Microstructural Analyses of Inter-Granular Corrosion Behavior for 6082-T6 Aluminum Alloy

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Abstract. The microstructural analyses of the 6082-T6 aluminum alloy were conducted after electro-chemical corrosion tests utilizing the Optical Microscope (OM), Scanning Electrical Microscope (SEM), Transmission Electrical Microscope (TEM), and Electrical Backscattered Spectrum Diffraction (EBSD). In addition, the systematic analysis of the mechanism of inter-granular corrosion was carried out by the application of the theory of electro-chemical reaction. It can be concluded that the light-etched zone is a single crystal. Whereas, the deep-etched zone is polycrystalline. Moreover, the fine granulated β'-Mg2Si precipitates are continuously precipitated along grain boundaries, and Precipitate Free Zone (PFZ) are also formed bilaterally along the β'-Mg2Si precipitates with the width of 100~150nm. The mechanism that causes the inter-granular corrosion is the difference in the micro-electrode potentials between the β'-Mg2Si precipitates and PFZ. In addition, the coarse block-like Mg2Si particles, which were not dissolved when it was subjected to the solid solution treatment, play a certain role in connecting of the corrosion cracks, as a result, the inter-granular corrosion is being accelerated accordingly.

1. Introduction
Along with the serious global situations of the heavy energy consumption and environment issues, light weighting of an automobile is the common ambition of the auto industries. Generally, 6xxx series of aluminum alloys have not inter-granular corrosion susceptibility. If there is some compositional mismatch of Cu, Mg and Si or an inappropriate heat treatment process. The inter-granular corrosion susceptibility would be increased accordingly [1-4]. As the territory of China is relatively large, the snow coverage of the highway for the northern regions in winter season affects road transportation safety seriously. Therefore, the traffic department normally utilizes the industrial salt such as sodium chloride to dissolve the ice on the road. Whereas, it is highly likely that the inter-granular corrosion would be gradually generated in the 6082 forgings used as drivetrain parts because of their long-term exposure in the corrosion environment. These kinds of corrosion are localized and very destructive, and substantially weaken the binding force among the grains or sub grains. As a result, it would cause the auto parts catastrophic failure and even fracture accident. Hence, it is significant to specifically examine the inter-granular corrosion of the 6082 forgings. In this paper, using 6082 forgings after T6 treatment, we carefully investigate the effects of the microstructures on the corrosion situation and the mechanism of inter-granular corrosion (here termed as IGC).
2. Experimental

2.1. Materials
The materials used were all from the drivetrain parts of the Company B after forging process, which were formerly extruded from the Company A. The forging process was as sequential as following series, which were saw cutting bar, heating bars to 500°C, four-pass roll forgings, 525°C×45 min. solid solution treatment followed by the water quenching, 170°C×5hr peak hardness artificial ageing, Ф1.6mm Al alloy shot blasting, and sizing & adjusting process etc. Table 1 listed the extrusion process parameters, homogenous temperature and time of raw materials that are provided by the Company A, whose chemical compositions were 0.82Mg-1.03Si-0.01Cu-0.27Fe-0.61Mn-0.18Cr (all in weight percent, Al-balanced).

| Raw Materials before Extrusion (mm) | Extrusion Speed (m/min) | Extrusion Ratio | Diameter after Extrusion (mm) | Homogeneous Treatment Temperature and Time |
|------------------------------------|------------------------|-----------------|-----------------------------|------------------------------------------|
| 254                                 | 4.20                   | 6.45            | 100                         | 510°C×6hr                                |

2.2. Experimental Procedures
Etchant solution used for IGC test was the mixture solution of 100ml distilled water, 2grams of sodium chloride, and 6.6ml hydrochloric acid (concentration of 38 per cent), which was totally same as the etchant solution utilized by the company B at the IGC test for the auto parts. The argon ion beam jet with the model of IlionII697 polished the samples used for the EBSD analysis in order to remove the retained internal stress after mechanical rough polishing. The parameters used were 6KV for 20min, 4KV for 30 min, and 1KV for 20min, respectively. The transmission electron microstructural analysis was carried out in the model of JEOL JEM-2100F with the accelerate voltage of 200KV. The TEM was mainly utilized to characterize the secondary precipitates. In addition, Selected Area Diffraction (SAD) and TEM-EDS analysis were also conducted to reveal the details of the orientations and compositional differences between the precipitates and matrix.

