The mechanism of anneal-hardening phenomenon in extruded Zn–Al alloys

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ARTICLE INFO

Article info
Received 22 December 2012
Accepted 24 February 2013
Available online 5 March 2013

Keywords:
Extruded Zn-based alloys
Anneal-hardening
Phase transformation

ABSTRACT

An anomalous anneal-hardening phenomenon was studied in extruded Zn–Al alloys. The extruded Zn–Al alloys were isothermally heated above the eutectoid point for 10 h, and then cooled with furnace. The anneal-hardening phenomenon was observed in specimens with aluminum content ranging from 5 wt% to 25 wt%. Microstructure evolution during the annealing process was investigated. The annealing–hardening phenomenon was accompanied by phase transformation from a suspensive Zn-rich $\gamma_1$ phase to an equilibrium Al-rich $\gamma_2$ phase and a Zn-rich $\eta$ phase. The hardness of the alloys increased with the decreasing volume fraction of the $\gamma_2$ phase. The hardness of the $\gamma_1$ phase and the $\eta$ phase was measured and the hardness of the $\gamma_2$ phase was calculated. The mechanism of the anneal-hardening phenomenon in extruded Zn–Al alloys can be attributed to phase transformation from the soft $\gamma_2$ phase to the harder $\gamma_1$ + $\eta$ phases.

1. Introduction

Zinc–aluminum based alloys have been widely used for several decades [1,2]. Extruded Zn–Al alloys could provide potential applications for instead of brass and cast iron, due to their favorable comprehensive characteristics (low melting point, exceptional castability, super plasticity, easy machinability, moderate strength, and excellent wear resistance) [3–7]. However, as we know, the two properties—plasticity and hardness—are usually contradictory. So developing Zn–Al alloys, which not only have high hardness, but also keep high plasticity, is advantageous to extend the application.

Annealing is a heat treatment which can relieve the residual stress, reduce the structure defects, and homogenize the composition. Usually, annealing can improve the plasticity and reduce the hardness. However, annealing may harden alloys in some cases. The anneal-hardening phenomenon was found in copper-based alloys, which was explained by the solute segregation to the stacking faults formed by deformation [8–10] and the re-establishment of the short range ordering partially destroyed by deformation [11,12]. The mechanism of anneal-hardening in dilute copper alloys was investigated by Vitek and Warlimont [13]: (1) the solute segregation to dislocations and the resulting binding force is the primary cause, (2) the short range ordering is not a primary cause but may contribute to it.

Recently, it has been found that the matrix phase transformation during the annealing process may lead to the hardening phenomenon in eutectoid Cu–Al alloys [14], near-eutectic Al–Si alloys [15], eutectoid Ti–Cu alloys [16] and deformed nanocrystalline Ni alloy [17]. Compared with the precipitation hardening which relies on fine particles of an impurity phase precipitated from an initially supersaturated solid solution at the low temperature [18], the matrix phase transformation induced hardening is caused by the increase of the phase volume fraction of the matrix phase which has higher hardness.

For Zn–Al alloys, heat treatments usually result in the decrease of the hardness and strength because of the reduction in the dislocation density and the coarsening of grains [19–22]. Recently, an anneal-hardening phenomenon was observed in rolled (90%) Zn–22Al (22 wt%Al) alloys [23]. Annealing at 250 °C, the hardness of Zn–22Al alloys increased when the heating time was smaller than 180 min. Grain size increased during the annealing process. However, the detailed mechanism of the hardening phenomenon in Zn–Al alloys has not been well studied.

In this work, the conditions required for the anneal-hardening phenomenon in extruded Zn–Al alloys were explored. The microstructure evolution during heat treatments was investigated. The mechanism of the hardening phenomenon can be attributed to a decomposition of a soft suspensive Zn-rich $\gamma_2$ (fcc) phase. The present study can help people understand the relationship between the phase structure and the properties in Zn–Al alloys, which is combined with experimental verification. High plasticity and high hardness can be obtained by controlling the phase volume fractions using proper heat treatments.
2. Experimental procedure

A medium frequency induction furnace was used to produce the Zn–Al alloys (the aluminum content ranges from 5 wt% to 40 wt% with a step width of 5%) by melting the corresponding amounts of Zn (99.99% purity) and Al (99.90% purity). Then the alloys were obtained by casting the melt in a steel mold. The ingots were subsequently hot extruded at 280 °C by a 315 T vertical extruder with a deformation ratio of 1:28.

The extruded specimens were subjected to an annealing process: isothermally heated at 300 °C for 10 h, and then cooled slowly to room temperature with furnace.

