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EFFECT OF QUENCHING RATE ON AGE HARDENING IN AN Al-Zn-Mg ALLOY SHEET

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ABSTRACT

The effect of the quenching rate on age hardening in an Al-6.0mass%Zn-0.75mass%Mg alloy sheet was investigated. The quenching rates and aging conditions were as follows: water quenching (WQ) or furnace cooling (FC) followed by pre-aging at 20°C, then artificial aging at 120, 160 or 200°C were performed. The peak strength of the FC and the WQ are very similar at 120°C aging. It is important high strength was obtained even at the extremely slow quenching rate. On the other hand, the strength of the WQ significantly decreased compared to the FC at 200°C aging. GP (I) zones were formed during the pre-aging at 20°C even if the cooling rate was very slow like the FC, and were transformed into the GP (II) ones at 70°C or higher and then into the η' phase. However, these zones were dissolved by reversion during heating to 200°C. Thus the strength of the WQ decreased. On the other hand, it is considered that an unknown cluster or GP zone with a thermal stability formed during the FC was not dissolved up to 200°C and was transformed into the η' phase. Therefore, a higher strength was obtained in the FC for the 200°C aging.

KEYWORDS

Al-Zn-Mg alloy, Quench sensitivity, Furnace cooling, Pre-aging at room temperature, GP zone

INTRODUCTION

Al-Zn-Mg alloys are widely available in commercial production because these alloys have lower quench sensitivity and can be produced by air cooling (AC). Heat treatable aluminum alloys are usually produced by water quenching (WQ) to increase their strength because a high cooling rate inhibits the precipitation of the stable phase during cooling and increases supersaturated solute atoms. However, Baba (1967) reported the strength of an Al-6%Zn-1.8%Mg (mass%) alloy without additional elements quenched by very slow cooling (15°C/min) was 96% of that quenched by WQ. Furthermore, the age hardening at room temperature (RT) occurs after annealing at 410°C followed by furnace cooling（FC, 0.5ºC/min or less）in these alloys. Therefore, the process of annealing at 410 to 430°C for 120 min followed by AC, and reheating at 230°C for 240 min, then cooling is recommended in the specifications (Japan Aluminum Association, 2011). Matsuda and Yoshida (1996) also recommended annealing at 300°C for Al-Zn-Mg alloy extruded products to inhibit age hardening at RT by precipitating the solute atoms and decreasing them in the matrix. It has been considered that the higher the content of excess quenched-in vacancy becomes by WQ, the higher aging rate at RT is obtained. Therefore, it is theoretically and commercially important to clarify the reason why the age hardening occurs relatively quickly in almost no excess quenched-in vacancies such as the FC, and why the same strength as the WQ can be obtained in the FC.

Many studies about the phase decomposition of Al-Zn-Mg alloys have been published (Lorimer & Nicholson, 1966; Suzuki, Kanno, & Asami, 1972; Asano, Abe, & Fujiwara, 1976; Ryum, 1975; Groma, Kovács-Csetenyi, Kovács, Lenvai, & Ungár, 1976; Ungár, Lendvai, Kovács, Groma, & Kovács-Csetényi, 1976; Radomsky et al., 1979; Inoue et al., 1981). To summarize these studies, the solubility limit of the GP zone is in the range of 120 to 155°C, depending on the content and measuring method. However, recent studies about two-step aging indicated the existence of two kinds of GP zones. Ryum (1975) suggested the existence of vacancy-rich nuclei. Stiller, Hansen, Knustson-Wedel, and Gjønnes, (1998) called these vacancy-rich nuclei the GP (II) zone. Berg et al. (2001) and Hansen, Karlsen, Langsrud and Gjønnes (2004) also investigated the phase decomposition of Al-Zn-Mg alloy extrusions. Their results are as follows: there were two kinds of GP zones, that is, the GP (I) and GP (II) zones. The GP (I) zone was formed at RT in spite of the solution heat temperature and could exist up to 120°C or less. It was decomposed during heating to 150°C. On the other hand, the GP (II) zone was formed as a precursor of the η’ phase at 70 to 170°C after quenching from 450°C or higher and was decomposed at 170°C or higher.

