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Microstructural Investigations of Al_2O_3 Scale Formed on FeCrAl Steel during High Temperature Oxidation in SO_2

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The results of microstructure observations of the Al_2O_3 scale formed on a Fe-Cr-Al steel during high temperature oxidation in the SO_2 atmosphere are presented. Morphology of the scale has been studied by SEM and TEM techniques. Phase and chemical compositions have been studied by EDX and XRD techniques. The alumina oxide is a primary component of the scale. TEM observations showed that the scale was multilayer. The entire surface of the scale is covered with "whiskers", which look like very thin platelets and have random orientation. The cross section of a sample shows, that the "whiskers" are approximately 2 μm high, however the compact scale layer on which they reside is 0.2 μm thick. The scale layer was composed mainly of small equiaxial grains and a residual amount of small columnar grains. EDX analysis of the scale surface showed that the any sulfides were found in the formed outer and thin inner scale layer. A phase analysis of the scale formed revealed that it is composed mainly of the θ-Al_2O_3 phase and a residual amount of α-Al_2O_3.

Keywords *: SEM, TEM, XRD, Al_2O_3, Fe-Cr-Al alloy*

1. Introduction

Alumina former alloys present a good protective behavior under the high temperature oxidizing and corrosive environments. Their high aluminum content allows the formation of an alumina scale, which protects them well.[1)] This oxide may occur in a few different crystallographic forms: γ, δ, θ and α. The meta-stable γ-, δ- and θ-Al_2O_3 appear on the surface of FeCrAl steels in the initial period of high temperature oxidation and their amount decreases with increasing temperature. α-Al_2O_3 is the only phase stable thermodynamically at high temperature.[6),7)] It is commonly accepted that the θ-Al_2O_3 scale grows due to the outward diffusion of the Al^{3+} cations *via* point defects in the cation sublattice,[3),4)] while the α-Al_2O_3 scale grows due to the inward grain-boundary diffusion of oxygen. According to some studies,[5)] the α-Al_2O_3 scale grows by simultaneous outward diffusion of the Al^{3+} cations and inward diffusion of oxygen. Therefore the growth mechanism of alumina scales is continuously a subject of investigation. A sequence of phase transformations: $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ in the Al_2O_3 scale proceeds at different rates, depending both on the temperature and the gas phase composition. These phase transformations are reflected in the decreasing rate of oxidation because the meta-stable aluminas grow faster than the stable one, i.e. α-Al_2O_3.[7)-9)] Microscopic observations show that the phase transformations of Al_2O_3 are accompanied by morphological changes in the oxide scale. The γ phase occurs as small cubic crystals, the δ and θ phases - as platelets and whiskers, while the α phase was present as fine equiaxial grains.[9)] The well-developed plate-like structure on the surface of the FeCrAl alloys is related to the $\gamma \rightarrow \theta$ phase transformation.[8)] As follows from previous papers,[9)] formation of the plate-like structures is strongly affected by the composition of the gas phase. It means that the mechanism of alumina scale grows is still not yet known well.[8),9)]

This paper presents result of microstructures investigations of Al_2O_3 scale formed on FeCrAl steel during its thermal oxidation in the sulphur dioxide atmosphere.

2. Experimental procedure

In this study a commercial cold rolled foil of the FeCrAl

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Table 1. Chemical composition of the FeCrAl alloy (wt%).

Elements	Fe	Cr	Al	C	Other
% mass	matrix	18,50	4,60	0,020	0,20

steel was used. This material has recently been used as an automobile catalytic converter, which is exposed to the exhaust gas at high temperature. Chemical composition of the foil is given in Table 1.

To obtain the Al_2O_3 scale on a FeCrAl foil an experiment was carried out at 820℃ in SO_2+1% oxygen gas mixture during 24 hours. The partial pressures of oxygen and sulfur in SO_2+1% O_2 gas mixture under a pressure of 10^5 Pa and temperature of 820℃, calculated on the basis of equilibrium, are the following: $p_{S2} = 0,21 \cdot 10^{-5}$ Pa and $p_{O2} = 22,14$ Pa.[10] Before oxidation the sample was degreased using an ultrasonic washer and a water bath with addition of detergent. Subsequently, the sample was washed with ethanol and dried in a hot air flow.