Vickers hardness (applying load of 1.96 N, 10 s) of the specimens was measured following each heat treatment according to ISO 6507-1:2005(E) standard [24]. At least 10 points were taken for each specimen to obtain an average value.

The specimen for tensile testing was 10 mm (within the gauge length) in diameter with 50 mm gauge length according to ISO 6892-1:2009(E) standard [25]. Tensile specimens were machined parallel to the extrusion direction. The tensile deformation was carried out at room temperature with a crosshead speed of 7.00 × 10^{-3} mm s^{-1}. Each test was repeated five times and the mean value was taken.

The electrical conductivity measurements were carried out by a SB2230 DC digital resistance tester according to IEC 60468:1974 standard [26]. The system was calibrated on the calibration blocks with known conductivity values. The measured values were considered to be accurate within ±0.05% International Annealed Copper Standard (IACS).

The morphologies of the specimens were observed by a Hitachi S-4800 field emission microscope (SEM). Ground and polished specimens were examined for 30 s in 3%HNO_{3} + 3%HCl aqueous solution.

The phase structures of the specimens were investigated by a FEI Tecnai F20 transmission electron microscope (TEM) with an accelerating voltage of 200 kV.

The single-phase specimens of the γ1 phase and the η phase were characterized by XRD (D8 Advance X-ray diffractometer).

3. Results and discussion

Fig. 1 shows the changes of the mechanical properties ((a) tensile strength, (b) elastic modulus, (c) elongation, and (d) hardness) of Zn–Al alloys with increasing aluminum content for both extruded state and annealed state. The tensile strength and the elastic modulus of the extruded Zn–Al specimens with the aluminum content ranging from 10 wt% to 25 wt% were improved after the annealing. The elongation of the extruded Zn–Al specimens was reduced after the annealing. An anneal-hardening phenomenon took place in the extruded Zn–Al specimens with the aluminum content ranging from 5 wt% to 25 wt%.

Fig. 2 shows the changes of the electrical conductivity of Zn–Al alloys with increasing aluminum content for both extruded state and annealed state. The electrical conductivity of the extruded Zn–Al specimens was improved by the annealing, which can be attributed to the decrease of electronic scattering from structure defects [27].

Figs. 3 and 4 show the SEM images of the Zn–Al alloys with the aluminum content ranging from 5 wt% to 40 wt% for both extruded state and annealed state. Cracks paralleling to the extrusion direction were found in extruded Zn–Al specimens. After annealing, the amount of cracks was reduced. It should be noticed that lamellar structures were found in annealed Zn–Al specimens with the aluminum content ranging from 10 wt% to 30 wt%. The amount of lamellar structures increased as the aluminum content was close to 22 wt% (the eutectoid point). The anneal-hardening phenomenon was more notable in specimens with more lamellar structures.

Fig. 5 shows the dependence of the hardness of extruded Zn–20Al alloys of various isothermal temperatures on cooling rate. Extruded Zn–20Al specimens were isothermally heated at 250–320 °C for 10 h and then cooled at various rates (0.02–50 K s^{-1}).

When the isothermal temperature was below the eutectoid point (277 °C), the hardness of Zn–20Al specimens decreased with the decreasing cooling rate. Previous reports found that heat treatments (aging below the eutectoid point) led to the decrease of strength and hardness in Zn–Al alloys [19–22]. The softening was explained by the relief of the residual stresses [20,21], the decrease of the structure defects [21] and the grain-coarsening [22]. However, when the isothermal temperature was above the eutectoid point, the hardness of Zn–20Al specimens increased with the decreasing cooling rate. Similar results were found in eutectoid Cu–Al alloys [14], near-eutectic Al–Si alloys [15], and eutectoid Ti–Cu alloys [16]. The hardness was dependent on the kinetics of the eutectoid decomposition in Cu–Al alloys [14], the amount of dendritic γ2-Al phase in Al–Si alloys [15], and the volume fractions of eutectoid structure and martensite in Ti–Cu alloys [16].

Considering the Zn–Al phase diagram [28], it suggests that the decomposition of the suspensive γ2 phase may play an important role in the anneal-hardening phenomenon in extruded Zn–Al alloys.

Fig. 6a–c shows the SEM observations of extruded Zn–20Al alloys isothermally heated at 250 °C (below the eutectoid temperature) for 10 h and then cooled in (a) water, (b) air, and (c) furnace, respectively. It can be found that the grain size increased slightly with the decreasing cooling rate. The hardness decreased with the decreasing cooling rate (shown in Fig. 5).

