PRE-PRECIPITATION AND TWO-STEP AGING BEHAVIOR OF Al-Mg-Si ALLOYS

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ABSTRACT The mechanism of two-step aging behavior of Al-Mg-Si alloys is discussed based on the results of low temperature aging and effects of quenching conditions including water-quenching(W.Q.) and step-quenching(S.Q.) treatments. In an Al-0.57%Mg-0.31%Si alloy (mass%), the S.Q. treatment gives little effect on the electrical resistivity change at room temperature, while a characteristic effect is observed on the resistivity increment at 373K. In addition, the peak hardness of the two-step aged alloy at 453K after pre-aging at 373K becomes higher in the S.Q. treatment than that in the W.Q. treatment. These results suggest that two types of clusters are formed during pre-aging and that quenched-in excess vacancies affect the formation behavior of these clusters.

Keywords: *Al-Mg-Si alloys, two-step aging, pre-precipitation, step-quenching, quenched-in vacancies, Si-vacancy clusters*

1. INTRODUCTION

Recently, Al-Mg-Si alloys have become attractive as heat treatable aluminium alloys for bodysheets of automobiles. However, it is well known that the two-step aging behavior of these alloys is rather complicated. Therefore, this complicated behavior stands in the way of practical applications of these alloys for bodysheet materials. The artificial aging treatment for these alloys is usually performed at about 453K after quenching from solid solution states. However, in a case that the alloys are exposed at low temperatures before artificial aging, the age-hardening behavior of these alloys during artificial aging is variously changed depending on the temperature and time of exposure conditions. In addition , the two-step aging behavior of Al-Mg-Si alloys also differs depending on the chemical compositions of alloys ; i.e. contents of Mg_2Si , excess Si and Mg for Mg_2Si quasi-binary compositions.

It is considered that these complicated behaviors are associated with the pre-precipitation during low temperature aging (pre-aging). Therefore, in this work, both the effects of pre-aging conditions on the subsequent artificial aging (second aging) behavior and the pre-precipitation behavior have been investigated for the quasi-binary Al-Mg-Si alloys and excess Si alloys. The precipitation and microstructures were examined using hardness, electrical resistivity measurements, and transmission electron microscopy. Furthermore, the effects of quenching conditions including water-quenching(W.Q.) and step-quenching(S.Q.) treatments on the above behaviors have been also discussed in terms of the quenched-in vacancies.

2. EXPERIMENTAL PROCEDURE

The chemical compositions of the alloys are listed in Table 1. The quasi-binary alloys(balanced alloys) were prepared with the Mg_2Si contents of 0.9%(9B) and 1.4%(14B). Excess Si alloys containing 0.6%Si(9S) and 0.3%Si(14S) for the corresponding quasi-binary alloys were also prepared. The ingots were homogenized, then hot and cold-rolled to 1.2-1.5mm thick sheets. All of the sheet specimens were solution-treated at 833K for 1.8ks and quenched into ice water at 273K directly (W.Q.) or after interrupted at 523K for 30s (S.Q.). All the specimens were held in ice water for 50s and subsequently age-treated in various conditions. The pre-aging was carried out at temperature T_1 (R.T.-373K) for aging time t_1 and followed by the second aging at temperature T_2 (453K). Hardness measurements were performed on the as-polished specimens using a micro Vickers hardness tester with a 0.5kg load. The foils for the transmission electron microscopy (TEM) were prepared by the twin-jet polishing technique in a 25vol.% nitric acid-75vol.% methanol solution at about 250K. The precipitate microstructures were observed at an accelerating voltage of 200kV using a JEM200CX transmission electron microscope. The electrical resistivity changes were measured by the four-probe potentiometric technique on wire specimens with dimensions ϕ 1.0mm × 300mm at liquid nitrogen temperature.

Table 1 Chemical compositions of alloy specimens (mass%).

