STUDY ON ALUMINA OXIDE LAYER GROWTH ON FeCrAl ALLOY USING A FOCUSED ION BEAM/TRANSMISSION ELECTRON MICROSCOPY SYSTEM

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ABSTRACT

STUDY ON ALUMINA OXIDE LAYER GROWTH ON FeCrAl ALLOY USING A FOCUSED ION BEAM/ TRANSMISSION ELECTRON MICROSCOPY SYSTEM. Study on alumina oxide layer growth on FeCrAl alloy has been done. Materials of FeCrAl alloy were isothermal oxidized at 1200°C in air for 2 minutes, 10 minutes, 2 hours, 20 hours, 100 hours, 600 hours and 1000 hours. Preparation of the specimens was carried out by using Focused Ion Beam (FIB) system. The specimens produced were characterized using Transmission Electron Microscope (TEM), Energy Dispersive X-Ray Spectroscopy (EDX), Electron Energy Loss Spectroscopy (EELS) and Electron Probe Microscope Analyzer (EPMA). The results show that after isothermal oxidation in increased period will result in increased thickness of oxide layer. Some elements found to be diffused from the matrix to outer part, in this case the oxide layer, to form oxide compound. The diffusion of Mg leads to the formation of spinel ($MgAl_2O_4$). Traces of Zr, Mg, and Si were observed.

Key words : Alumina oxide layer growth, focused ion beam system, transmission electron microscope

ABSTRAK

STUDI PERTUMBUHAN LAPISAN ALUMINA OKSIDA PADA PADUAN FeCrAl DENGAN MENGGUNAKAN SISTEM *FOCUSED ION BEAM/TRANSMISSION ELECTRON MICROSCOPY.* Studi pertumbuhan lapisan alumina oksida pada paduan FeCrAl telah dilakukan. Bahan paduan FeCrAl dioksidasi isothermal pada 1200°C di lingkungan udara selama 2 menit, 10 menit, 2 jam, 20 jam, 100 jam, 600 jam dan 1000 jam. Preparasi sampel dialakukan dengan menggunakan system *Focused Ion Beam (FIB)*. Spesimen yang dihasilkan kemudian dikarakterisasi menggunakan Mikroskop Elektron Transmisi (MET), *Energy Dispersive X-Ray Spectroscopy (EDX)*, *Electron Energy Loss Spectroscopy (EELS)*, dan *Electron Probe Microscope Analyzer (EPMA)*. Hasil yang diperoleh menunjukkan bahwa semakin lama waktu oksidasi isothermal, maka ketebalan lapisan oksida juga meningkat. Beberapa unsur diketahui berdifusi dari matriks menuju bagian luar, dalam hal ini, lapisan oksida, membentuk senyawa oksida. Difusi Mg membentuk spinel ($MgAl_2O_4$) dan beberapa bagian menunjukkan *trace* Zr, Mg, dan Si.

Kata kunci : Pertumbuhan lapisan alumina oksida, focused ion beam system, mikroskop elektron transmisi

INTRODUCTION

Several studies on advanced material for metal supported catalytic converter have been done. One of studied material was FeCrAl alloy. This material has superior oxidation resistance up to very high temperature. The application of FeCrAl alloys in industry is in large variety [1-3]. The recent application of FeCrAl alloys is for substrate material of modern car catalytic converter [4]. Thermally-grown, external Al_2O_3 thick films (or scales) play an important role in limiting the environmental degradation of many high temperature alloys. In general, Al_2O_3 scales are dense, relatively inert and slow-growing, and therefore protect the underlying metal from severe oxidation. To reach the stability of the converter for a long time, the alloy

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relies significantly on the thickness of the oxide, its scale growth rate, microstructure, and adherence [5].

In this paper, we will report the result from the study on alumina oxide layer growth on FeCrAl alloy after isothermal oxidation. The oxidation experiment on FeCrAl alloys were carried out at isothermal temperature of 1200 °C with the time exposure variations of 2 minutes, 10 minutes, 2 hours, 20 hours, 100 hours, 600 hours, and 1000 hours. The isothermal oxidation kinetics was measured by a Stearam Thermo Balance in synthetic air at that respective condition. The specimen oxide scale cross section were prepared by FIB technique [6-7], to reach large transparent area of the specimen which can be analyzed from the top of the oxide layer to the alloy matrix. For obtaining detailed information some characterizations were carried out by using TEM for microstructure analysis and diffraction pattern, EDX to determine elements distribution, EELS for determination of light element and oxygen, and EPMA to detect the elements and their distributions in the sample part, and grains as well as several types of oxide and carbide.

