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Transmission Electron Microscopy Characterization of High-Temperatur Oxidation of Fe-20Cr-5Al Alloy Prepared by Focused Ion Beam Technique

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Abstract

The Focused Ion Beam (FIB) technique was applied for cross section preparation of the oxidized alloy for Transmission Electron Microscopy (TEM) study. Prior to preparation, the specimens of Fe-20Cr-5Al alloy sheet were oxidized in air at 1200 ^{o}C for 2 minutes, 10 minutes, 2 hours, and 100 hours. The microstructure and elemental composition of the samples were characterized using TEM equipped with an Energy Dispersive X-Ray Spectroscopy (EDX). The Electron Energy Loss Spectroscopy (EELS) was used to determine of the light elements. The TEM investigation reveals remarkable microstructure evolution of the specimens during oxidation which generally exhibit a typical multi-layer structure. The TEM images, however, can provide detailed description about the phases occur after oxidation such as the Tungsten (W) and the Gallium (Ga) layers on top of the samples obviously formed during FIB preparation, the formation of Al_2O_3 and Cr_2O_3 layer, $MgAl_2O_4$ spinel, porosity, Zr/Hf/Mg phases or clusters inside the oxide scale. Hence, the FIB technique has been proven to be reliable preparation technique for microstructural and elemental studies of Fe-20Cr-5Al alloy using TEM.

Abstrak

Karakterisasi TEM pada Paduan Fe-$_{20}$Cr-$_{5}$Al Oksidasi Temperatur Tinggi Menggunakan Teknik Preparasi FIB. Teknik Berkas Ion Terfokus atau *Focused Ion Beam* (FIB) diterapkan untuk persiapan melintang (*cross section*) aloi teroksidasi jenis Fe-20Cr-5Al untuk kajian Mikroskop Transmisi Elektron atau *Transmission Electron Microscopy* (TEM). Sebelum persiapan dilakukan, spesimen lembar aloi Fe-20Cr-5Al dioksidasi di udara pada suhu 1200 ^{o}C selama 2 menit, 10 menit, 2 jam, dan 100 jam. Struktur mikro dan komposisi elemen dari sampel tersebut dianalisis menggunakan TEM yang dilengkapi dengan Spektroskopi Sinar-X Energi Dispersif atau *Energy Dispersive X-Ray Spectroscopy* (EDX). Spektroskopi Kehilangan Energi Elektron atau *Electron Energy Loss Spectroscopy* (EELS) digunakan untuk menentukan elemen cahaya. Penggunaan TEM memperlihatkan evolusi struktur mikro yang luar biasa pada spesimen ketika oksidasi dilakukan, yang biasanya memperlihatkan struktur berlapis yang tipikal. Citra TEM memberikan deskripsi yang mendetail mengenai berbagai fase yang muncul setelah oksidasi, seperti lapisan Tungsten (W) dan Gallium (Ga) yang terbentuk di atas sampel selama masa persiapan FIB, pembentukan lapisan Al_2O_3 dan Cr_2O_3, spinel $MgAl_2O_4$, porositas, berbagai fase atau kelompok Zr/Hf/Mg di dalam skala oksida. Maka dari itu, teknik FIB telah terbukti sebagai teknik persiapan yang dapat diandalkan untuk meneliti struktur mikro dan elemen dari aloi Fe-20Cr-5Al dengan TEM.

Keywords: EELS, EDX, Fe-20Cr-5Al alloy, FIB, Oxidation, Preparation, TEM

1. Introduction

It is among the material scientists widely agreed that high quality ultra thin and defect free specimens are required for investigation of almost any materials down to atomic level by using of the Transmission Electron Microscope (TEM). New materials and their variations either in the compositions or in the art they are produced often behave differently during TEM specimen preparation. This requires new innovations in the

methods of specimen preparation instead of the very time consuming and complex conventional technique. Since its introduction in 1991 as a method of specimen preparation for TEM analysis, today Focused Ion Beam (FIB) has been become an important instrument in materials science, especially for fine structure studies down to atomic level [1].