3. Results and Discussion

3.1. Microstructures of the Deep-Etched and Light-Etched Zones
Figure 1(a) showed the microstructural photo of the section area of the extruded sample from the Company A after IGC etching. As can be observed, there is IGC development that was uniformly distributed throughout the whole Ф100mm extruded raw material. In another word, there was not any “coarse-grain ring” caused by the severe extrusion plastic deformation. Whereas, after four-pass roll forging process, the specimen showed the different etching situation (shown in Figure 1(b)), that is to say, light-corroded area unevenly appeared at the shell of the section, but the deep-corroded area was developed within the core. After enlargement of the edge of two different etched zones in Figure 1(b), it was clearly observed that the light-corroded area was uniformly etched, there was not any IGC happened. In contrast, the severe IGC developed within the deep-corroded area and formed the IGC networks as can be seen in Figure 1(c).
Figure 1. The IGC morphologies of the 6082 alloy, (a) the IGC morphology of the section of the extruded specimen, (b) section of the forged steering knuckle showing the light-corroded area in the shell and deep-corroded area in the core, (c) microstructural details of the light-etched area and deep-etched area.

3.2. Ebsd Analyses of The Light-Corroded Area and Deep-Corroded Area
Figure 2 showed the EBSD analytical photo of the light-corroded area and deep-corroded area. It can be seen that the deep-corroded area was polycrystalline, and belonged to the period of recovery, and did not experience the recrystallization process. Some grains showed the elongated textural microstructures after plastic deformation, some grains showed the equiaxial shape related to the recrystallization. In addition, there were some sub-grains whose sizes were at the range of 10~15μm. Moreover, it was easily observed that the light-corroded area was a single crystal whose orientation was {101} Miller index. Whereas, the orientations of the polycrystalline grains mainly consisted of {001}, {101}, and {111} Miller index, and the same orientated crystal lattice faces appeared the linear arrangement.

Figure 2. EBSD analytical photos of the light-etched area and deep-etched area after forging

3.3. Tem Analyses of Light-Corroded Area after Forging Process
Figure 3 showed the TEM bright field images of the light-corroded area. It was noticed that there was no any grain boundary being observed when the TEM incident electron beam rotates around the hole of the foil specimen, only the different forms of the equal-thickness interference stripes can be seen because of the wedge-shaped foil sample. To identify whether the microstructure nearby the central hole was single crystal, the Selected Area Diffraction (SAD) analysis was carried out. The results of it were shown in the top right corner of Figure 3(a)-(b) and bottom right corner of the Figure 3(c)-(d). It was revealed that the electron diffraction patterns, gotten from the up, bottom, right, and left side of the center hole, are totally same. Thus, it is firmly verified that the microstructure around the center hole is absolutely a single crystal, just as same as light-corroded area mentioned in the EBSD analysis.
According to some of literature [5-8], the cause for generating the single crystal is correlated to many factors such as chemical compositions, homogenization treatment, extrusion process, forging process, and solid solution etc. Normally, the coarse grains or single crystal is produced at the shell parts of bar raw materials when it experiences the severe plastic deformation. Many documents termed it as “coarse grain ring”. It will seriously cause the microstructures and mechanical properties uneven at the whole section. Some works of literature [9-16] indicated that the formation of the coarse grains or single crystal is related to Mn and Cr alloy elements. As these alloy elements would be combined to become dispersive compound $\text{MnAl}_6$ and $\text{CrAl}_7$ and play a primary role on preventing the grain grows by pinning the grain boundaries. Whereas, when component experiences the high temperature solid solution process, as some of the $\text{MnAl}_6$ and $\text{CrAl}_7$ can be dissolved into the $\alpha$-Al matrix, there are no many secondary particles to be acting as the function of pinning the grain boundaries, thus, the system loses the ability to inhibit the grain grows. As a result, the drastically deformed unstable grains will rapidly grow through the emergence of the nearby defects such as vacancies and dislocations, and become coarse grain ring or single crystal.