EXPERIMENTAL

Materials

The chemical composition of the studied FeCrAl alloy in mass % and mass ppm showed in Table 1. Specimens in size of 20 mm x 10 mm x 2 mm were abraded on the successive finer Si-C papers, and then mechanically polished with 1 μm diamond paste and then degreased ultrasonically in a detergent prior to oxidation. The specimens were then isothermal oxidized at 1200°C, for 2 minutes, 10 minutes, 2 hours, 20 hours, 100 hours, 600 hours, and 1000 hours.

Specimen Preparation Using FIB System

Specimen preparation using a FIB system is as described by T. Yaguchi et.al. [6-7]. The specimens were cut using a dicing saw into a piece of approximately 0.5 mm wide, 1.5 mm long, and 0.02 mm thick. The sliced block was mounted on a TEM specimen washer with partial cut, and then transferred to the FIB system. To prevent scale loss during TEM specimen preparation, the specimens were sputtered with a thin gold layer. The milling conditions are summarized in Table 2 [6-7].

Characterization

Characterizations were carried out by using 200 kV TEM for microstructure analysis and diffraction pattern, EDX to determine elements distribution, Electron Energy Loss Spectroscopy (EELS) for determination of light element and oxygen, and Electron Probe Micro Analyzer (EPMA) to observe the elements and their distribution.

RESULTS AND DISCUSSION

Figure 1 shows TEM images of FeCrAl alloy after 2 minutes exposure. Figure 1a shows Gallium (Ga) as ion source in FIB preparation clearly observed as layer on the top of the surface and Al-oxide layer was grew during isothermal oxidation. Cr-oxide scales were formed within and near the interface of oxide layer and matrix, while pore also formed near the interface as shown in Figure 1b. Their amounts were still relative small, however, they were spread almost homogenously.

Figure 2 shows the image of FeCrAl alloy after 10 minutes exposure. Tungsten (W) from sample preparation clearly shown on the top of the layer. The spinel ($MgAl_2O_4$) grains and Cr-oxide scale began to form within Al-oxide layer during exposure. The possible explanation for the spinel formation is that Mg diffused from the bulk alloy into the oxide scale, and then reacted with existed Al-oxide. Their amount and formation were not so different from the result after 2 minutes exposure.

Results from characterization and analysis of FeCrAl alloy specimen after 2 hours exposure will be shown in series of figures as follow. Figure 3a, b and c show TEM images of FeCrAl alloy after 2 hours exposure. The Al-oxide layer formation was confirmed by results from EDX analysis and diffraction pattern (in Figure 3a). The diffraction pattern shows that the Al-oxide has a hexagonal pattern. The thickness of the oxide layer was approximately 1.66 μm. The spinel ($MgAl_2O_4$) grains at the top of the oxide layer were formed, confirmed by The EDX analysis result, is shown

Table 1. Chemical compositions of the studied FeCrAl alloy in mass-% and mass-ppm.

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 Focused Ion Beam (FIB) system.