Fig. 6d–f shows the SEM observations of extruded Zn–20Al alloys isothermally heated at 300 °C (above the eutectoid temperature) for 10 h and then cooled in (d) water, (e) air, and (f) furnace, respectively. Granular structures transformed into lamellar structures as the cooling rate decreased. The hardness increased with the decreasing cooling rate (shown in Fig. 5).

Fig. 7 shows the TEM observations of extruded Zn–20Al alloys isothermally heated at 300 °C for 10 h and then cooled in (a) water and (b) furnace, respectively. In the water-cooled specimen (shown in Fig. 7a), the granular structure was consisted with three kinds of phases: suspensive Zn-rich γ2 phase (the dark area), equilibrium Al-rich γ1 phase (the bright area) and equilibrium Zn-rich η phase (the dark area). The γ2 phase and the γ1 phase have the face-centered cubic lattice with almost the same lattice parameters. The two phases can be distinguished from the EDX spectrums. The η phase has the close-packed hexagonal lattice. From the EDX spectrums (the test was repeated five times to obtain the average value), the γ2 phase is Al-rich phase (94.9 ± 1.0 wt% Al, balance Zn), the γ1 phase is Zn-rich phase (79.9 ± 1.1 wt% Zn, balance Al) and the η phase is Zn-rich phase (98.2 ± 0.5 wt% Zn, balance Al).

It suggests that the suspensive γ2 phase and the equilibrium γ1 + η phases were co-existed in the water-cooled specimens. In the furnace-cooled specimen (shown in Fig. 7b), the lamellar structure was consisted with the equilibrium Al-rich γ1 phase and the equilibrium Zn-rich η phase. The suspensive γ2 phase cannot be found in lamellar structures.

From the mentioned results, it suggests that the suspensive γ2 phase has not completely decomposed into the equilibrium γ1 + η phases by rapid cooling. After annealing, the hardening phenomenon takes place in specimens containing lamellar structures. The lamellar structure is consisted by equilibrium γ1 + η phases.

To further study the relationship between the phase structure and the hardness of Zn–Al alloys, the volume fraction of the γ2 phase was measured using SEM. Because both of the γ2 phase and the η phase are Zn-rich phases, the two phases cannot be dis-
tistinguished by the appearance directly. However, the Al-rich \( \alpha_1 \) phase can be measured directly from the photographs. Therefore, the volume fraction of the \( \alpha_2 \) phase can be calculated by the lever rule.

The proportion of the volume fraction of the \( \alpha_1 \) phase and the \( \eta \) phase is (the \( \alpha_1 \) phase and the \( \eta \) phase can approximate to pure aluminum and pure zinc respectively):

\[
\frac{f_{\alpha_1}}{f_\eta} = \frac{w_{\alpha_1}/\rho_{Al}}{w_\eta/\rho_{Zn}} = \frac{(20 - 0)/2.7}{(100 - 20)/7.1} = \frac{0.40}{0.60} = 0.66
\]

(1)

The volume fraction of the \( \alpha_2 \) phase can be calculated as:

\[
f_{\alpha_2} = 1 - (f_{\alpha_1} + f_\eta) = 1 - \frac{f_{\alpha_1}}{0.40}
\]

(2)

Fig. 8 shows the relationship between the volume fraction of the \( \alpha_2 \) phase and the hardness of extruded Zn–20Al specimens isothermally heated at 300 °C for 10 h and then cooled by different rates. It can be seen that the hardness increased with the decreasing volume fraction of the \( \alpha_2 \) phase. It suggested that the suspensive \( \alpha_2 \) phase has higher plasticity and lower hardness than the equilibrium \( \alpha_1 + \eta \) phases. The decomposition of \( \alpha_2 \) phase during the annealing can cause the reduction in plasticity and the improvement in hardness.

To determinate the hardness of the \( \alpha_1 \) phase and the \( \eta \) phase respectively, the single-phase specimens were produced with the corresponding elemental contents based on the EDX spectrums in TEM observations. Fig. 9 shows the XRD patterns and the hardness of the single-phase specimens. The hardness of the \( \alpha_1 \) phase and the \( \eta \) phase was about 143.5 HV and 63.2 HV respectively. It indicated that the \( \alpha_1 \) phase was the hardening phase. It also coin-
The hardness of the Zn–Al alloys increased with the increasing aluminum content, because the volume fraction of the $\alpha_1$ phase increased with the increasing aluminum content.

The hardness of the alloy containing mixture phases can be calculated by the rule of mixture (ROM) based on the iso-strain model when the hardness of the hard phase is much higher than that of the soft phase [29]:

$$H = \frac{f_s H_s + f_h H_h}{f_s + f_h},$$

where $H$ is the hardness of the mixture, $f_s$ and $f_h$ are the volume fraction of soft and hard phases, and $H_s$ and $H_h$ are the hardness of soft and hard phases, respectively.