Oxidation conditions were chosen on the basis of our previous studies.[11] These investigations point out that the morphology of Al_2O_3 scale is dependent on the oxidation temperature and on the composition of the oxidizing atmosphere (i.e., the ratio of SO_2 to O_2 in gas mixture).

It has been found that in pure SO_2 atmosphere at 850℃, independently of the composition of the oxidizing atmosphere, the α-Al_2O_3 scale is strongly deformed and poorly adherent to a metallic substrate. Upon applying slightly lower temperatures (800-830℃), the scale obtained is good adherent and composed of α-Al_2O_3 and θ-Al_2O_3, with a characteristic plate-like structure morphology of the external surface (Fig. 1).

3. Results and discussion

3.1 Morphological and phase studies

As was mentioned above a well-developed Al_2O_3 plate-like structure were obtained by oxidation of FeCrAl steel

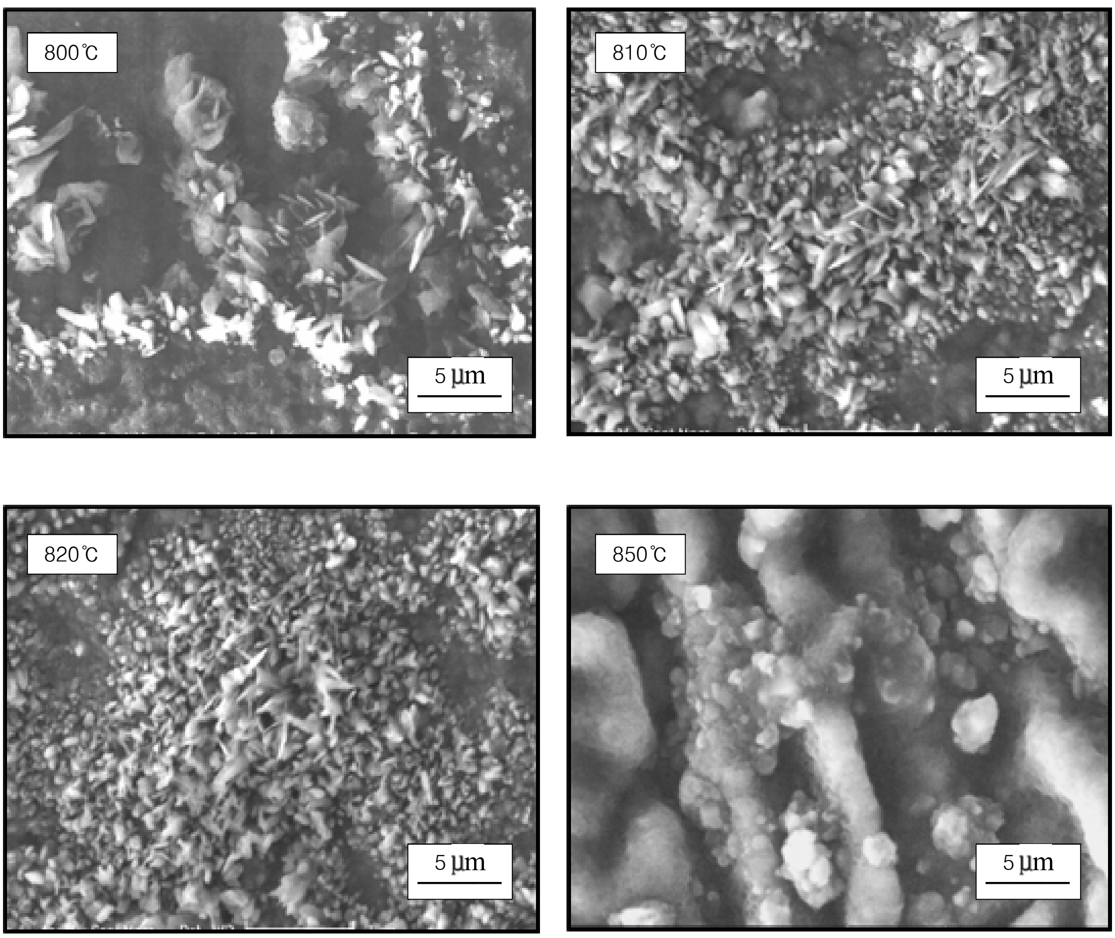

Fig. 1. External surface of the Al_2O_3 scale formed on a steel FeCrAl during 24 h oxidation in SO_2+0,01% O_2 gas mixture at temperatures 800, 820, 830 and 850℃, respectively.