Elements Specimens	Mg	Si	Al	Mg_2Si	Ex.Si
9B	0.57	0.31	bal.	0.84	—
9S	0.58	0.94	bal.	0.92	0.60
14B	0.94	0.51	bal.	1.39	—
14S	0.96	0.84	bal.	1.51	0.29

3. RESULTS

3.1 Two-step aging behavior

The peak hardness of the alloys two-step aged at 453K was examined for different pre-aging temperatures. Fig.1 shows the examples for 9B and 9S alloys two-step aged at 453K for 36ks(for a 9B alloy) or 18ks(for a 9S alloy) after pre-aged at R.T. for 60s to 604.8ks for W.Q. and S.Q. treatments. The so-called negative effects of the pre-aging at R.T. are recognized in a 9S alloy, while the changes in a 9B alloy are little. The hardness changes for the pre-aging at 373K are presented in Fig.2. The negative effects of the pre-aging are similarly observed in a 9S alloy, however,

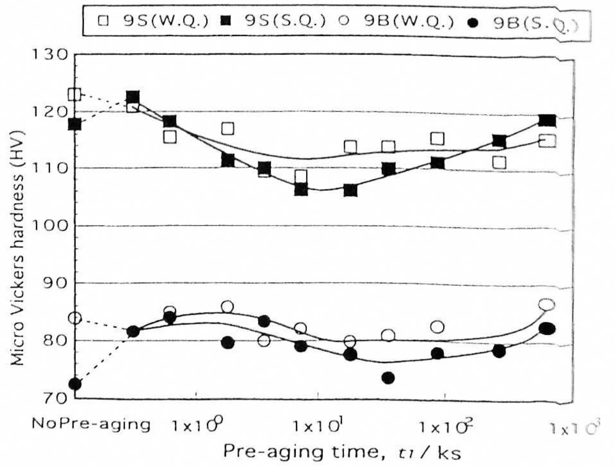

Fig.1 Hardness of a 9B alloy aged at 453K for 36ks and a 9S alloy for 18ks after pre-aging treatment at R.T..

the positive effects are obviously found in a 9B alloy. These results basically well agree with a large number previous results.

TEM micrographs are shown for the alloys single aged and two-step aged in Fig.3. In all micrographs needle shaped precipitates are observed. These precipitates are identified to be G.P. zones, which cause marked precipitation hardening in Al-Mg-Si alloys. In Fig.3 it is found that the pre-aging at 373K results in the increased number density of precipitates for a 9B alloy (see(a) and(b)), while the decreased number density for a 9S alloy (see(c) and (d)). These results clearly indicate that the hardness changes of 9B and 9S alloys are associated with the number density of G.P. zones.

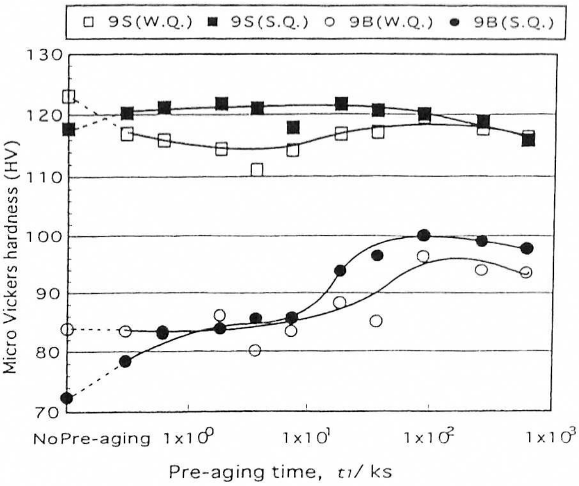

Fig.2 Hardness of a 9B alloy aged at 453K for 36ks and a 9S alloy for 18ks after pre-aging treatment at 373K.

The effect of the S.Q. treatment on the hardness changes is also demonstrated in Fig.1 and Fig.2. The hardness of both 9B and 9S alloys single aged (no-preaging) after the S.Q. treatment are smaller than those of the alloys after the W.Q. treatment. These results are explained in terms of quenched-in excess vacancies. It should be noted that the S.Q. treatment results in the increased hardness for both alloys pre-aged at 373K, while results in the decreased hardness for the alloys pre-aged at R.T.. These results suggest that the two-step aging behavior is also closely related with the amount of quenched-in vacancies.