For the extruded Zn–Al alloys, the $\alpha_2$ phase can be considered as the soft phase and the equilibrium $\alpha_1 + \eta$ phases can be considered as the hard phases. And the hardness of annealed specimens can be considered as the hardness of the equilibrium $\alpha_1 + \eta$ phases. Based on the results in Fig. 8, the hardness of the $\alpha_2$ phase can be calculated, which was about 30.1 HV.

Therefore, a model can be suggested for the anneal-hardening phenomenon in extruded Zn–Al alloys. In the hot extrusion, a
part of the softer $\sigma_2$ phase was formed in Zn–Al alloys with the aluminum content ranging from 5 wt% to 25 wt%, because the hot extrusion temperature (280°C) was above the eutectoid temperature (277°C). After the annealing, the softer $\sigma_2$ phase decomposed into the harder equilibrium $\sigma_1 + \eta$ phases, which caused the hardening phenomenon. A similar model was reported in deformed nanocrystalline Ni alloy [17]. A soft $\sigma$ phase was obtained in the deformation process, and transformed into a hard $\gamma$ phase in the annealing. That leads to the work-softening and the anneal-hardening of nanocrystalline Ni alloy.

The changes of hardness after the annealing and the corresponding calculated volume fraction of the $\sigma_2$ phase was shown in Fig. 10. For the extruded Zn–Al specimens (Al: ≥30 wt-%), the hardness decreased after the annealing. That can be explained by the grain-coarsening and the removal of crystal defects and the internal stresses. For the extruded Zn–Al specimens (Al: 5–25 wt-%), the phase transformation induced hardening effect influenced the hardness more than the above-mentioned softening effects. Therefore, the increase of the hardness caused by the phase transformation was at least about 6.9–19.9 HV (12–32%), respectively. The corresponding volume fraction of the $\sigma_2$ phase can be calculated.

4. Conclusion

In the present study, the mechanism of anneal-hardening phenomenon in extruded Zn–Al alloys was investigated. The conclusions can be drawn as following:

1. For extruded Zn–Al alloys showing the anneal-hardening phenomenon, the aluminum content should range from 5 wt% to 25 wt% and the isothermal heating temperature should be above 280°C. The electrical conductivity was improved after the annealing.
The annealing-hardening phenomenon was accompanied by phase transformation from a suspensive Zn-rich \( \alpha_2 \) phase to an equilibrium Al-rich \( \alpha_1 \) phase and a Zn-rich \( \eta \) phase. After isothermal heating above the eutectoid point for 10 h, the \( \alpha_2 \) phase can be obtained by rapid cooling. As the cooling rate decreases, the \( \alpha_2 \) phase decomposes into equilibrium \( \alpha_1 + \eta \) phases. The hardness of the alloys increased with the decreasing volume fraction of the \( \alpha_2 \) phase. The hardness of the \( \alpha_1 \) phase and the \( \eta \) phase was measured and the hardness of the \( \alpha_2 \) phase was calculated. The suspensive \( \alpha_2 \) phase has higher plasticity and lower hardness than the equilibrium \( \alpha_1 + \eta \) phases.

A model can be suggested for the anneal-hardening phenomenon in extruded Zn–Al alloys. In the hot extrusion, a part of the softer \( \alpha_2 \) phase was formed in Zn–Al alloys with the aluminum content ranging from 5 wt% to 25 wt%, because the hot extrusion temperature (280 °C) was above the eutectoid temperature (277 °C). After the annealing, the softer \( \alpha_2 \) phase decomposed into the harder equilibrium \( \alpha_1 + \eta \) phases, which caused the hardening phenomenon. The plasticity and hardness of extruded Zn–Al alloys can be manipulated by modifying the phase structures using proper heat treatments.

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**Fig. 8.** Relationship between the volume fraction of the \( \alpha_2 \) phase and the hardness of extruded Zn–20Al specimens isothermally heated at 300 °C for 10 h and then cooled by different rates.

**Fig. 9.** XRD patterns (a) and hardness (b) of the single-phase specimens (the \( \alpha_1 \) phase and the \( \eta \) phase).

**Fig. 10.** Changes of hardness of extruded Zn–Al alloys after the annealing and the corresponding calculated volume fraction of the \( \alpha_2 \) phase.
Acknowledgement

This work was financially supported by three foundations in China (2009BAE71B05, 2009A31004 and 2012A610057).

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