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Microstructural characterization of aluminum alloys using Weck's reagent, part II: Coloring mechanism

Li Gao [a], Yohei Harada [b], Shinji Kumai [b,*]

[a] Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan
[b] Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8550, Japan

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ABSTRACT

This paper is the second part of the study focusing on the color metallography using Weck's reagent for Al alloys. Following the first part of the study which demonstrated a wide application of Weck's reagent, this paper investigates the coloring mechanism of color etching with Weck's reagent in detail by various characterizations of the specimen surface after etching. The results show that after the Al specimen is etched with Weck's reagent, a thin film consisting of Mn oxide is formed on the surface with different morphologies and thicknesses from location to location, which causes different colors observed by optical microscopy correspondingly. Further investigations show that the film is characterized by a relatively smooth surface but a rough interface with the substrate. Such structure may cause interference of light reflected from different sites. The growth of film is strongly influenced by the solute micro-segregation in the Al phase. Film starts to form first on the area with higher solute (Ti) concentration. As the etching time increases, film also grows on other areas. 12 s etching yields to the best color contrast because the difference in the film morphology and thickness is the most obvious at this time.

1. Introduction

As a color etchant, Weck's reagent was developed by Weck and Leistner in 1980s for alloys including Al alloys. After etching Al alloys with Weck's reagent, the microstructure observed under an optical microscope (OM) become colorful. According to Weck and Leistner, those different colors represent micro-segregations in Al phase although no convincible prove was provided. In our recently published paper [1] dealing with micro-segregations in semi-solid processed A356 Al alloy, we have successfully proved that the micro-segregations of Ti in Al phase has a strong correlation with the color difference revealed by Weck's reagent. The diffusion coefficient of Ti in Al is extremely low so that the micro-segregation of Ti can be preserved after semi-solid treatment. This find is very important because it implied that using Weck's reagent, solute micro-segregation can be conveniently visualized which used to be done by mapping of electron probe micro-analysis (EPMA).

In the first part of this study [2], we have already found more applications of Weck's reagent for Al alloys besides A356 Al alloy, as well as the fact that micro-segregations of solutes such as Si and Mg can also cause the color difference. As a continuance of the first part, the second part of this study focuses on coloring mechanism. We want to know why the microstructure turned colorful after etching. Recently, some coloring mechanisms of color etchants for alloys have been studied [3–12]. In those studies, the surface morphology has been proved to be the key factor that produces the color after etching. Before the present study, Suárez-Peña et al. [13] has supposed that a MnO_2 film is formed during etching via the following chemical reaction:

$$Al + MnO_4^- + 2\,H_2O \rightarrow Al(OH)_4^- + MnO_2. \quad (1)$$

In the protective coating industry, this chemical reaction is known as the permanganate conversion coating (PCC) of Al alloys as a substitute of chromate conversion coating (CCC) since the later one produces toxic Cr (VI). However, due to the lack of experimental confirmation, as well as the fact that the solution for PCC is different from Weck's reagent, we can still not assert that MnO_2 film is formed after etching by Weck's reagent.

In this part of the study, we carried out various observations and analyses of the specimen surface which was etched with Weck's reagent. Through these experiments, we characterize the morphology and the composition of the etched surface. Based on these experimental results, we propose the coloring mechanism of Weck's reagent and

* Corresponding author.
E-mail addresses: gao.l.ab@m.titech.ac.jp (L. Gao), harada.y.ah@m.titech.ac.jp (Y. Harada), kumai.s.aa@m.titech.ac.jp (S. Kumai).

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Table 1
Main chemical compositions of the materials used in this research (wt.%).

Alloy	Si	Mg	Fe	Ti	Sr	Mn	Al
Ti-contained A356	6.90	0.39	0.10	0.14	0.025	<0.10	Bal.
Ti-free A356	7.04	0.43	0.13	0.0006	0.0024	0.006	Bal.

furthermore discuss the influence of the solute micro-segregation and etching time on the coloration.