It was clearly indicated from this experiment and analyses shown in Figure 1(a)-(b) that the coarse grains or single-crystal was generated at the forging and solid solution process instead of extrusion region. As is well known, when parts experience the forging process, the plastic deformation degree is substantially different in terms of the geometry of the forging dies. That is to say, the severely plastic deformed area should be in the unstable situation because it is stored much amount of deformation energy induced by the lattice defects. When the sample under goes the thermal activation energy such as the solid solution, the unstable high-energy microstructures characterized by the lattice distortions would be converted into the stable state through devouring the crystal defects such as the vacancies and dislocations. During the solid solution process, as the materials are in the high temperature for a long period, the atoms can be self-diffused to a long distance promoted by the thermal activation energy. In addition, as some area is in the high-energy condition, the high-angle grains that have strong movability will rapidly grow up by means of the sub-grain aggregation. As a result, the recrystallization would be carried out in the short period, and the low energy state coarse grains or single-crystal would be produced. All in all, the root cause for the coarse grains or single-crystal is the solid solution treatment after inhomogeneous plastic deformations. Moreover, the temperature and time of solid solution also play a certain role in the coarse grain formation. Normally, higher the temperature and longer the time, the severer the coarse grains, even forming a single crystal. Besides, the temperature has a bigger influence on the formation of the coarse grains or single-crystal compared to the time in the solid solution process.

3.4. TEM Observation and TEM-EDS Analysis after Forging Process

Figure 4 showed the TEM photographs of 6082 alloy after forging process, 525°Cx45 min solid solution and 170°Cx5hr peak hardness artificial ageing. It was shown that there are massive rod-shaped precipitates formed within the grains (shown in Figure 4(a)). The rod-like precipitates were strictly coherent with the matrix. In addition, its morphology was appeared to be perpendicularly cross-like when they were shown in the direction of normal to the incident electron beam. Accordingly,
it showed the small black circles when appeared on the direction of parallel to the incident electron beam. Because its rod-like precipitates were located in the different depth within the TEM foil, the size, which was shown in the bright field image, is different. The length of the rod was almost in the range of an order of 100–150nm, the section area was 1~3nm2. Reports [17-19] shown that the highest precipitate hardness contributor $\beta''$-Mg2Si would be coherently formed in the matrix of crystallographic direction families of the <100> when specimen experiences the peak hardness ageing process (T6). Thus, here it can be carefully predicted that the precipitates, which were formed along the orthogonal <100> crystal directions, are $\beta''$-Mg2Si secondary phase.

In addition, as can be observed in the Figure 4(b), after 170˚Cx5hr artificial ageing process (T6), there were also many small granular precipitates coupling with a precipitate free zone (PFZ) along the grain boundary. The width of the PFZ was approximately 100~150nm. It is revealed after careful observation that the granular precipitates formed along the grain boundary were short rod-like, and its orientations were same as the rod-like precipitates grown within the grains. Thus, it can be concluded that the continuously precipitated short rod-like secondary phase is also $\beta''$-Mg2Si precipitates, nothing but it grows in the grain boundaries, which exists much of the defects such as vacancies and dislocations.

Through the TEM-EDX analysis of the short rod-like precipitates grown in the grain boundary (the point 1 in the Figure 4(b)) and matrix (the point 2 in the Figure 4(b)), it was known that there was much alloy segregation such as Mg, Si, and Cr within the short rod-like ones. The amount of Mg, Si, Cr (shown in Figure 4(c)) is 2.8%, 2.2% and 0.7%, respectively (all in weight percent, Al-balanced) after quantitative analysis. On the contrary, the matrix only included 1.2%Mg, 0.5%Si and 0.6%Cr (shown in Figure 4(d)). The results confirm that the main elements segregated within the short rod-like precipitates are Mg and Si, which are 2.33 and 4.40 times larger than in the matrix, respectively. It once again verifies that, the short rod-shaped precipitates grown at the grain boundary are Mg and Si rich $\beta''$-Mg2Si secondary phase.

