed at low pre-aging temperatures as shown in Fig. 3. Fig. 5 shows the S-T curves of Alloy C aged at 433 K for various

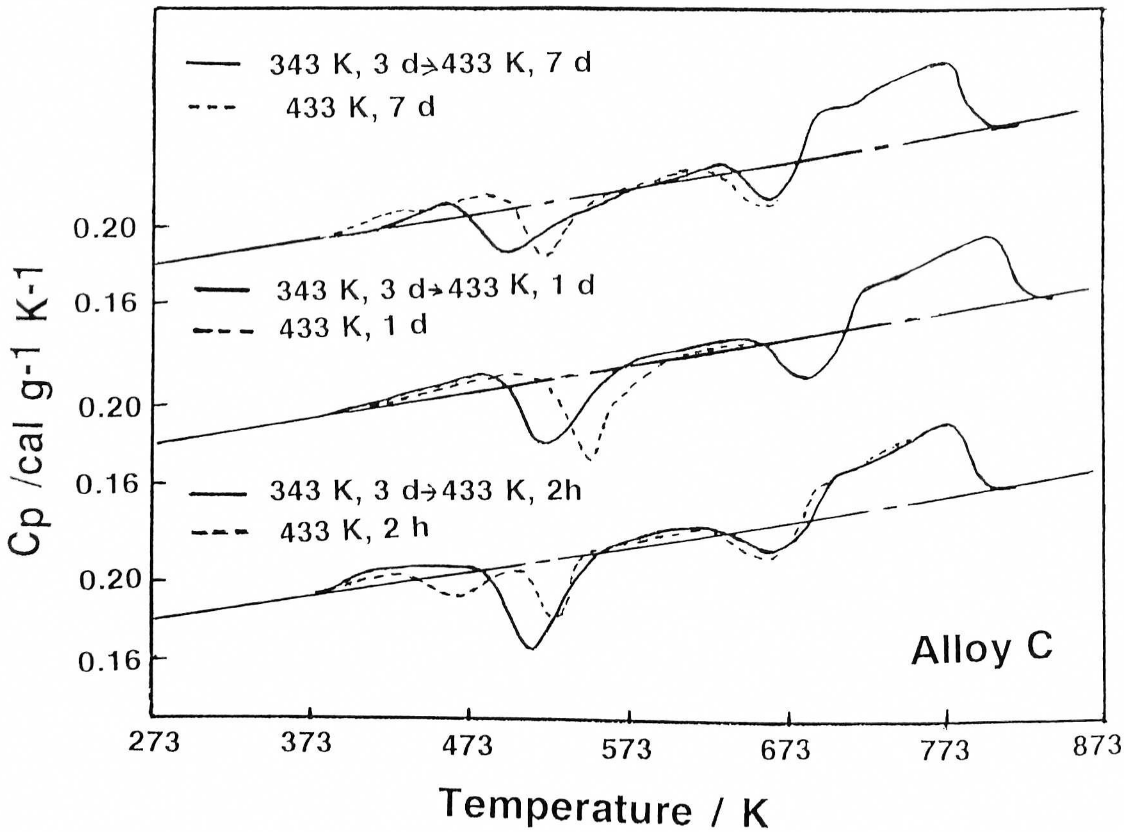

Fig. 5 Effects of final aging time at 433 K on specific heat vs. temperature curves of Al-1.31 mass% Mg_2Si-0.06 mass% Mg alloys after pre-aging at 343 K for 3 days.

times after pre-aging at 343 K for 3 days. When the aging time at final aging is very short (2 hours), small P peak was observed for direct aging and then P and Q peaks clearly were separated, while L and P peaks extremely increased by 2 steps aging. Thus, pre-aging accelerated the formation of G. P.-I zones and extremely suppressed β" phase formation. With increasing aging time at final aging temperature the effect decreased. Finally, the results of the thermal analysis in the present work are summarized as follows: (1) The species of precipitates mainly formed at pre-aging and final aging are not same, when both aging temperatures are much different each other, (2) G. P.-I zones are mainly formed at low pre-aging temperatures below about 373 K. On the other hand, β" and β' phases mainly are produced at high final aging temperatures such as 433 K, (3) G. P.-I zones have high thermal stability and the temperature range of existence overlaps with that of β" phases and (4) The G. P.-I zones formed by pre-aging at low aging temperatures extremely retard the β" formation by final aging at high aging temperatures such as 433 K. Pashley et al. [11] and Asano, Hirano [12] have explained the 2 steps aging behaviors in Al-Mg-Si alloys in terms of the kinetic stability of the G. P. zones formed on pre-aging, and the difference in the number of G. P. zones at pre-and final aging temperatures, respectively. However, it is in both models facitly assumed that the same G. P. zones are formed during pre-and final aging in the 2 steps aging of Al-Mg-Si alloys. This assumption is clearly in conflict with the results in the present work. Many electron-microscopic studies of the 2 steps aged Al-Mg-Si alloys show that the pre-aging tends to decrease the number density of β" phases and to coarsen β" phase in comparison with the direct aged alloys. Based on the results and our results, it is proposed that the G. P.-I zones formed by pre-aging decrease solute concentration in the matrix and the solute concentration available for precipitation of β" phases is much insufficient.

4. CONCLUSION

The effect of 2 steps aging on the precipitation process was investigated for the Al-1.31 mass% Mg_2Si alloy accompanying the deterioration in strength by 2 steps aging using an adiabatic calorimeter. It is found that the formation of G. P.-I zones by the pre-aging at lower temperatures than final aging temperature retards the formation of β" phases responsible for the age-hardening of Al-Mg-Si alloys. It is proposed that the deterioration in strength of Al-Mg-Si alloys by 2 steps aging is attributed to the decrease in solute concentration available for precipitation of β" phases at final aging.

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