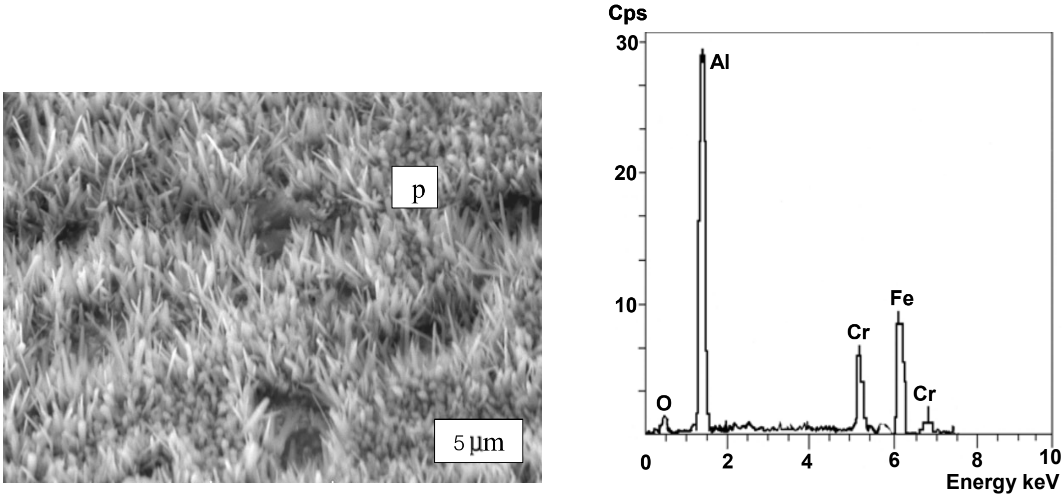

Fig. 2. External surface of the Al_2O_3 scale formed on FeCrAl steel oxidized 24 h in SO_2+1% O_2 atmosphere at 820℃ and EDX analysis at point P.

at 820℃ in SO_2+1% O_2 gas mixture during 24 hours. Under this conditions whiskers on surface of the scale were formed.

The morphology of external scale surfaces formed on the FeCrAl steel was examined by a scanning electron microscope Philips Electron Optics, type SEM XL30, equipped with an energy dispersive spectrometer, LINK IBIS, Oxford Instruments (Fig. 2).

Morphological studies of the oxide layer have shown various crystalline forms present on its outer surface. Three types of crystal morphology were observed, differing in size. The smallest ones, taking approximately up to 5% of the overall surface, were regions with poorly developed crystals. Bigger, oval-shaped areas, constituting about 20% of the surface, were covered with fine, regular columnar crystals. The major part of the surface was built of oxide whiskers, up to 2 µm in length. The surface of the scale was built exclusively of alumina; sulfur was not detected by EDS.

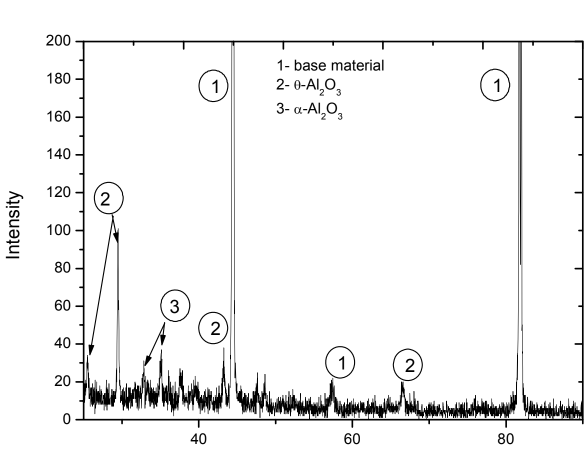

Fig. 3. Diffraction patterns of the Al_2O_3 scale formed on a FeCrAl steel oxidized 24 h in SO_2+1% O_2 atmosphere at 820℃.