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

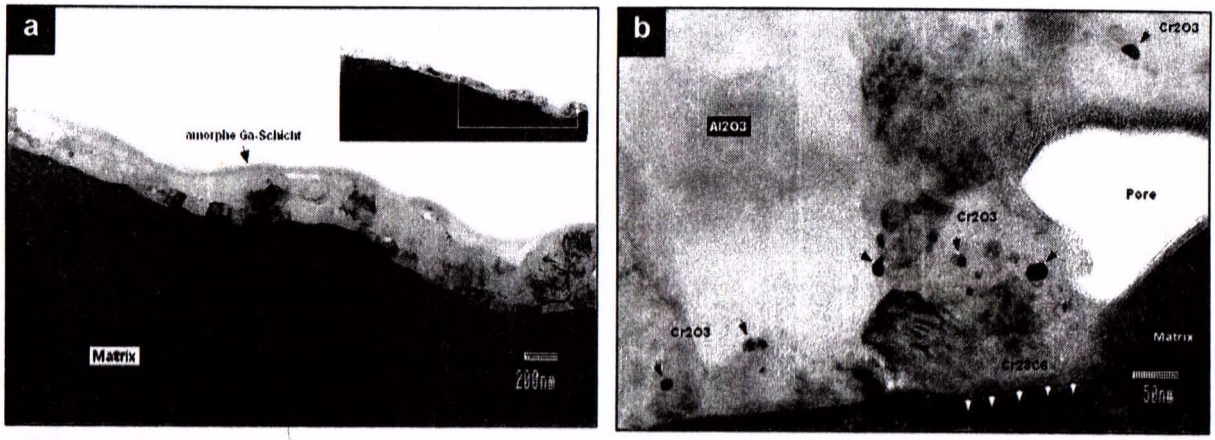

Figure 1. TEM images after 2 minutes exposure showing multi-layer of amorphous Ga, Al-oxide layer and matrix (a), and Cr-oxide scales and pore within Al-oxide layer (b).

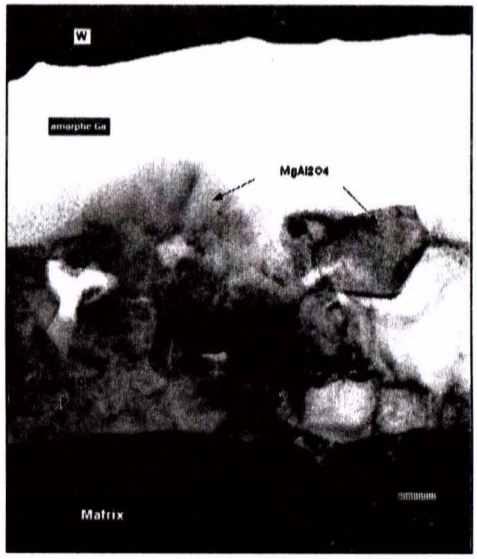

Figure 2. TEM image after 10 minutes exposure.

in Figure 3a. The result from diffraction mode shows the cubic pattern of the spinel. The order of detected elements from high to low was Al, Cu and Mg. The spinel was dominated by Al and Mg elements, and Cu was appeared due to the sample holder made of copper. In Figure 3b, the TEM image shows Mg traces and Al-oxide of columnar grain formed after 2 hours exposure as confirmed by the EDX and EELS analysis results. The result from EELS analysis shows detected K-edges of O, Mg and Al. In Figure 3c, the TEM image shows Si traces formed after 2 hours exposure as confirmed by the EDX result.

Figure 4 shows TEM image of FeCrAl alloy after 20 hours exposure, where Zr traces was observed and confirmed by EDX analysis result. Zr traces, seems likely, also diffused from the bulk alloy into Al-oxide scale. The thickness of the oxide layer was approximately 4.0 μm.

Figure 5 shows TEM image of FeCrAl alloy after 100 hours exposure, where (Zr-Hf-Mg)-oxide were observed. The EDX analysis and diffraction pattern results were obtained to confirm the observed (Zr-Hf-Mg)-oxide. The thickness of the oxide layer was approximately 5.42 μm.

Results from characterization and analysis of FeCrAl alloy specimen after 600 hours exposure will be shown in series of figures as follow. Figure 6a and Figure 6b show TEM images of FeCrAl alloy after exposure. The image shows that Y-C precipitates were clearly observed within the matrix. After isothermal oxidation, Hf/Zr-carbide diffused from the matrix to the oxide layer.

The Electron Probe Micro Analyzer (EPMA) analysis was carried out to observe the elements and their distribution. The results are shown in Figure 6c, Figure 6d and Figure 6e. The colored figure shows the distribution of each element. The dominated element is represented by the brightest parts or dots of each square of micrograph. In Figure 6c, the colored figure shows the element distribution, and gray-scale figure was shown as position reference. In Figure 6d, the analysis result of the overlap of Mg, Y, Zr, and Hf-oxide is also

