Application of Color Metallography on As-cast Al-Mg-Si-Cu-Mn Alloy during Heat Treatment

Xiaoguo Wang¹², Jian Qin²³*, Fangzhen Liu²³, Yifeng Li²³ and Hiromi Nagaumi²³

¹College of Engineering, Shanxi Agricultural University, Taigu, Shanxi, 030801, China
²High Performance Metal Structural Materials Research Institute, Soochow University, Suzhou, Jiangsu, 215021, China
³Shagang School of Iron and Steel, Soochow University, Suzhou, Jiangsu, 215021, China

*Corresponding author’s e-mail: james.qin@suda.edu.cn

Abstract. Color etching was performed to characterize microstructure evolution and phase transformation on as-cast and homogenized Al-Mg-Si-Cu-Mn alloys. Initial intermetallic phases in microstructure of as-cast Al-Mg-Si-Cu-Mn alloy are mainly composed of primary Mg2Si, α-Al(FeMn)Si and quaternary Q phase. Post-etching microstructure of as-cast alloy presents a typical dendritic morphology with distinctive intermetallic distributions. Micro-segregation of solute elements are visualized as color difference within grains. Q phase is mainly located between the dendrite arms, while Mg2Si and α-Al(FeMn)Si are arranged along the grain boundaries. Heterogeneous nucleation sites provided by Al3Ti during solidification are also observed and identified at the core of grains. The distribution of alloying elements and intermetallic exhibited by color micrograph presents a good agreement with outcomes of EPMA. The color metallography of etched sample reveals the distribution of α-Al(MnCr)Si dispersoids and dispersoids free zone (DFZ), after the alloy is subjected to two-step homogenization. Micro-segregation of solute elements within solid solution is dramatically eliminated, associated with reduction of color difference. The dissolution of primary Mg2Si and Q phase during two-step homogenization are also directly detected. Therefore, color etching is an effective and reliable auxiliary approach to reveal microstructural evolution and phase transformation of as-cast Al-Mg-Si-Cu-Mn alloy during homogenization process.

1. Introduction

Color etching has been proved to be a not only feasible but also effective approach to real microstructural characterizations of materials during different stages. A film with thickness of hundreds of microns was developed on the surface of color etched sample, which causes light interference under optical microscope and yields to color difference. It was reported that the color variation was related to distribution of chemical compositions [1] and grain orientation[2]. B. Suárez-Peña et.al [3] pointed out that electrochemical potential difference ascribed to micro-segregation of alloying elements intensified the color difference of post-etching samples.

Al-Mg-Si-Cu-Mn alloys (6XXX) are in great demand due to their excellent mechanical properties and environment-friendly recyclability, making them appealing to various industrial applications,
including electrical power transmission and transportation [4,5]. As it is known to all, 6XXX alloys are
typical heat-treatable wrought alloys and subjected to homogenization, solution as well as aging heat
treatments. During these heat treatment processes, multiple phase transformations took place associated
with diffusion and aggregation of solute atoms, such as dissolving of primary Mg_2Si and Q,
transformation of β-AlFeSi to α-Al(FeMn)Si, precipitation of α-Al(MnCr)Si dispersoids and β.
Therefore, it is urgent to efficiently and quickly characterize microstructural evolution during different
heat treatments.

The present study aimed to use color etching reagent to (5g KMnO_4+1g NaOH+100ml water) detect
micro-segregation of alloying elements, reveal distribution of second phases in as-cast Al-Mg-Si-Cu-
Mn alloy and characterize transformation of second phases as well as precipitation of dispersoids during
homogenization treatment.

2. Experimental
In this study, the studied Al-Mg-Si-Cu-Mn ingots with 150 mm in diameter were manufactured by direct
chill casting. The Al-Mg-Si-Cu-Mn alloy’s chemical composition were detected by SPECTROLAB
optical emission spectroscopy and listed in Tab.1. Samples (15mm×15mm×8mm) were taken from the
half center of the ingots. An optimized two-step homogenization heat treatment (Fig.1) were applied on
the samples to alleviate micro-segregation and precipitate Mn/Cr containing dispersoids.