2. Experimental

2.1. Materials and process

There are two kinds of A356 aluminum alloy billets used in this research, one with 0.14 wt.% Ti included and the other free of Ti. Their chemical compositions are indicated in Table 1. The Ti-contained A356 billet was direct-chill cast and supplied by Kyushu Mitsui Aluminium Co., Ltd, while the Ti-free A356 billet was cast in a ship-shaped Cu-mold and provided by Nissan Motor Co., Ltd. The reason for using these two Al alloys is that in the first part of this study [2], Ti was found to increase the color contrast after etching by Weck's reagent. This phenomenon will be further investigated in this paper.

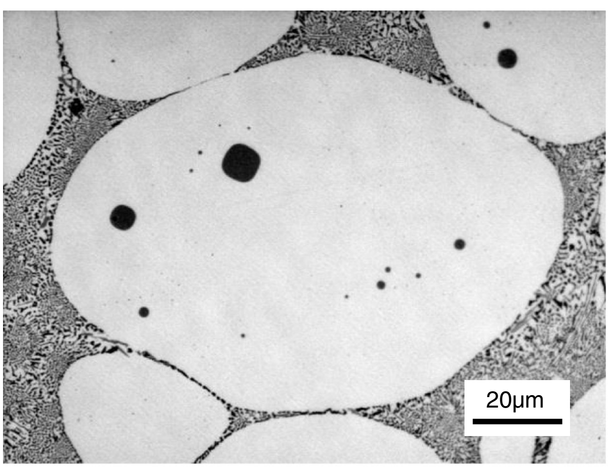

Fig. 1. A spheroidal Al grain in Ti-contained A356 Al alloy observed by optical microstructure before (a) and after (b) etching with Weck's reagent.

As a specialty of our study, not only the conventional microstructure containing dendritic Al phase, but also the microstructure with spheroidal Al phase is characterized using Weck's reagent. The spheroidal Al phase is obtained by a deformation-partial re-melting process. In order to induce plastic deformation to the billets, they were compressed at room temperature. Compression was carried out axially by a 500 ton compressing machine. The compressing rate is 0.2 mm/s. The billet's temperature was increased to about 44 °C when the target height (100 mm, 33% reduction) was reached.

Small specimens were cut from the compressed billet and heated to semi-solid state. Once the temperature of specimen reaches 581 °C, specimen was quickly water quenched. The solid fraction of A356 Al alloy at 581 °C is about 0.5 according our previous investigation [14].

2.2. Etching and optical microstructure observation

Specimens were polished via standard metallographic techniques, finished using Struers OPS colloidal silica. Subsequently, specimens were immersed in Weck's reagent for approximately 12 s at room temperature. Then the microstructure was observed by optical microscopy (OM) without any filters or analyzers. In order to study the influence of etching time, one specimen was etched for five times, for 4 s, 8 s, 12 s, 20 s and 28 s. Before each time of etching, slight polishing of the previous etched surface was done to remove the etching layer. The micrographs were taken for the same location in the specimen.

2.3. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM)

Imaging with secondary electrons by both SEM and FE-SEM was applied to characterize the etched surface. The accelerating voltage was set at 5 kV. FE-SEM (accelerating voltage is set at 12 kV) was used for observations with higher resolution at high magnifications. Different locations within one spheroidal Al grain were observed in terms of their surface topography.

2.4. Laser microscopy and atomic force microscopy (AFM)

Both Keyence VX-200 laser microscope and Olympus OLS4500 Nano search microscope with AFM function were used to characterize the etched surface. Both of these two microscopes are able to accurately select a certain area to observe with the help of an optical microscope equipped together. The surface average roughness (R_a) of a selected area can be measured by both these two microscopes and the results were compared with the color expressed in RGB values obtained by a VX-200 laser microscope.

2.5. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM)

A high-voltage electron microscopy (HVEM) using a Hitachi H1250 microscope operated at 1000 kV was used for TEM observation. The observation was carried out with the observation angle vertical to the etched surface. The TEM specimen was made by first mechanically polishing the alloy side of the specimen to less than 100 μm and then electro polishing ($HClO_4$:C_2H_5OH = 3:7, 13 V) until a tiny hole appeared on the surface. Diffraction pattern was also taken. In the case of STEM, a JOEL JEM-2100F microscope operated at 200 kV was used. In the beginning, carbon was deposited on the etched surface to protect the surface. Then, a focused ion beam (FIB) was used to slice a small specimen vertical to the surface, namely a

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