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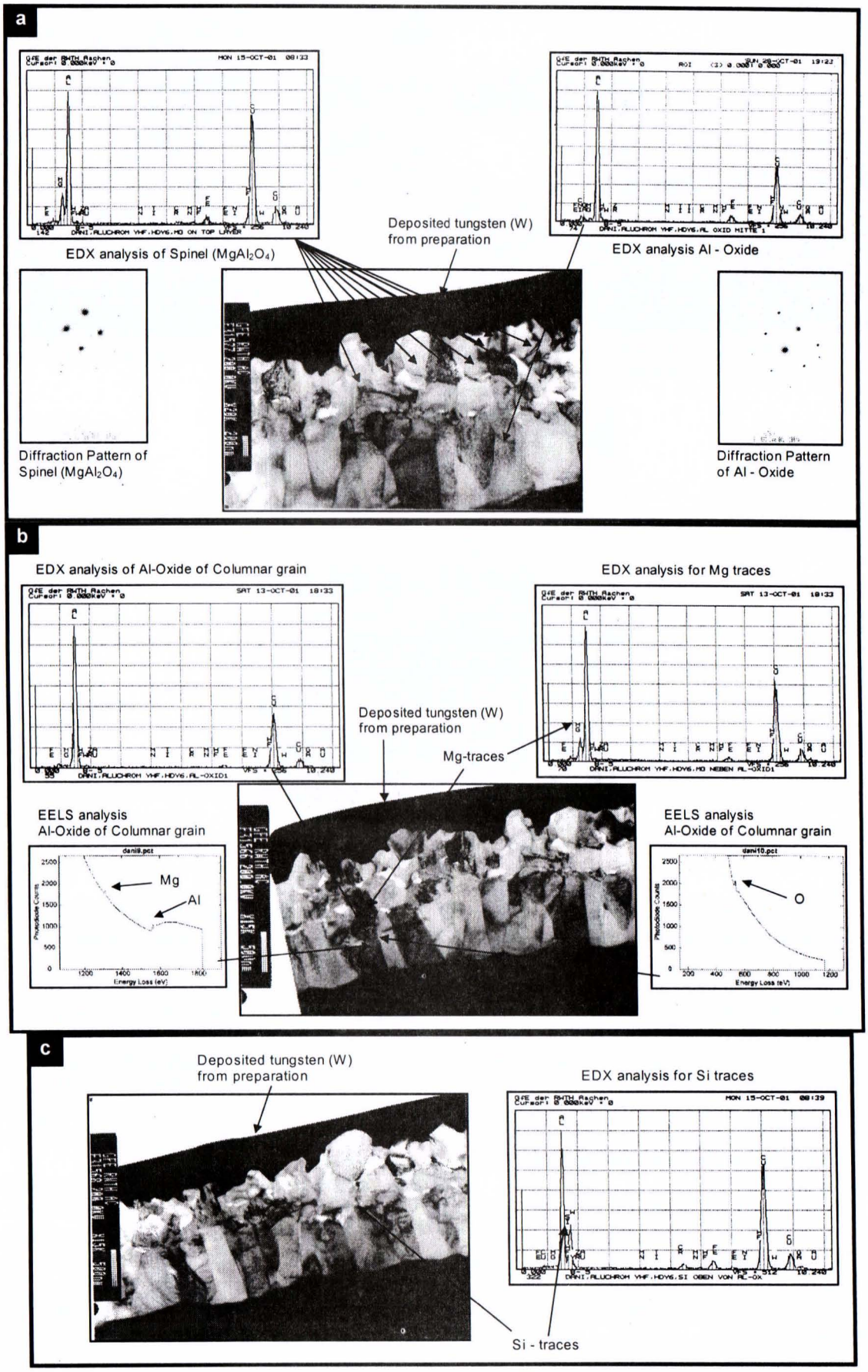

Figure 3. TEM images and analysis results after 2 hours exposure showing Al-oxide and spinel (a), Al-oxide of columnar grain and Mg traces (b) and Si traces (c).