All samples were prepared by standard metallographic procedures. Afterwards, the samples were
immersed in color etching reagent for around 15 s at ambient temperature or 0°C. For comparison, the
homogenized samples were etched using both 0.5% HF solution and color etching reagent. The
microstructure of as-cast and homogenized samples was characterized by Olympus GX53 optical
microscope without any filter in light-field mode. Additionally, the microstructure of as-cast Al-Mg-Si-
Cu-Mn alloy was investigated via back scattered electron imaging (BSE), electron probe micro-analysis
(EPMA) and energy disperse spectroscopy (EDS) to show the micro-segregation of solute elements and
identify the types of intermetallic phases. EPMA tests were conducted at acceleration voltage of 15 kV
with beam current of 100 nA. Subsequently, the EPMA and EDS data were compared to that of color
etching to validate the effectiveness of color etching.

![Figure 1. Schematic diagram of two-step homogenization heat treatment](image)

3. Results and Discussions

3.1 The as-cast microstructure before and after etching
The microstructures of as-cast Al-Mg-Si-Cu-Mn alloys before and post etching are illustrated in Fig.2.
As labelled in Fig.2a, there are mainly three different intermetallic phases: round Q phase as well as
primary Mg_2Si and α-Al(FeMn)Si along grain boundaries. The corresponding EDX results of the
intermetallic phases are listed in Tab.2. Unlike microstructure prior to etching, significant color contrast
can be observed after the same alloy is color etched, as is shown in Fig.2b. It is reported [2,7] that the
color contrast is resulted from micro-segregation of alloying elements. Additionally, it is noticed that there are light areas around intermetallic phases with similar shape of those phases, which is owing to solute atom depletion. This phenomenon helps to locate and distinguish the different types of intermetallic phases in the as-cast Al-Mg-Si-Cu-Mn alloy.

Table 1. Chemical composition of Al-Mg-Si-Cu-Mn alloy (wt.%)

| Element | Si  | Mg  | Cu  | Mn  | Cr  | Ti  | Fe  | Al  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Composition | 1.12 | 0.79 | 0.59 | 0.74 | 0.19 | 0.04 | 0.06 | Bal. |

3.2 Identification of heterogeneous nucleation sites

To slow down the color etching rate, the as-cast alloy was etched at 0°C for 15s. Normally, it is hard to observe the shape of dendritic phase without color etching. However, interestingly, the typical dendritic shape of Al phase are clearly revealed with distinguishable dendrite arms as well as grain boundaries, as marked in Fig. 3a. Comparing Fig. 3a with the BSE result of color etched Al-Mg-Si-Cu-Mn alloy, it can be seen that there is a strong connection between the color difference revealed by color etching and distribution of solute atoms, since color difference are observed inside one single dendritic grain. Furthermore, intensified color contrast at the core of the marked grain is noticed at both OM and BSE of color etched Al-Mg-Si-Cu-Mn alloy. EDX was carried out to confirm the chemical composition of the core part within grains and the corresponding outcomes are exhibited in Tab. 3. The results indicate that Ti concentration is much higher at the core than in the other regions to form Al₁Ti and act as a heterogeneous nucleation site during casting, which is consistent with the research of Li [7]. Therefore, it is reasonable to assume that the observed color difference in dendritic grain mainly associates with micro-segregation of Ti element.
Table 2. EDX results of intermetallic phases in as-cast Al-Mg-Si-Cu-Mn alloy (wt.%)

| Phase        | Si  | Mg  | Cu  | Mn | Fe | Cr | Al  |
|--------------|-----|-----|-----|----|----|----|-----|
| Q            | 19.16 | 1.56 | 22.02 | -  | -  | -  | 57.27 |
| Al(MnFe)Si   | 8.62  | -   | -   | 16.37 | 5.14 | 2.63 | 67.23 |
| Mg2Si        | 27.14 | 28.71|     |     |    |    | 44.16 |