Generally, the FIB works with the same principle as Scanning Electron Microscope (SEM), but it uses a very different beam source. Instead of using tungsten (W) filament or lanthanum hexaboride (LaB_6) tip which emits the electrons, a liquid Gallium (Ga) metal as ion source is used in FIB. During FIB operation, individual Ga ions are extracted and accelerated using a high voltage, usually up to 30 kV [2-4]. The Ga ion beam is focused by the electromagnetic condenser lenses onto a spot of less than 7 nm in diameter. Because of this, the FIB has a resolution comparable to that of a conventional SEM. Analogous to the SEM work, by means of a pair of scan coils, the Ga ion beam is scanned over the sample surface to produce image or by controlling the beam current to cut a thin lamellae of the sample at every interesting location. In the imaging mode, depending upon the polarity of the collector voltage of the detector, both secondary electrons and secondary ions can be detected. Secondary electrons are detected as they have a much better signal to noise ratio than secondary ions. Secondary ions, however, are used to produce images of materials, which exhibit only slight differences in composition across the specimen.

The FIB technique has several advantages such as the secondary electron (SE) imaging of the specimen, which can alternately be observed during milling. This enables the operator to locate the milled area precisely, to obtain high degree of accuracy in a specific area and produce high precision sample cross-sections. This technique also enables us to handle specimens of different material properties that are too fragile to be mechanically thinned and to reach large area of transparent specimens, which can be investigated by TEM. In their work, Dimyati et al. in [5,6] reported for the first time the application of FIB for HRTEM specimen preparation of layer system consisting of materials with very different hardness and chemical properties such as Zn galvanized high strength steels. Additionally, by many scientific works the FIB preparation has been proven to be the best TEM sample preparation technique with the fastest process time by relatively good results compared with conventional methods.

In the present paper, a specimen preparation technique using FIB workstation in conjunction with the study of Al_2O_3 layer formation on Fe-20Cr-5Al alloy will be described. Fe-20Cr-5Al alloy has been used for various applications, from fuel cell to nuclear power plant, as structure material. With addition of tiny rare earth oxide particles such as Yttria, this alloy becomes a well-known Oxide Dispersed Strengthened alloy with exceptionally high creep resistance at elevated temperature.

2. Experimental

Material. The material used in this work was commercial Fe-20Cr-5Al alloy provided by the Emitec GmbH as a sheet of 1 mm thickness. The chemical composition of the alloy is presented in Table 1. Some elements were counted to be the trace elements which were systematically added to the alloy in order to improve its oxidation properties at elevated temperature. The Fe-20Cr-5Al alloy is often found as the active elements (Pd, Ti) carrier material in catalytic converters of modern cars which is assumed to be the future candidate in substitution of the heavy and expensive ceramic substrate. After some standard pre-treatment and metalographic preparation the alloy specimens size of 10 mm x 10 mm were isothermally oxidized at 1200 ^oC for 2 minutes, 10 minutes, 2 hours, and 100 hours in a resistance heated furnace in ambient atmosphere. Detailed information about the preparation and oxidation experiment is described else where [7].

FIB Preparation. The TEM sample cross sections were prepared in FIB workstation, with the so called Lift-Out technique consisting the following steps. Firstly, the sample sheet was cut into pieces (0.5 mm x 1.5 mm) with a diamond wire saw and then mounted with a special adhesive on a circular washer with the oxide scale/substrate interface oriented to the Ga ion beam direction. The surface roughness was then removed with the focused Ga ion beam at low beam current. This was followed by amorphous tungsten deposition on the surface to form a cover layer up to 3 μm of thickness which aimed to protect the surface against destructive Ga ion bombardment and Ga implantation during milling. TEM lamellae was then produced by removing the left and right side material with ion beam at higher current. By adjusting the current density, the amount of material to be removed can be limited to the amount and area of the specimen required. The FIB mill procedure is described schematically in Figure 1 whereas the milling conditions are summarized in Table 2 [8,9].