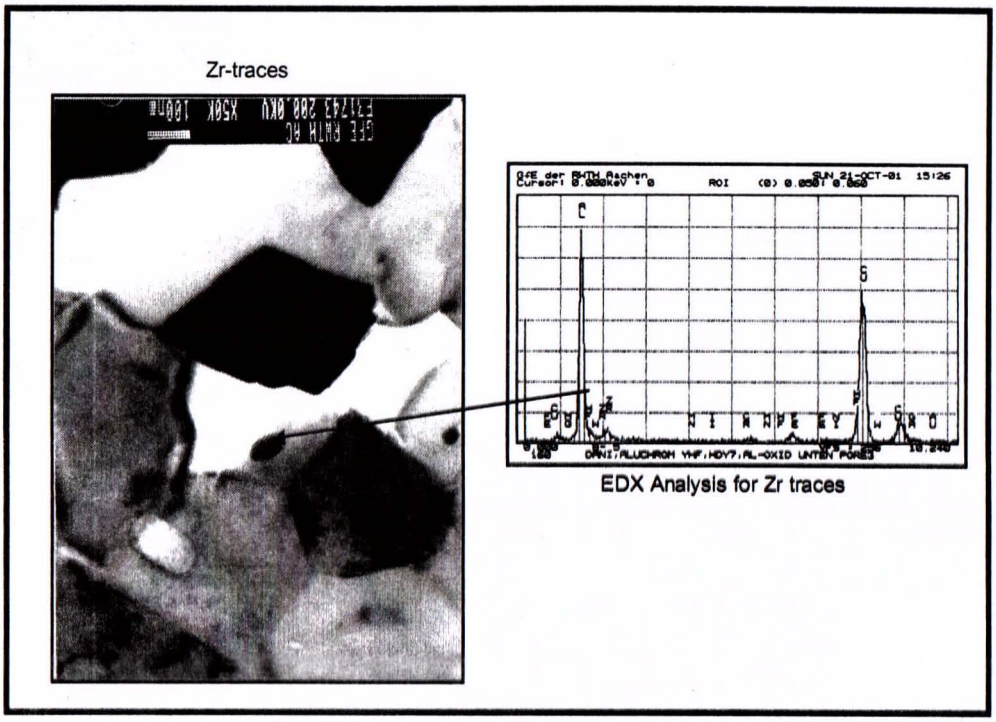

Figure 4. TEM image of FeCrAl alloy after 20 hours exposure and EDX analysis result of Zr-traces.

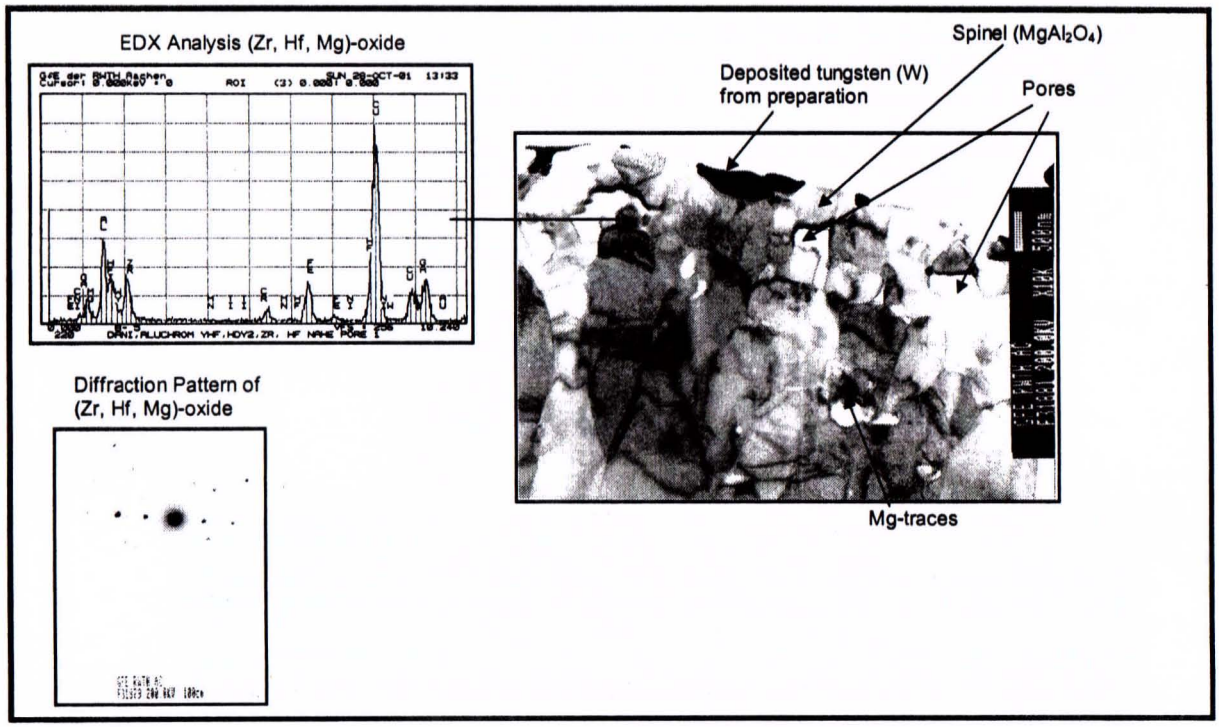

Figure 5. TEM image of FeCrAl alloy after 100 hours exposure and EDX analysis result of (Zr-Hf-Mg)-oxide.

presented. The micrograph also shows the interface between Al-oxide and spinel. Figure 6e shows the overlap of Zr, Hf-carbide and the interface between Al-oxide and substrate (FeCrAl).