Table 3. EDX results of core part within grains

| Elements | Atomic concentration (%) | Mass concentration (%) |
|----------|--------------------------|------------------------|
| Al       | 72.10                    | 59.30                  |
| Ti       | 27.90                    | 40.70                  |

3.3 EPMA analysis of as-cast Al-Mg-Si-Cu-Mn alloy

The studied alloy contains a variety of elements. In order to further determine the relationship between the color difference of etched samples and micro-segregation of alloying elements, EPMA analysis was carried out. Solute distributions of Mg, Si, Cu, Mn, Cr and Fe in a dendritic grain are presented in Fig.4.
Figure 4. BSE images with corresponding element distribution maps of as-cast sample

Fig.4 (b) and (c) indicate that both Mg and Si elements mainly distribute at eutectic particles and interdendritic regions, rather than dendritic areas. Cu and Fe elements tend to concentrate in Q and eutectic phase, respectively, as shown in Fig4 (d) and (g). Mn and Cr elements are found to be rich in dendritic areas, which matches the visualized dendritic morphology of color etched as-cast alloy. Thus, micro-segregation of Mn and Cr elements can be held accountable for color difference of etched samples.

3.4 Microstructures of homogenized alloys post etching

The studied Al-Mg-Si-Cu-Mn alloys were subjected to two-step homogenization heat treatment (300°C*8h+550°C*10h). For comparison, the homogenized alloys were etched by 0.5% HF solution and color reagent at ambient temperature.

Figure 5. Microstructures of homogenized alloys etched by (a) 0.5% HF solution and (b) color reagent

It is known that 0.5% HF solution is commonly applied to characterize dispersoids’ distribution in 6XXX [8,9] and 3XXX [10,11] Al alloys. As illustrated in Fig.5a, it reveals high-density dispersoids and DFZ around intermetallic phases when the homogenized alloy was etched in 0.5% HF solution. Yet,
the microstructure fails to provide more information about the homogenized alloy.

After color etching, the alloy reveals sharper color contrast. Besides, grain boundaries are clearly visible, which is not shown in Fig.5a. Primary Mg2Si and Q phase, which exist in as-cast alloy, are undetectable in Fig.5b. Another noteworthy phenomenon is that the color difference that appears after as-cast alloy is color etched disappears, which indicates the elimination of micro-segregation due to diffusion of solute atoms during homogenization heat treatment. (Fig.5b), the microstructure also reveals high-density dispersoids and DFZ, but with more clarity.

Figure 6. (a) TEM image of homogenized alloy and (b) EDS of dispersoids

TEM was conducted to identify the morphology and composition of the observed dispersoids in Al-Mg-Si-Cu-Mn alloy. It can be seen from Fig.6a that the dispersoids mainly consists of two shapes: plate-shaped (marked by red arrows) and cubic-shaped (marked by yellow arrows). Based on quantitative analysis of TEM image of dispersoids in studied alloy, the average equivalent diameters were determined as 121±23 nm. Fig.6b shows the EDS results of the dispersoids. Though Cu is detected, Cu is not considered as certain element in dispersoids [12,13]. Thus, based on the morphology observation [14] and composition analysis, the dispersoids were identified as α-Al(MnCr)Si dispersoids [15].

4. Conclusion

(1) After color etching, color differences related to element micro-segregation appear in the microstructure of as-cast Al-Mg-Si-Cu-Mn alloy, which facilitates detection and localization of intermetallic compounds.

(2) It is easy to identify heterogeneous nucleation sites provided by Al3Ti, when the as-cast Al-Mg-Si-Cu-Mn alloy is color etched.

(3) The color difference shaped as dendritic structure should be related to the micro-segregation of Ti, Mn and Cr elements.