Table 1. Chemical Composition in Mass (%) or Mass (ppm) of the Fe-20Cr-5Al Alloy Used in this Work

Fe	Cr	Al	Ni	Mg	Mn	Mo	Si	Y	Ti	Zr	Hf	S	N	C
(%)	(%)	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Base	20.10	5.68	1550	80	2040	60	900	600	35	33	340	2	2.1	23

Table 2. Conditions for Ga Ion Beam in FIB

Milling	Acc. Voltage (kV)	Beam Current (nA)	Beam Diameter (nm)
Rough	30	15	600
Medium	30	1.0	70
Fine	30	0.04	30

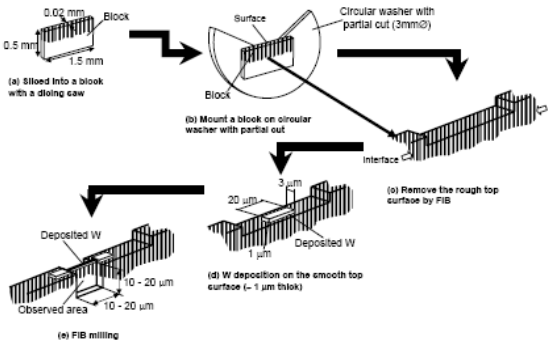

Figure 1. FIB Procedure for TEM Specimen Preparation [8,9]

Characterization. The characterization of the FIB lamellae was carried out using TEM JEOL FX2000 and FEI Tecnai F2 with electron acceleration voltage 200 kV for microstructure analysis at GfE-RWTH Aachen Germany. Both TEM were equipped with EDX detectors and EELS for determination of elements and their distribution.

3. Results and Discussion

Figure 2 shows TEM lamella of the Fe-20Cr-5Al sample after 2 hours of oxidation prepared using FIB technique as described above. The lamella was put on the surface of a thin carbon film inside the copper (Cu) TEM sample grid for TEM observation (Figure 2a). The related Brightfield TEM image of the sample is shown in Figure 2c.

The result shows that FIB technique was reliable to produce TEM specimens for microstructure study of Fe-20Cr-5Al alloy oxidation with sufficient large transparent area.

Figure 3 shows Brightfield TEM image and EDX spectrum of Fe-20Cr-5Al alloy sample after 2 minute of exposure. After 2 minute of oxidation at the temperature of 1200 ^{o}C, two layers of dense Al_2O_3 scale with the total thickness between 200 – 300 nm were formed. It might be α-Al_2O_3 as indicated by Selected Area Electron Diffraction (SAED) analysis. However, amorphous Ga layer with thickness about 53 nm on the top most surface was present. Large number of Cr_2O_3 particles distributed in the boundary between large and small Al_2O_3 grains parallel to the substrate/oxide scale interface could be clearly observed [10-12].

Figure 4 shows TEM brightfield image of Fe-20Cr-5Al alloy after 10 minutes of exposure. The W protective layer was located on top of the layer. After 10 minutes of exposure, the oxide scale reached a total thickness of about 500 nm. The inner part of the oxide scale showed

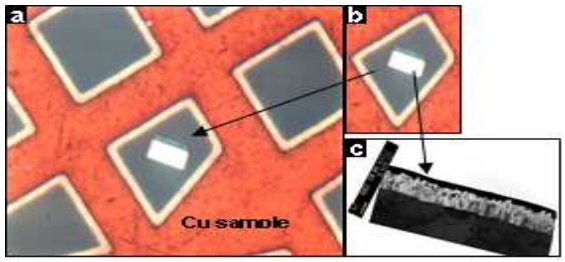

Figure 2. Light Microscope Images of TEM Lamella of the Fe-20Cr-5Al Alloy after 2 Hours of Isothermal Oxidation at 1200 °C in Air Prepared by Using FIB Technique Located in a Cu Sample Grid (a, b) and their Related Brightfield TEM Image (c)