Figure 7 shows the TEM images of FeCrAl alloy after 1000 hours exposure. The TEM image in Figure 7a shows Hf/Zr-carbide cluster on the top of Al-oxide surface. The observed gold (Au) was from sample preparation. During isothermal oxidation for 1000 hours, crack on the top of oxide layer was begun, as shown in Figure 7b.

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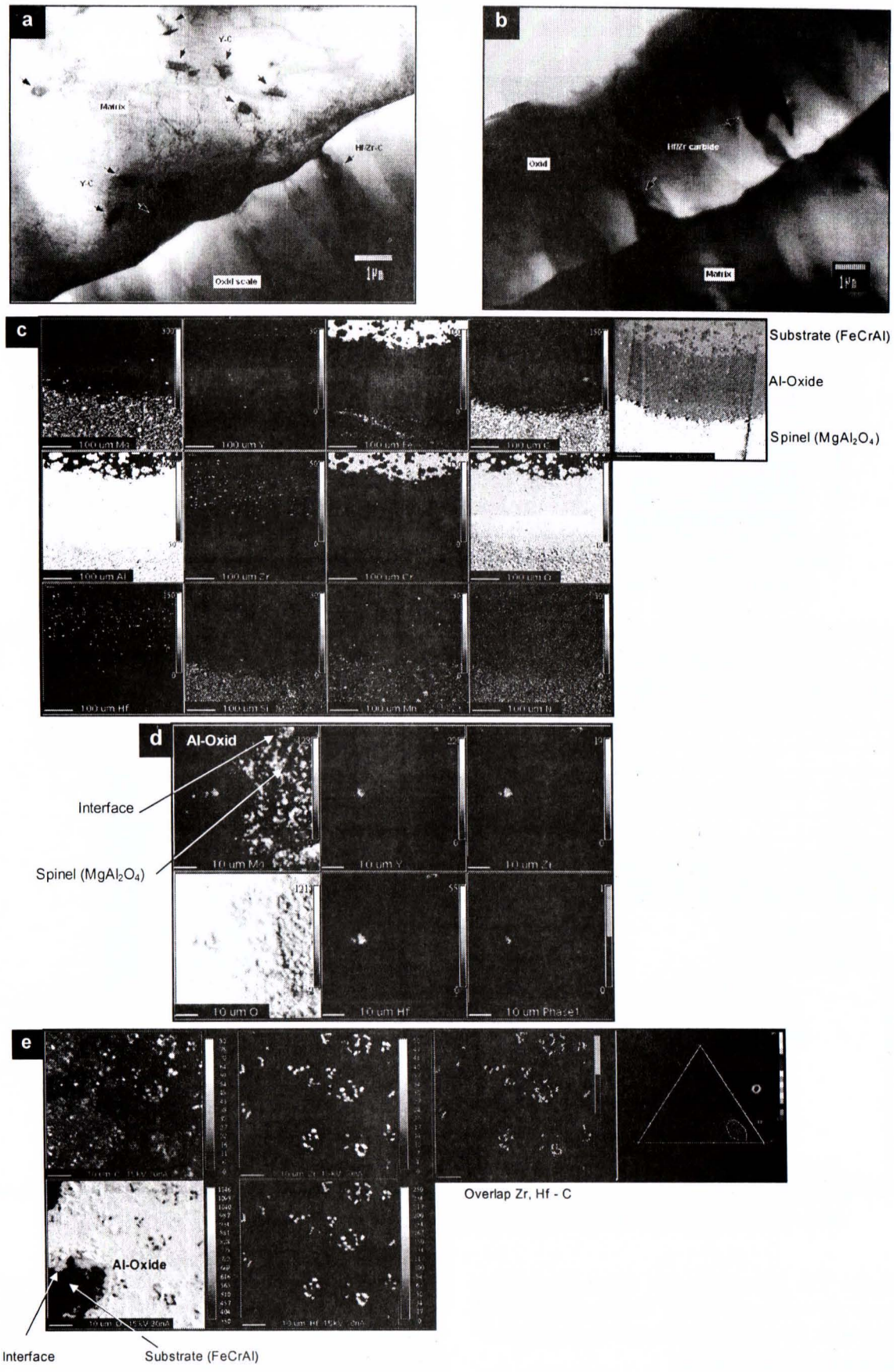

Figure 6. TEM images of FeCrAl alloy after 600 hours exposure (a-b) and EPMA analysis results (d-e).