Minoda and Yoshida (2012) also investigated the two-step aging of a 7204 alloy and discussed the mechanism of the two-step aging to increase the strength based on the result of Berg et al. (2001) and Hansen et al. (2004). High strength was obtained by a long pre-aging at RT followed by step aging at 100 and 150°C. A significant number of the GP (I) zones was formed at a long pre-aging and were decomposed during heating. The GP (II) zone were formed at 70°C or higher by recombining with the decomposed GP (I) one. The formation of the GP (II) zone was further accelerated by aging at 100°C for 180 min. This GP (II) zone was transformed into the η’ phase during heating to 150°C. They concluded that these fine η’ phase particles dispersed at a high density were produced by two-step aging and increased the strength.

In this study, the effect of the quenching rate (WQ or FC) and the pre-aging time at RT followed by artificial aging on the strength of Al-6%Zn-0.75%Mg was investigated. The formation of the GP zone and the precipitation process of η’ during aging in the sheet quenched by the WQ or FC were discussed.

EXPERIMENTAL

The Al-Zn-Mg alloy ingot with a cross section of 175 mm square was DC cast using 99.99% aluminum. The chemical compositions (mass%) of the ingot were 5.99%Zn and 0.76%Mg, and the amount of each impurity, that is, Fe, Si, Cu, Mn, Cr, Ti, Zr was less than 0.01%. The ingot was homogenized at 500°C for 480 min followed by WQ. The homogenized ingot was hot-rolled from a thickness of 25 mm to 2 mm by 10 passes, and then cold-rolled to 1mm by 12 passes. The rolled sheets were solution-heated at the heating rate of 0.83°C/min (50°C/h) to 450°C and kept for 60 min followed by WQ, or FC at the cooling rate of 0.33°C/min (20°C/h). These sheets were then pre-aged at 20°C for 10080 min in an oil bath followed by aging at 120°C for 1440 min, 160°C for 500 min, or 200°C for 50 min. The pre-aging at 20°C for 120 min followed by aging at 160°C for 500 min was also performed to investigate the effect of the pre-aging time. The Vickers hardness of the aged sheets was measured. To make the aging curve at 160 or 200°C, a tensile test (JIS 13B tensile test piece) was performed on the pre-aged specimens at 20°C for 120 or 10080 min followed by aging at 160 or 200°C for various aging times. The processes of rolling and heat treatment are shown in Figure 1. Furthermore, to analyze the precipitation phenomena, the electrical conductivity by the eddy current method using the SIGMATEST made by FOERSTER Instruments, Inc., a differential scanning thermal analysis using the Pyris 1 DSC made by PerkinElmer, Inc., and TEM observations using the JEM-2010 made by JEOL, Ltd., were performed.

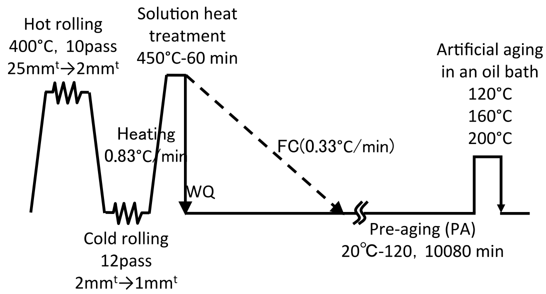
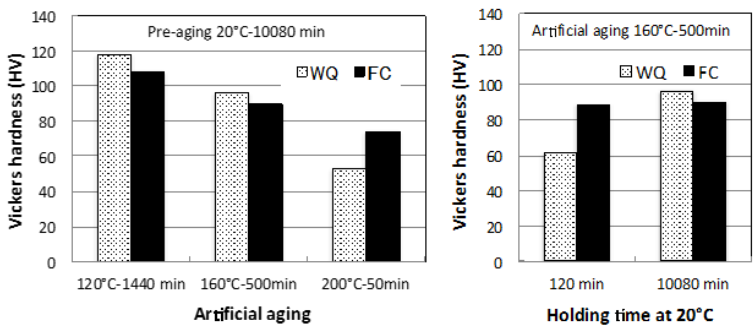