The two-step aging behavior of Al-Mg-Si alloys and the effect of the S.Q. treatment on the precipitation behavior should be understood based on the phenomena taking place during pre-aging at low temperatures. Therefore, it is necessary to elucidate the pre-precipitation behavior in more details.

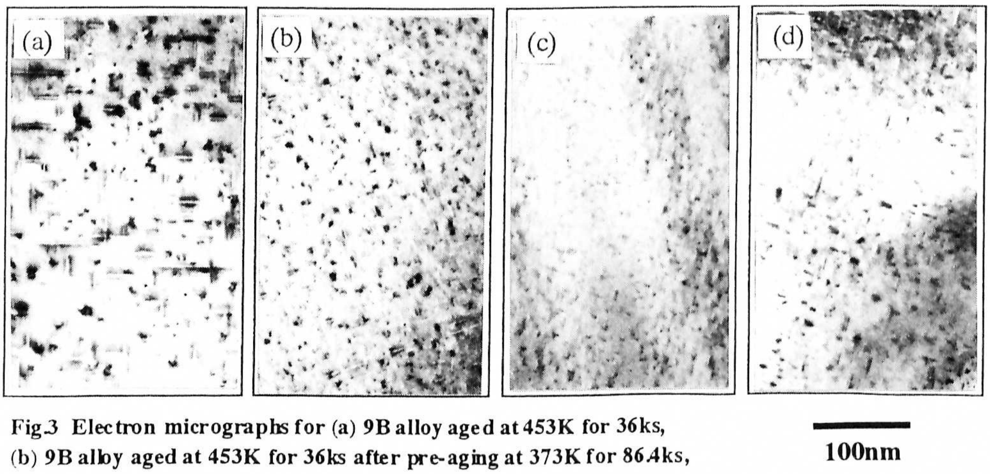

**Fig.3 Electron micrographs for (a) 9B alloy aged at 453K for 36ks,
(b) 9B alloy aged at 453K for 36ks after pre-aging at 373K for 86.4ks,
(c) 9S alloy aged at 453K for 18ks,
(d) 9S alloy aged at 453K for 18ks after pre-aging at 373K for 86.4ks.**

3.2 Pre-precipitation behavior

Fig.4 shows isothermal aging curves of hardness for a 9B alloy during pre-aging at R.T. to 373K. It is noteworthy that the shapes of aging curves change depending on the pre-aging temperature. Two curves of R.T. and 373K aging are different from each other in their shapes; i.e. the curve of R.T. aging shows a gradual increase from the beginning of aging, while the curve of 373K aging shows a delayed increase at the beginning of aging. The curves of 323 and 348K aging exhibit a two-stage increase in hardness, indicating that two types of clusters are formed. In this work, the two-stage increase is designated as Stage 1 and Stage 2, respectively. The positive effects on the second aging at 453K is observed when the pre-aging temperature is 323 to 373K for a 9B alloy, as mentioned in the section 1. In the present results, the products formed at Stage 1 of pre-aging give a negative effect on the peak hardness of the second aging at 453K, while the products formed at Stage 2 cause a positive effect.

The similar behavior was also observed in a 9S alloy during low temperature aging. However, basically only negative effects are observed in a 9S alloy at all pre-aging temperatures examined. The behavior of the negative effect in excess Si alloys can not be simply explained by the mechanism working in quasi binary alloys. Some additional effects should be taken into consideration in excess Si alloys. The increased number of Si-vacancy clusters, for example, are possibly formed in excess Si alloys compared with quasi-binary alloys. This is considered later in more details.

The electrical resistivity changes during pre-aging at R.T. and 373K were also examined and are shown in Fig.5 and Fig.6. These increment behaviors of the resistivity well agree with the previously reported results. The results for the S.Q. treatment are also

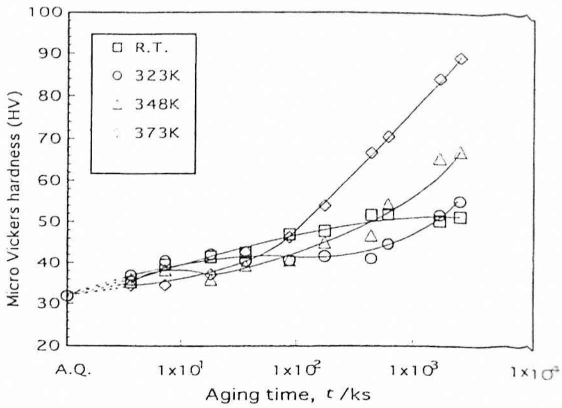

Fig.4 Isothermal aging curves of hardness for a 9B alloy during pre-aging at R.T. to 373K.