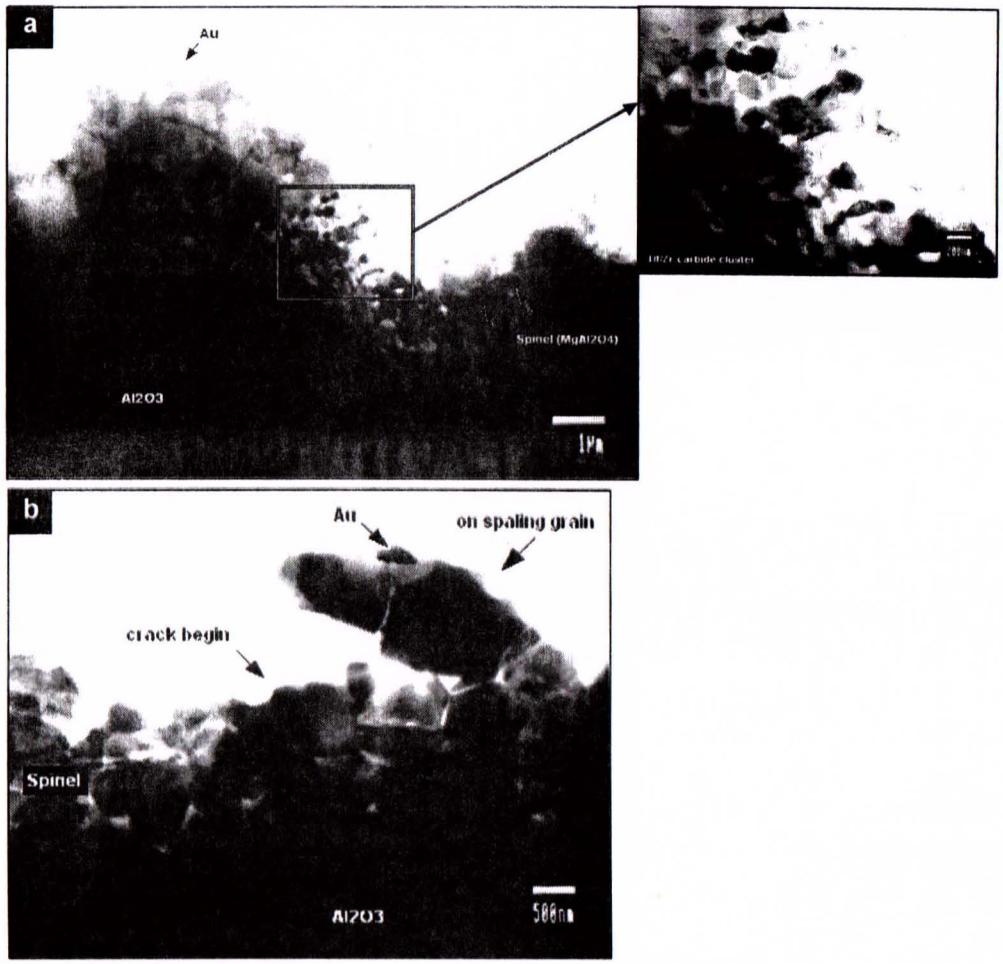

Figure 7. TEM images of FeCrAl alloy after 1000 hours exposure.

CONCLUSION

The studies on oxidation behavior of alumina oxide growth on FeCrAl lead to several conclusions. The FIB system used in this study proved its ability to produce high quality specimens. The TEM studies results shows the growth of Al-oxide layer in varied thickness related to varied exposure time in isothermal temperature. The top of oxide layer and the surrounding area consisted of spinel ($MgAl_2O_4$) with cubic lattice structure, Al-oxide layer with hexagonal lattice structure, and pores. Through EELS study, the light elements and oxygen were detected. All of the elements forming the bulk such as Fe, Cr, Al, the spinel, oxide element, as well as Mn, Mg and O were detected by EPMA analysis.

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TANYA JAWAB

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Pertanyaan

1. Apa keuntungan teknik perparasi FIB

Jawaban

1. Dengan teknik FIB dapat menganalisis sampel dengan daerah yang luas, mulai dari lapisan oksida yang terluar sampai daerah matriks yang terdalam.