Figure 1. Conditions of rolling and heat treatment for the rolled sheets of an Al-Zn-Mg alloy

RESULTS

Vickers Hardness

The effect of the quenching rate (WQ or FC) followed by the pre-aged at 20°C for 10080 min and aging at 120°C for 1440 min, 160°C for 500 min, or 200°C for 50 min on the Vickers hardness is shown in Figure 2a. For the long pre-aging (10080 min) at 20°C, the hardness of the FC followed by aging at 120 or 160°C was, respectively, 92 or 94% of that by the WQ. Thus it is considered that the hardness of the FC and WQ are very similar. On the other hand, the hardness of the WQ followed by aging at 200°C was 72% of that of the FC. For the short pre-aging (120 min) followed by aging at 160°C for 500 min, a similar result was obtained as shown in Figure 2b. The hardness of the WQ was 69% of that of the FC. Generally speaking, it has been believed that the higher the quenching rate, the higher strength is obtained after artificial aging because the higher quenching rate inhibits the precipitation of the stable phase during cooling and increases the solubility of the supersaturated solute atoms. However, we found that the strength of the FC was higher than that of the WQ under certain aging conditions. This is an important result both theoretically and practically.

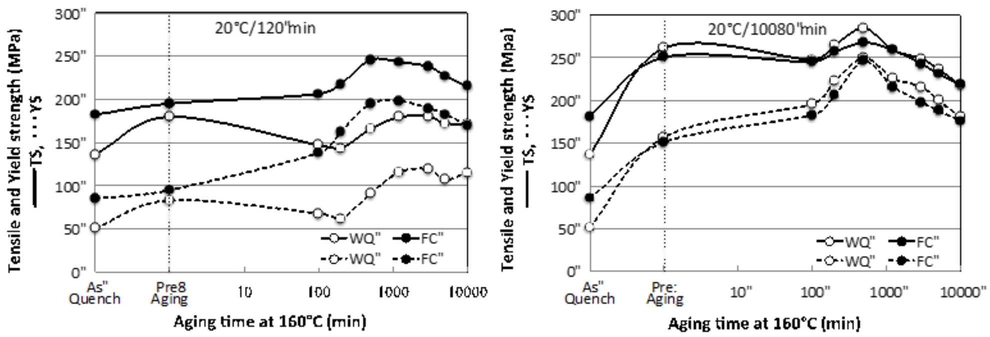


(a) pre-aging at 20°C for 10080 min (b) aging at 160°C for 500 min

Figure 2. Effects of quenching rate, pre-aging time and aging temperature on the Vickers hardness of the sheet, (a) pre-aging at 20°C for 10080 min, and (b) aging at 160°C for 500 min

Tensile and Yield Strength

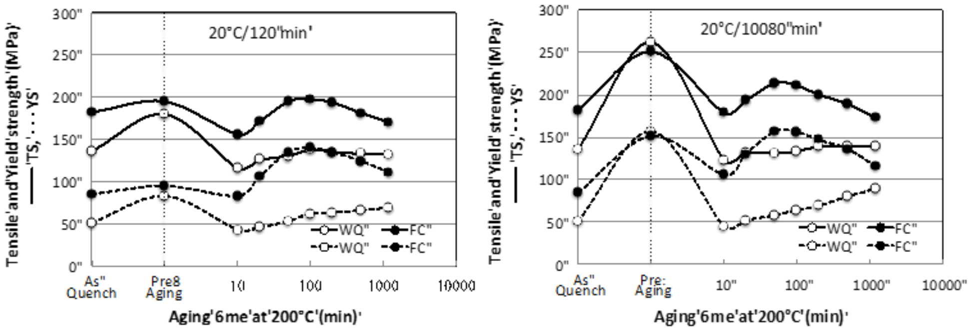
Furthermore, we investigated the change in the tensile properties during aging at 160 or 200°C to clarify the effect of the quenching rate on the artificial aging rate. Figures 3a and 3b show the effect of the quenching rate on the change in the tensile and yield strength during 160°C aging after pre-aging at 20°C for 120 or 10080 min, respectively. The changes in the pre-aging (left) and artificial one (right) are distinguished by the dotted line. Under the as-quenched conditions, the strength of the FC was higher than that of the WQ in spite of the pre-aging times at 20°C. For the short pre-aging, the age hardening at 20°C of the FC slightly increased, but that of the WQ furthermore increased as shown in Figure 3a. On the other hand, for the long pre-aging, age hardening at 20°C significantly increased in spite of the quenching rate, and the almost same strength after pre-aging at 20°C for 10080 min were obtained as shown in Figure 3b. During the aging at 160°C after the short pre-aging, the strength of the WQ decreased until 200 min of aging time by reversion, then increased. However, the strength of the FC increased without reversion and is higher than that of the WQ. The peak tensile strength of the WQ was 73% of that of the FC for the 160°C aging. On the other hand, based on the aging at 160°C after the long pre-aging, the peak tensile strength of the FC is 94% of that of the WQ as shown in Figure 3b. The peak tensile strength of the FC is almost the same as that of the WQ as well as the hardness shown in Figure 2.