![Figure 4. TEM photographs and TEM-EDS analysis of the deep-corroded zone after 170˚Cx5hr ageing (T6), (a) precipitates within the grains and at the grain boundaries, (b) continuously distributed precipitates along the grain boundary, (c) (d) showing the TEM-EDS profiles of point 1 and point 2, respectively.](image)

After the TEM observation and EBSD analysis of deep corroded zone and light-corroded zone for 6082 alloy (T6), it was finally to be understood that the deep-etched area is definitely polycrystalline, and massive granular $\beta''$-Mg2Si precipitates are generated along the grain boundaries coupling with the PFZ of 100~150nm. Besides, the light-corroded area is just a single crystal. Secondary precipitates $\beta''$-Mg2Si are uniformly distributed within the single crystal. As there is no any grain or sub grain boundary, the micro-corrosion potential is almost equal anywhere, as a result, it appears the uniform light-etching color at the OM observation.
3.5. Analysis of the IGC Propagation Root

The corrosion, happened on the surface of the 6082 alloy, appears the form of networks (shown in Figure 5(a)). In addition, as can be observed in Figure 5(b) showing the IGC root through the section of the specimen, when the IGC meets the Si crystal, it is ceased to development. At the same time, the boundaries between Mg2Si and matrix is cracked ahead.

Figure 5. The generated IGC for the 6082-T6 aluminum alloy, (a) the networks of the corrosive surface, (b) corrosion development root at the section.

The IGC is essentially one kind of the electro-chemical corrosions. The corrosion potentials of Mg2Si, α-Al matrix, and Si in the sodium chloride solution are as sequential as -1.160, -0.876, and -0.547SCE/V shown in Table 2 [20], respectively, meaning the Mg2Si and Si exhibit the lowest and highest corrosion potentials individually. The potential differences among the phases must show the different corrosion characteristics. For example, as the potential of α-Al matrix is lower than that of the Si, the α-Al matrix would be dissolved anodically when they constitute the micro-galvanic cell. Besides, the Mg2Si phase will be dissolved firstly when Mg2Si and α-Al matrix form the micro-galvanic cell as the potential of Mg2Si is lower than that of α-Al.

Table 2. The corrosion potentials of α-Al matrix, Mg2Si and Si in the sodium chloride solution [20]

| phases    | α-Al   | Mg2Si  | Si   |
|-----------|--------|--------|------|
| Ecorr, SCE/V | -0.876 | -1.160 | -0.547 |

In a summary, the corrosion initiates at the bigger solidified Mg2Si and/or small granular precipitates β’-Mg2Si, and then, when corrosive cracks developed and occasionally met with the grain or sub grain boundaries, the corrosive cracks will further propagate along the grain boundaries as the electrode potential β’-Mg2Si are lower than that of the PFZ. In addition, as the granular β’-Mg2Si are continuously precipitated along the grain boundaries, the corrosive crack would follow the grain boundaries, leading to the formation of corrosive crack networks, the IGC. Besides, in this test, we do not observe the corrosion happened in the boundaries between the Si and α-Al matrix (shown in Figure 5(b)). It can be predicted as follows that, although the literature [21-22] mentioned that, there is a chemical potential difference between Si and α-Al matrix. But, as every series of the 6082 aluminum alloy have their own specific compositional proportions, different materials have their own specific potentials of Si and α-Al. In this case, the potential difference between Si and α-Al must be smaller. As a result, we cannot observe the α-Al matrix dissolution between the boundaries of Si and α-Al matrix.

4. Conclusions

Through the systematic analysis of the electro-chemical, corrosion and its IGC mechanism of 6082 alloy using the OM, SEM, TEM-EDS and EBSD, it can be concluded as follows.
5. References

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