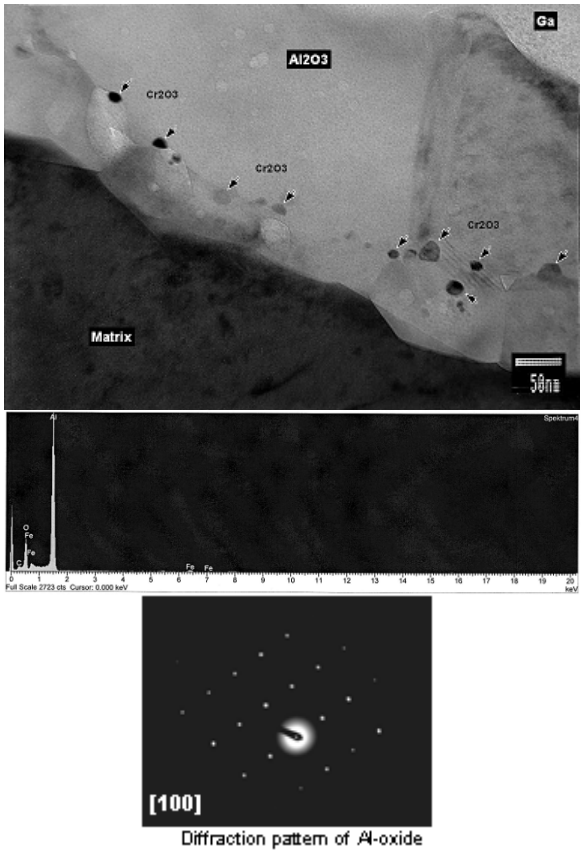

Figure 3. TEM Image, EDX and SAED Results of Fe-20Cr-5Al Alloy after 2-Minute of Exposure

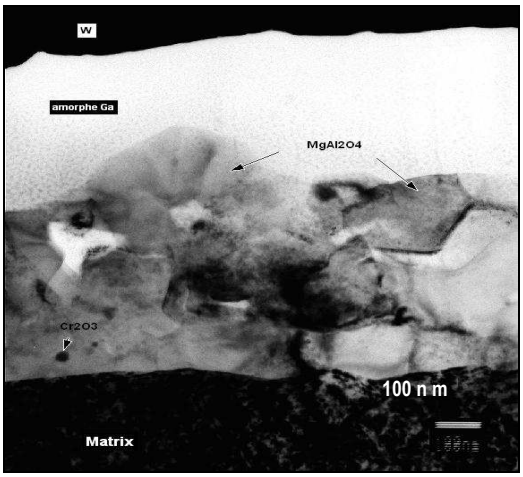

Figure 4. TEM Image after 10 Minutes Exposure

the same characteristic features, i.e. a layer of small Al_2O_3 grains terminating the oxide scale towards the matrix. This third layer was characterized by the occurrence of small voids with typical dimensions of 50–100 nm and the existence of $MgAl_2O_4$ spinel grains at the top near surface. The spinel grains had typical dimensions of 100 to 200 nm as, at high temperature, Mg diffused from the bulk alloy into the oxide scale and then reacted with existed Al-oxide. Small Cr_2O_3 particles can still be observed at grain boundaries near the matrix but with more reduced number compared to the sample after 2-minute oxidation. After the particles become embedded in the alumina scale, they tend to be dissolved, depending on the actual prevailing growth mechanism. The mechanism of Mg spinel formation and Chromium oxides dissolution is discussed in depth in different publication [13].

Figure 5 shows TEM images of FIB lamella of the Fe-20Cr-5Al alloy sample after 2-hour oxidation. The Al-oxide layer formation was confirmed by the EDX result and SAED analysis. The SAED showed characteristic hexagonal pattern of stable α-Al_2O_3. The microstructure of the oxide scale showed columnar structure indicating characteristic downward growing toward the substrate. The thickness of the oxide layer was measured to be 1.66 µm. The grains of Mg spinel at the top of the oxide layer were formed, as confirmed by the EDX result, as shown in Figure 5b. Additionally, SAED shows the typical cubic pattern of the Mg spinel indicating $MgAl_2O_4$ phase. The EELS analysis showed fine structure of K-edges of O, Mg, and Al, which confirmed the electronic bonding of $MgAl_2O_4$ phase. As shown in Figure 5c, in the EDX spectrum a trace of Si atoms was found. The cause of the existence of Si inside the dense alumina scale was unclear and needed further investigation. Cu also appeared in the EDX spectrum, possibly due to the diffracted X-ray signals from the TEM sample grid which was made of copper.