Phase analysis of the scale formed was carried out using an X-ray diffractometer Philips, type PW1710, equipped with a filtered CoK_a X-Ray beam (Fig. 3).

The analysis of phase composition indicated that the oxide scale contains two varieties of alumina, i.e. θ- and α-Al_2O_3, total volume of the stable phase α-Al_2O_3, being much less than that of the metastable θ-Al_2O_3 (Fig. 3). Due to small thickness of the oxide layer (about 5 µm) some peaks corresponding to the underlying alloy were also visible in the diffraction pattern. The δ phase was not detected at all, probably because its amount was below the detection limit.

According to TEM, the Al_2O_3 scale consisted of two layers (Fig 5). The outer one was composed of whiskers, 1-2 µm in length and about 0.2 µm in thickness.

3.2 TEM observations

Microstructure, phase and local chemical composition analysis of the Al_2O_3 scale formed on the FeCrAl steel oxidized under SO_2+1% O_2 at 820℃ was examined with Transmission Microscopes (PHILIPS CM 20 (200 kV) TWIN (Fig. 4-5).

On Fig. 4 chemical microanalysis (mapping) of the scale formed on the FeCrAl steel is presented. It shows that scale was built with Al_2O_3 layer. The alumina oxide is a primary component of the scale. Analysis of the scale surface shows that no sulfides were found in the thin scale layer formed.

Fig. 5 presents a cross-section of the scale formed on

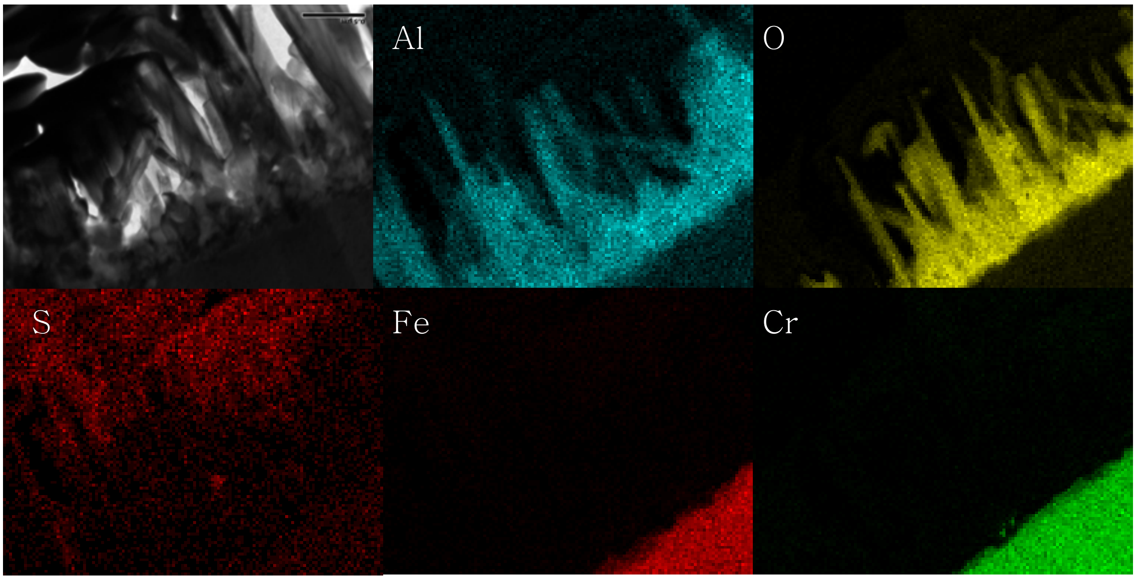

Fig. 4. Chemical microanalysis from TEM image of the Al_2O_3 scale formed on the FeCrAl steel oxidized 24 h in SO_2+1% O_2 atmosphere at 820℃.

the FeCrAl foil oxidized for 24 hours and diffraction patterns at points 1 to 4. Fig. 5 shows diffraction patterns of the crystal elements presented in Fig. 6. Point (1) small equiaxial grain from inner oxide layer corresponds to γ-Al_2O_3, (2) small columnar grain from inner oxide layer corresponds to α-Al_2O_3, while (3) blade-like crystal and (4) the next neighbour crystal are all composed of θ-Al_2O_3 (Fig. 6).