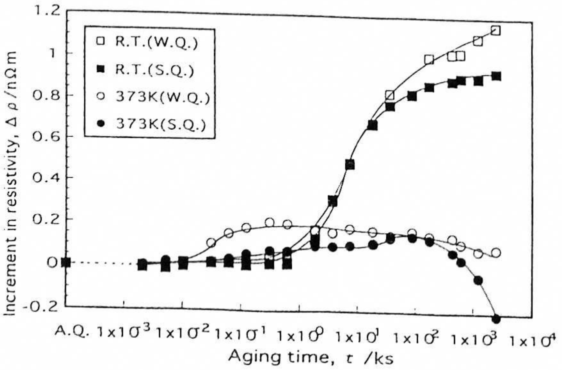

Fig.5 Increments in resistivity for a 9B alloy during pre-aging at R.T. and 373K. ($\Delta\rho = \rho - \rho_{A.Q.}$)

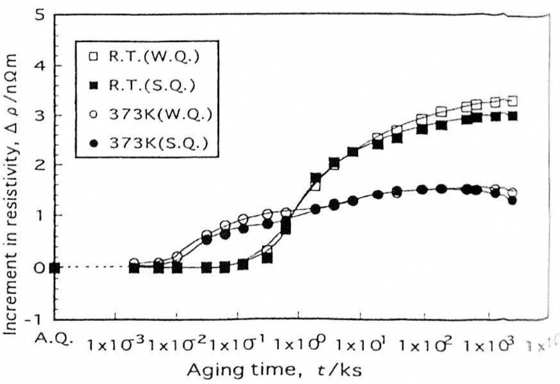

Fig.6 Increments in resistivity for a 9S alloy during pre-aging at R.T. and 373K.

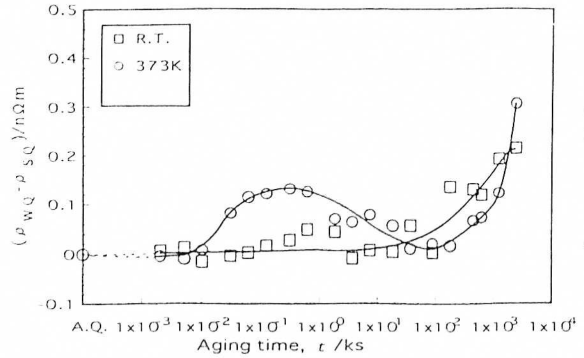

Fig.7 The difference of resistivity between W.Q. and S.Q. treatments, as a function of aging time at R.T. and 373K for a 9B alloy.

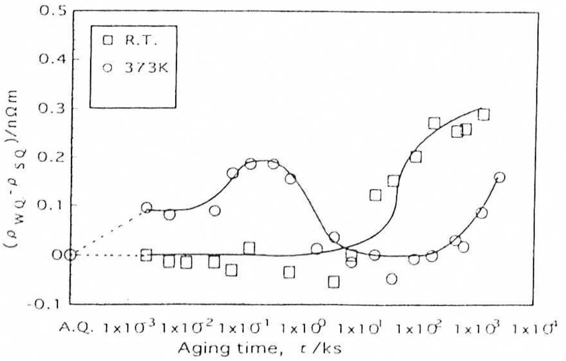

Fig.8 The difference of resistivity between W.Q. and S.Q. treatments, as a function of aging time at R.T. and 373K for a 9S alloy.

represented in Fig.5 and Fig.6. The increments in resistivity become small by the S.Q. treatment compared with the W.Q.treatment. If carefully observed, the resistivity discrepancy between the W.Q. and S.Q. treatments is found to be large at different stages of aging for R.T. and 373K. To demonstrate these points, the difference of resistivity between the W.Q. and S.Q. treatments, $(\rho_{WQ}-\rho_{SQ})$, is shown in Fig.7 and Fig.8. Both of Fig.7 and Fig.8 show that the value of $(\rho_{WQ}-\rho_{SQ})$ becomes increased at Stage 1 at 373K. These results indicate that the formation of products at Stage 1 is suppressed by the S.Q. treatment due to the decreased amount of quenched-in vacancies.