(a) pre-aging at 20°C for 120 min (b) pre-aging at 20°C for 10080 min

Figure 3. Effects of quenching rate and pre-aging at 20°C for (a) 120 min or (b) 10080 min on the change in the tensile and yield strength of Al-Zn-Mg alloy sheets aged at 160°C

Figures 4a and 4b show the effect of the quenching rate on the strength during the aging at 200°C after pre-aging at 20°C for 120 or 10080 min, respectively. The age hardening at 20°C of the WQ is higher than that of the FC. However, the strength of the WQ and FC after pre-aging at 20°C for 10080 min is almost the same. Regardless of the pre-aging time, the strength of the FC decreased until 10 min of the aging time by reversion, then age hardening occurred during the 200°C aging. The strength peaked in 50 to 100 min. However, the strength of the WQ slowly increased after reversion and was much lower than that of the FC. The age hardening behavior after reversion for the 200°C aging is almost the same between the short pre-aging and the long one. The strength of the 200°C aging was not affected by the pre-aging time unlike the 160°C aging. The peak tensile strength of the WQ is 65 to 70% of that of the FC.



(a) pre-aging at 20°C for 120 min

(b) pre-aging at 20°C for 10080 min

Figure 4. Effects of quenching rate and pre-aging at 20°C for (a) 120 min and (b) 10080 min on the change in the tensile and yield strength of Al-Zn-Mg alloy sheets aged at 200°C

The experimental results are summarized as follows:

1) The quenching rate did not significantly affect the hardness for the artificial aging at 120°C for 1440 min after the long pre-aging. A high strength was obtained even though the quenching rate was very slow as FC. This is an interesting result not only in theory, but also in practise.
2) The effect of the pre-aging time on the strength of the aging at 160°C was remarkable. There was a slight influence of the quenching rate on the strength of the 160°C aging for the long pre-aging. However, for the short pre-aging, the age hardening rate at 160°C of the FC was faster than that of the WQ and the peak strength of the FC was higher than that of the WQ. The peak tensile strength of the WQ is 73% of that of the FC.
3) For the 200°C aging, the decrease in strength by reversion in the FC was lower than that in the WQ regardless of the pre-aging time. The age hardening rate of the FC after reversion was faster than that of the WQ and the peak strength was higher than that of the WQ. The peak strength of the WQ is 65 to 70% of that of the FC. It has not yet been reported that the age hardening rate of the FC was faster and the peak strength was higher under certain aging conditions compared to the WQ.