(4) Not only clear distributions of α-Al(MnCr)Si dispersoids and DFZ, grain boundaries can also be observed by color etching for homogenized Al-Mg-Si-Cu-Mn alloy. In addition, color etching can also characterize the degree of micro-segregation and evaluate the microstructural evolution of the alloy during homogenization heat treatment.

In summary, color etching can be used as an effective method for characterizing microstructural evolution and phase transformation of as-cast Al-Mg-Si-Cu-Mn alloy during homogenization process.

Acknowledgements

The authors acknowledge the financial support provided by Startup Project of Doctor Scientific Research of Shanxi Agricultural University ((No. 2020BQ80) and National Natural Science Foundation of China (Grant No. U1864209).

References

[1] C.F Yeung; H Zhao; W.B Lee (1998). The Morphology of Solidification of Thin-Section Ductile Iron Castings., 40(4-5): 201-208.
[2] P. J. Szabó; A. Bonyár (2012). Effect of grain orientation on chemical etching. 43(2-3): 349-351.
[3] B. Suárez-Peña; J. Asensio-Lozano (2006). Influence of Sr modification and Ti grain refinement on the morphology of Fe-rich precipitates in eutectic Al–Si die cast alloys. Rev. Metal., 54(9):1543-1548.

[4] T. Sakai, A. Belyakov, R. Kaibyshev. (2014). Dynamic and post-dynamic recrystallization under hot, cold and severe plastic deformation conditions. Progress in Materials Science, 60: 130-207.

[5] L. Donati, A. Segatori, M. El Mehtedi, L. Tomesani (2013). Grain evolution analysis and experimental validation in the extrusion of 6XXX alloys by use of a lagrangian FE code. International Journal of Plasticity, 46: 70-81.

[6] S.A. Kulinich; A.S. Akhtar; P.C. Wong; K.C. Wong; K.A.R. Mitchell (2007). Growth of permanganate conversion coating on 2024-Al alloy., 515(23), 8386-8392.

[7] G Li (2014). Color metallography of Al alloys using Weck’s reagent: applications and coloring mechanism Tokyo Institute of Technology: 20-30.

[8] Strobel K, Sweet E, Easton M, Nie JF, Couper M. (2010) Dispersoid Phases in 6xxx Series Aluminium Alloys.Materials Science Forum, 654-656

[9] Qian X, Parson N, Chen XG. (2019) Effects of Mn addition and related Mn-containing dispersoids on the hot deformation behavior of 6082 aluminum alloys. Materials Science and Engineering: A, 764: 138253

[10] Y.J. Li; A.M.F. Muggerud; A. Olsen; T. Furu (2012). Precipitation of partially coherent α-Al(Mn,Fe)Si dispersoids and their strengthening effect in AA 3003 alloy., 60(3): 1004–1014.

[11] Li Z, Zhang Z, Chen XG. (2017). Microstructure, elevated-temperature mechanical properties and creep resistance of dispersoid-strengthened Al-Mn-Mg 3xxx alloys with varying Mg and Si contents. Materials Science and Engineering: A, 708: 383-394.

[12] E.L. Huskins; B. Cao; K.T. Ramesh (2010). Strengthening mechanisms in an Al–Mg alloy., 527(6): 1292-1298.

[13] Y. Xu, H. Nagaumi, Y. Han, G.W. Zhang (2017). The Deformation Behavior and Microstructure Evolution of a Mn- and Cr-Containing Al-Mg-Si-Cu Alloy During Hot Compression and Subsequent Heat Treatment. Metallurgical and Materials Transactions A, 48(3), 1355-1365.

[14] L. Lodgaard; N. Ryum (2000). Precipitation of dispersoids containing Mn and/or Cr in Al–Mg–Si alloys. Materials Science and Engineering A, 283(1-2): 144-152.

[15] G.W Zhang, H. Nagaumi, Y. Han, Chad M. Parish, T.G Zhai (2016). Effects of Mn and Cr Additions on the Recrystallization Behavior of Al-Mg-Si-Cu Alloys. Materials Science Forum, 877: 172-179.