4. DISCUSSIONS

The hardness changes during aging at low temperatures exhibit a two-stage increase, suggesting the formation of two types products. This can be also detected in the resistivity changes. The increment in the resistivity at Stage 1 is higher in a 9S alloy than in a 9B alloy. Therefore, the products at Stage 1 are considered to be associated with Si atoms. The products are also influenced by vacancies. In this work, the products at Stage 1 are assumed to be Si-vacancy clusters, while the products at Stage 2 are assumed to be Mg-Si co-clusters. Based on the above assumption, the two-step aging behavior obtained in this work is well explained. The Si-vacancy clusters will suppress the formation of G.P. zones due to the reduced Si atoms and free vacancies in the matrix. On the other hand, the Mg-Si co-clusters formed at Stage 2 will act as nucleation sites for G.P. zones, resulting in the increased number of G.P. zones.

The effect of the S.Q. treatment is also explained in terms of the above assumption. The S.Q. treatment decreases the amount of quenched-in vacancies and results in the reduced Si-vacancy clusters. Then, the formation of Mg-Si co-clusters is resultantly accelerated and the number density of G.P. zones increases. Therefore, higher hardness is obtained in the S.Q. treated alloys. The above behavior should be also confirmed in 14B and 14S alloys in details. It is also important to detect and identify the Si-vacancy clusters and Mg-Si co-clusters experimentally.

5. CONCLUSIONS

The two-step aging behavior and the pre-precipitation behavior at low temperatures (R.T.-373K) for an Al-0.9%$\mathrm{Mg_2Si}$ alloy (9B) and an Al-0.9%$\mathrm{Mg_2Si}$-0.6%Si (9S) alloy were investigated with two kinds of quenching methods; i.e. water-quenching(W.Q.) and step-quenching(S.Q.). The obtained results are summarized as follows.

(1) The values of hardness for both 9B and 9S alloys single aged at 453K (no-preaging) after S.Q. treatment are smaller than those for the alloys after W.Q. treatment.

(2) The S.Q. treatment results in the increased peak hardness for both alloys pre-aged at 373K compared with the W.Q. treatment, while the S.Q. treatment results in the decreased peak hardness for the alloys pre-aged at R.T..

(3) The experimentally obtained results are well explained taking into account of the formation of two types clusters during pre-aging.

REFERENCES

(1) G.W. Lorimer and R.B.Nicholson: Acta Metallugica 14 (1966) 1009.

(2) D.W.Pashley, M.H.Jacobs and J.T.Vietz: Philosophical Magazine 16 (1967) 51.

(3) K.Asano, S.Fujikawa and K.Hirano:BULLETIN OF THE JAPAN INSTITUTE OF METALS 7 (1968) 457.

(4) C.Panseri and T.Federighi: Journal of the Institute of Metal 94 (1966) 99.

(5) M.Kanno, H.Suzuki and Y.Shiraishi: JOURNAL OF JAPAN INSTITUTE OF LIGHT METALS 28 (1978) 553.

(6) H.Suzuki, M.Kanno and Y.Shiraishi: JOURNAL OF JAPAN INSTITUTE OF LIGHT METALS 29 (1979) 197.

(7) G.A. Edwards, K.Stiller and G.L.Dunlop: Applied Surface Science 76/77 (1994) 219-225.

(8) I.Dutta and S.M.Allen: JOURNAL OF MATERIALS SCIENCE LETTERS 10 (1991) 323-326.

(9) L.Zhen, W.D.Fei, S.B. Kang and H.W.Kim: JOURNAL OF MATERIALS SCIENCE 32(1997) 1895-1902

(10) L.Zhen and S.B.Kang: Scripta Materialia 36 (1997) 1089-1094