Figure 6 shows TEM image of Fe-20Cr-5Al alloy after 100 hours of exposure, in which additional phases containing Zr, Hf, and Y were observed mainly in the upper part of the stable α-Al_2O_3 scale. In addition, the presence of reactive elements (Zr, Y and Hf) in Fe-20Cr-5Al alloy had positive impact on the growth and formation of an Al_2O_3 scale [14, 15]. The EDX analysis qualitatively confirmed the existent of those elements.

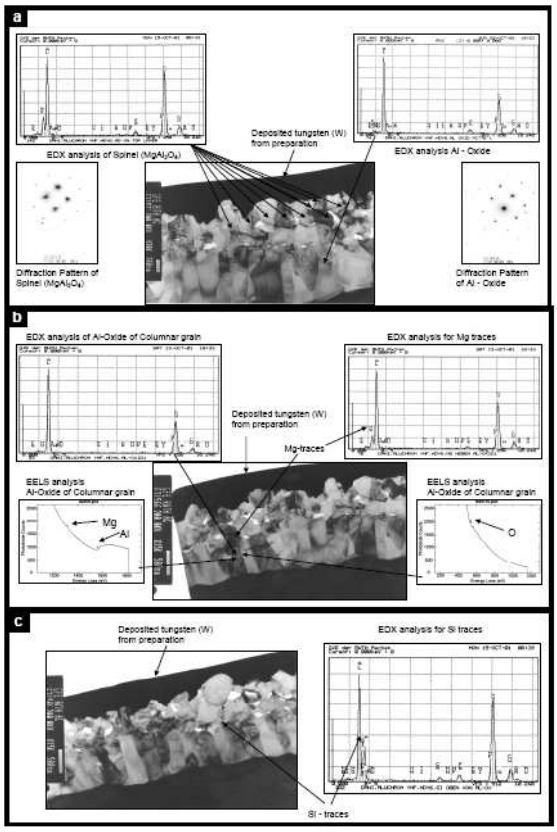

Figure 5. TEM Brightfield Image and EDX/EELS Spectra of the FIB Lamella of the Fe-20Cr-5Al Alloy after 2-Hour Oxidation

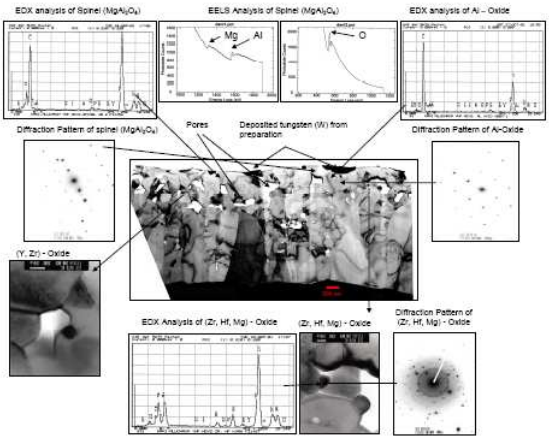

Figure 6. TEM Image and Analysis Results of Fe-20Cr-5Al Alloy after 100 Hours Exposure

Again the result of EELS analysis revealed the fine structure of the K-edges of O, Mg, and Al, indicating the presence of Mg spinel type $MgAl_2O_4$. The total thickness of the oxide layer was approximately 5.42 µm. The number of porosities increased significantly in the Mg spinel layer. It might be in correlation with phase transformations which may occur during oxidation, and this is in agreement with the results in [6].

4. Conclusion

The Focused Ion Beam (FIB) technique was applied for TEM specimen preparation of high temperature oxidation of Fe-20Cr-5Al alloy. All the FIB lamellae showed detailed insight into the microstructure on the entire interested area observable in TEM and almost defects free. The results of EDX and EELS analysis served undisputable results of elemental composition of the samples. It can be concluded that the FIB technique has proved its ability and reliability to produce TEM specimens for investigation of fine structure in the oxide scale on the Fe-20Cr-5Al alloy.

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