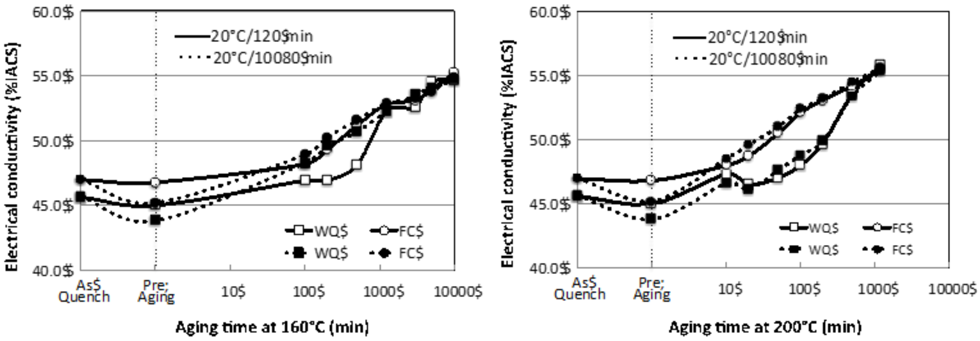
DISCUSSION

Electrical Conductivity

For the FC, the rate of artificial age hardening during the early stage was faster and the peak strength was higher compared to the WQ at the 160°C aging after the short pre-aging as shown in Figure 3a, and at 200°C regardless of the pre-aging time as shown in Figures 4a and 4b. This means some nucleation sites for the precipitation of the η’ phase were formed during the furnace cooling. The electrical conductivity was measured to confirm this idea.

<u>Electrical conductivity at 160°C</u>

Figure 5a shows the change in the electrical conductivity for the 160°C aging. The value of the electrical conductivity of the FC was higher than that of the WQ in the as-quenched condition. This means that some precipitation occurred during the furnace cooling. The decrease of the electrical conductivity was low for the short pre-aging, but this decrease was high for the long pre-aging regardless of the quenching rate. This decrease generally means that the GP (I) zone was formed during the pre-aging.



(a) aging at 160°C (b) aging at 200°C

Figure 5. Effects of the quenching rate and the pre-aging time at 20°C on the change of electrical conductivity in Al-Zn-Mg alloy sheets aged at 160°C and 200°C

During the aging at 160°C after the short pre-aging shown by the solid line in Figure 5a, the electrical conductivity of the FC increased from about 100 min, while that of the WQ increased from about 200 min. These increases of the electrical conductivity correspond to those of the age hardening shown in Figure 3a. The electrical conductivity of the WQ at 5000 min or more was nearly equal to that of the FC, but the strength of the WQ was lower than that of the FC as shown in Figure 3a. This indicates that the precipitation amount of the WQ is nearly equal to that of the FC, but the size and distribution of the precipitates in the WQ are larger and coarser compared to the FC. On the other hand, during the aging at 160°C after the long pre-aging shown by the dashed line in Figure 5a, the electrical conductivity of both the WQ and FC linearly increased in log time.

Electrical conductivity at 200°C aging

Figure 5b shows the change in the electrical conductivity for the 200°C aging. The electrical conductivity of the FC for the 200°C aging linearly increased in log time, while that of the WQ increased until 10 min of the aging time, then decreased, but again increased at 20 min. The GP (I) zone formed at RT and the GP (II) one formed during the heating were mostly dissolved by reversion during the 200°C aging, and this dissolution retarded the age hardening.

DSC Analysis and TEM Observations

Figure 6 shows a DSC analysis of the as-quenched sheets by WQ or FC without pre-aging at RT. It is considered that the endothermic peaks of A and B at 100 to 200°C corresponded to the dissolution of the GP (I) and the GP (II), respectively. The endothermic peak of A near 100°C was reported to be due to the dissolution of the GP (I) zone by Asano et al. (1976) and Suzuki et al. (1972). Broad exothermic peak C near 250°C corresponded to the precipitation of η’ and η phases based on the results of Mukhopadhyay, Yang and Singh (1994) and Jiang, Noble, Holme, Waterloo and Tafto (2000). The endothermic peak D near 320°C corresponded to the dissolution of η’ and η phases. For the WQ, the endothermic peak A corresponded to the dissolution of the GP (I) zone formed in the as-quenched condition or during DSC heating. It is considered that the GP (II) zone was quickly transformed from the GP (I) ones by recombining the decomposed GP (I) one, if the GP (II) one would form at 70 to 170°C according to Berg et al. (2001) and Hansen et al. (2004). The formation peak of the GP (II) zone is uncertain. The η’ and η were then formed and dissolved during heating. A gradual exothermic peak was slightly observed near 40°C in both the WQ and FC, which was estimated as the formation of the GP (I) zone. It is considered that the exothermic peak of the GP (II) zone was not observed on the DSC curve due to the overlap with the endothermic peak of the GP (I) one. The dissolution of the GP (I) and the GP (II) zones was not observed in the FC. It is assumed that an unknown cluster or GP zone with a thermal stability or metastable phase occurred during the FC. The unknown cluster or GP zone inhibited the formation of the GP (I) and the GP

(II) zones in the as-quenched condition. This is the reason why the clear endothermic peaks of the GP (I) or the GP (II) zones were not observed. The slight endothermic peak E near 190°C was observed in the FC. It is estimated that this is due to the dissolution of the unknown cluster or GP zone formed during the FC.

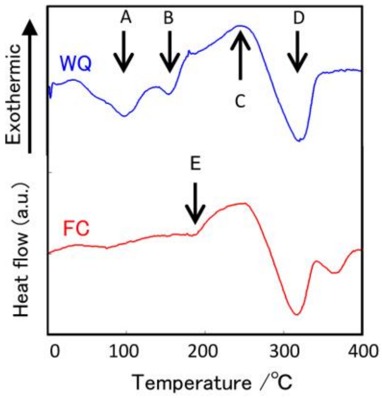


Figure 6. DSC analysis of as-quenched sheets produced at various quenching rates

Figure 7 shows TEM images of the FC in the as-quenched condition, that is, the bright field image showing the dispersion of black spots with a few nm diameters, and high resolution images of these black spots. From these images, it is considered that this is not the η' phase which has a different structure from the matrix. We could not identify these spots as the cluster or the GP zone. The formation of the GP zone generally causes a decrease in the electrical conductivity. The electrical conductivity of the FC in the as-quenched condition was higher than that of the WQ as shown in Figure 5 and the tensile strength of the FC was also 50 MPa higher than that of the WQ as shown in Figures 3 and 4. Therefore, it is considered to be the precipitation of the metastable phase, such as η', but we could not find such a precipitation in this study. It is considered that the unknown cluster or GP zone formed during the FC is different from the GP (I) or the GP (II) because it had a good thermal stability at the high temperature based on the DSC analysis. It is assumed that the unknown cluster or GP zone is a kind of a precursor of metastable phase from the TEM images. The unknown cluster or GP zone with a good thermal stability at high temperature near 200°C has not yet been reported. We will investigate the temperature range for the formation of this cluster or GP zone during the slow cooling, and the structures and properties as future research.

Figure 8 shows the TEM structures of the WQ and FC pre-aged at 20°C for 10080 min followed by aging at 200°C for 50 min. In the FC, granular precipitates estimated as the η' phase were finely dispersed at a high density in the matrix. On the other hand, rod-like precipitates estimated as η, except for the granular ones, were observed in the WQ. The results of the Vickers hardness in Figure 2a or tensile test in Figure 4b are supported by the dispersion of these precipitates

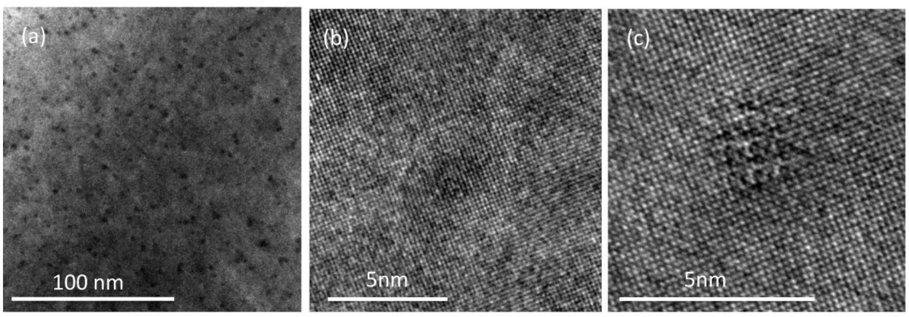
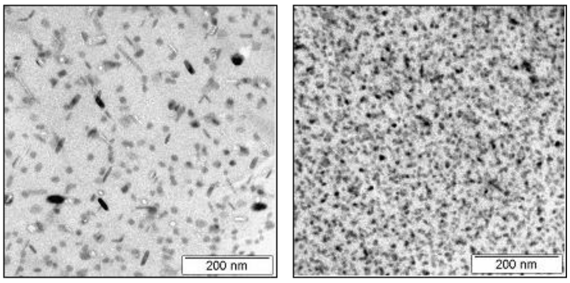


Figure 7. TEM images of FC in the as-quenched condition, (a) bright field image and (b), (c) high resolution images in [001] zone axis of Al matrix



(a) WQ (b) FC

Figure 8. Effect of quenching rate on TEM structures aged at 20°C for 10080 min followed by 200°C for 50 min

Mechanism of Precipitation

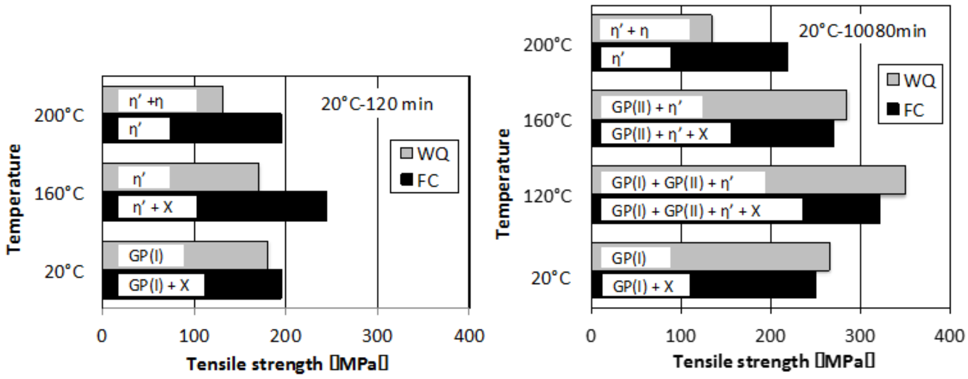
The strength and the artificial aging rate of the FC was higher than those of the WQ for the 160°C aging with the short pre-aging or the 200°C one with or without pre-aging. It is considered that the reason for this is as follows. The unknown cluster or GP zone with a good thermal stability was formed during cooling and transformed into the metastable phase at 160°C or higher because of the higher thermal stability compared to the GP (I) and GP (II) ones. Part of the cluster or GP zone would be also transformed into the metastable phase during cooling. Therefore, the strength of the FC in the as-quenched condition was higher than that of the WQ. We had the same experience with Al-Li alloys. Hirano and Yoshida (1989) reported that the strength of the FC was equal to that of the WQ for the same aging at 200°C for 24h in the Al-2.5%Li alloy. They considered that the reason for the high strength obtained in the FC was that a metastable phase, δ' was formed during slow cooling, but this was not easily transformed into the stable phase δ because of its thermal stability.

Mechanism of precipitation in water-quenched alloy

The GP (I) zone was formed during pre-aging at RT after quenching and the number of zones increased with the pre-aging time. For the 120°C aging, the GP (I) zone were decomposed during heating or aging at this temperature and immediately recombined into the GP (II) one. The GP (II) zone was then transformed into the η' phase that contributed to the increased strength. For the short pre-aging followed by 160°C aging in the WQ shown in Figure 3a, a small number of GP (I) zones was formed during the pre-aging. These GP (I) zones were decomposed and dissolved in the matrix during heating and aging at 160°C. The number of GP (II) zones formed from the GP (I) ones also decreased. Thus the strength decreased until 200 min of the aging time. The strength of the WQ then increased by the formation of the η' phase. However, the strength of the WQ was not so high because the number of η' phases formed from the GP (II) zones was small. For the long pre-aging followed by 160°C aging in the WQ, a significant number of GP (I) zones was formed at RT and they were decomposed and recombined into the GP (II) ones during the heating and aging at 160°C. As a result, age hardening increased because the number of η' phases formed from the GP (II) zones was high. During the aging at 200°C regardless of the pre-aging time, not only the GP (I) zones, but also the GP (II) ones were mostly decomposed and dissolved in the early stage of aging by reversion. Therefore, the strength of the WQ did not increase because the number of η' phases was significantly reduced.

Mechanism of precipitation in furnace-cooled alloy

We considered that the unknown cluster or GP zone with a good thermal stability was formed during the FC and transformed into the metastable phase during 160°C aging because the unknown cluster or GP zone was not dissolved up to about 200°C. This metastable phase is considered as the η' phase or a kind of η' phase. As a result, the age hardening increased. It has been known that the GP (II) zone has a thermal stability compared to the GP (I). But the temperature at which the GP (II) can exist is considered to be about 170°C or less from the literature referenced in the introduction and thermal analysis shown in Figure 6. The decrease in the electrical conductivity was not observed in the FC during aging at 200°C as shown in Figure 5b. This means that reversion did not occur and the unknown cluster or GP zone was immediately transformed into the metastable phase during aging. For the long pre-aging followed by 160°C aging in FC shown in Figure 3b, a large number of GP (I) zone was formed during aging at 20°C as well as the WQ in spite of the very slow cooling. These zones were decomposed and recombined into the GP (II) ones, which were transformed into the η’ phase that contributed to the increased strength. During the aging at 200°C, regardless of the pre-aging time, the tensile strength of the WQ decreased until 10 min of the aging time as shown in Figure 4 because the dissolution of not only the GP (I) zones, but also the GP (II) ones occurred. On the other hand, the strength of the FC did not decrease as much as that of the WQ. The peak strength of the FC was higher than that of the WQ because two kinds of metastable phases, that is, one was formed during the FC and the other was transformed from the unknown cluster or GP zone, contributed to the age hardening at 200°C. These metastable phases that occurred in the different processes are considered to be the same. The estimated phases existing during several aging conditions in which the highest strength was obtained are summarized in Figure 9. The values of the tensile strength were obtained by aging at 20°C for 120 or 10080 min, 120°C for 1440 min, 160°C for 500 min, or 200°C for 50 min. The values of the tensile strength at 120°C in Figure 9b were estimated from the Vickers hardness in Figure 2. X is an unknown cluster or GP zone with a good thermal stability, or a metastable phase formed during the FC. The η’ of the FC aged at 200°C in Figure 9 contains the above-mentioned metastable phases.



(a) Pre-aging: 20°C-120 min (b) Pre-aging: 20°C-10080 min

Figure 9. Estimated phases existing in several aging conditions in which the highest strength was obtained. X is an unknown cluster or GP zone with a thermal stability, or a metastable phase formed during furnace cooling. The values of the tensile strength at 120°C in (b) were estimated from the hardness in Figure 2

CONCLUSIONS

(1) The effect of the quenching rate (WQ or FC) followed by pre-aging at 20°C, then artificial aging at 120, 160 or 200°C on the hardness or strength of the Al-6.0%Zn-0.75%Mg alloy was investigated. For the 120°C aging, almost the same hardness was obtained regardless of the quenching rate. For the long pre-aging followed by aging at 160°C, the quenching rate did not affect the tensile strength, but in the short pre-aging, the tensile strength of WQ was 73% of that of the FC. For the 200°C aging, the tensile strength of WQ was 65 to 70% of that of the FC regardless of the pre-aging time. The tensile strength of FC was higher than that of WQ under certain aging conditions.

(2) The reason why the strength of the FC was higher than that of the WQ is considered as follows: there are two kinds of GP zones in the FC; one is GP (I) zone formed during pre-aging at RT and the other is an unknown cluster or GP zone with a good thermal stability formed during the FC. The GP (I) zone formed during the pre-aging was decomposed and recombined into the GP (II) one. The GP (II) zone was transformed into η’ during heating or aging at 160°C. However, these GP (I) and GP (II) zones were dissolved during heating to 200°C. On the other hand, the unknown cluster or GP zone with a good thermal

stability was not easily dissolved during heating to 200°C and was transformed into a metastable phase, such as η' phase, during 160 or 200°C aging. In the FC, this metastable phase contributed to the increase in the strength at high temperature. Therefore, the strength of the FC was higher than that of the WQ.

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