The inner layer was compact and built of equiaxed crystals identified as γ- and θ-Al_2O_3. At the alloy/scale interface there were small columnar grains of α-Al_2O_3.

The results of TEM analysis were consistent with the present understanding of temperature effect on the formation of different varieties of Al_2O_3 on the surface of FeCrAl steels upon exposure to oxidizing environments.[12),17)] When oxidation temperature falls in the range 600℃ - 800℃, the scale consists of a mixture of γ-, θ- and α-alumina. This composition is connected with phase transformations taking place in the following sequence:

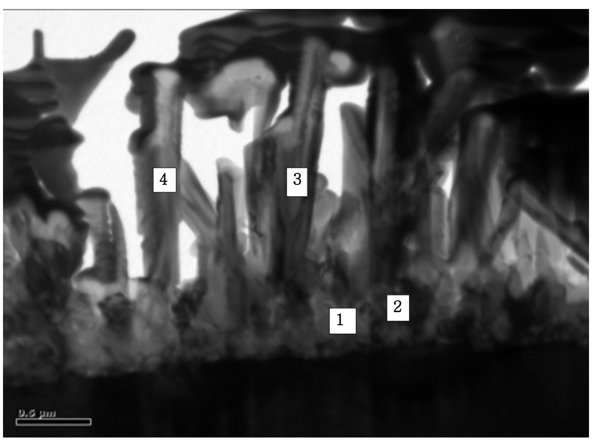

Fig. 5. TEM image of the Al_2O_3 scale formed on the FeCrAl steel oxidized 24 h under SO_2+1% O_2 atmosphere at 820℃.

$$\gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

In the experimental conditions applied in this work, a mixture of metastable oxide phases, γ, δ, and θ should have been expected. However, the X-ray diffraction analyses in different spots on the scale surface did not reveal any δ-Al_2O_3, which was probably due to its high transformation rate into θ-Al_2O_3. The α-Al_2O_3 phase, identified in the inner scale layer, may be related to chromium in the alloy, which is known to accelerate the θ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transformation.[13)] As a result of selective oxidation of aluminum, the subscale region of the alloy is rich in chromium.

As a summary of the above discussion we can propose a scheme of scale structure formed on FeCrAl steel oxidized 24h under SO_2+1% O_2 atmosphere at 820℃ (Fig. 7).

4. Conclusions

The oxidation studies presented in this contribution allow to draw the following conclusions:

1) The Al_2O_3 scales formed during the high-temperature

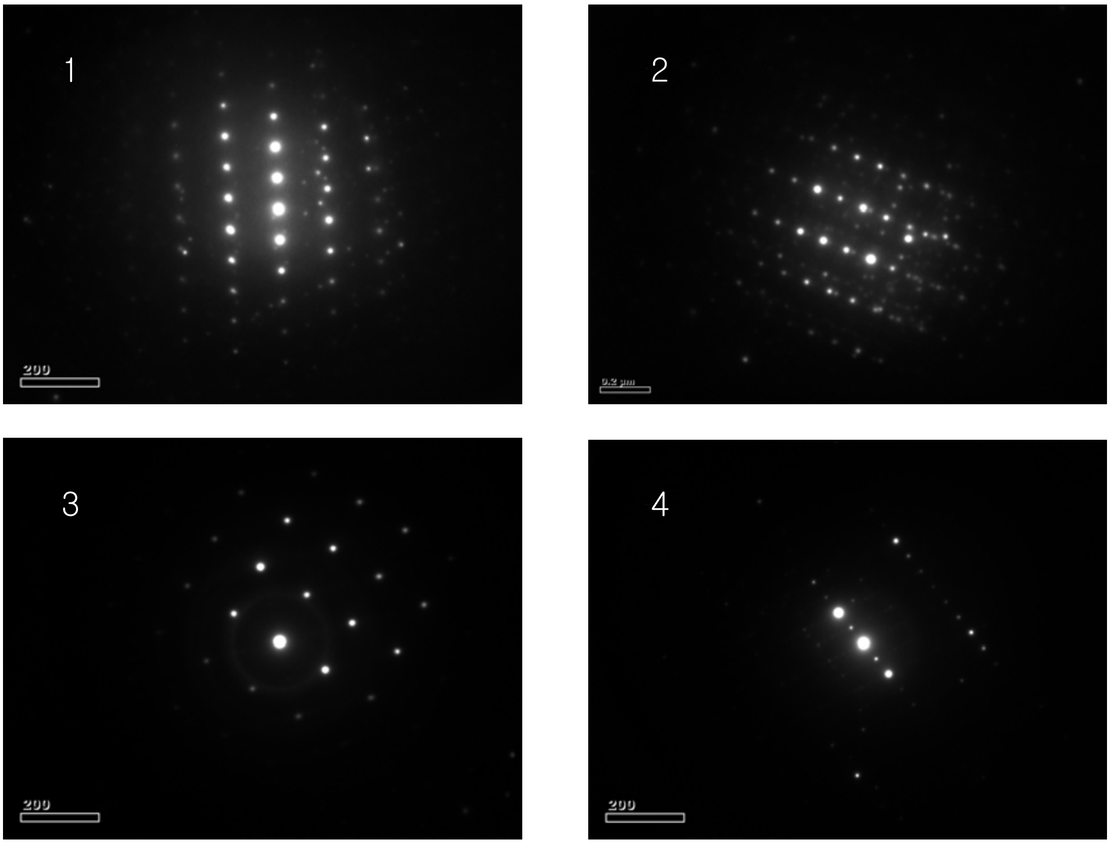

Fig. 6. Diffraction patterns of the Al_2O_3 scale formed on the FeCrAl steel oxidized 24 h under SO_2+1% O_2 atmosphere at 820℃: point (1) small equiaxial grain from inner oxide layer corresponds to γ-Al_2O_3, (2) small columnar grain from inner oxide layer corresponds to α-Al_2O_3, (3) blade-like crystal and (4) the next neighbour crystal are θ-Al_2O_3.

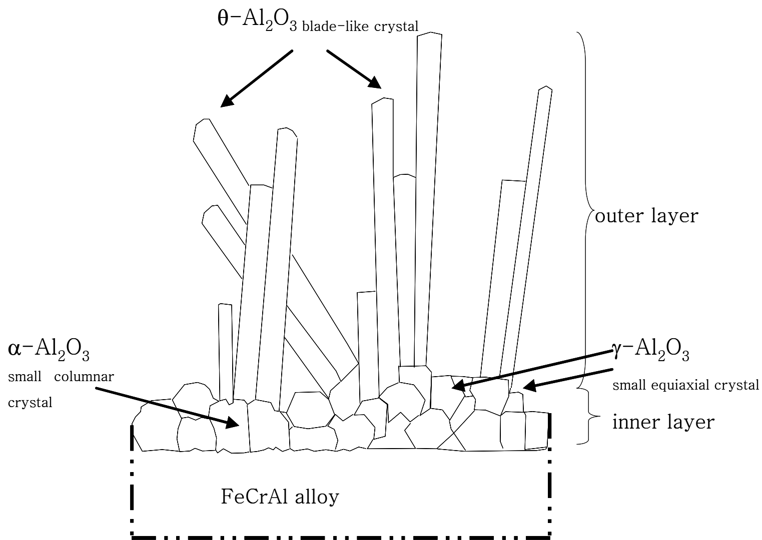

Fig. 7. Scheme of scale structure formed on the FeCrAl steel oxidized 24 h under SO_2+1% O_2 atmosphere at 820℃.

oxidation of the FeCrAl has a two-layer structure.

2) Entire surface of the scale is covered with blade-like crystals, while the outer scale is composed of small equiaxial and columnar grains.

3) The blade-like crystals start to grow at the interface of the two layers, pass through the outer layer and protrude

from the scale surface.

4) The internal scale is composed mainly of small equiaxial grains (γ- and θ-Al_2O_3 phase) and a residual amount of small columnar grains (α-Al_2O_3 phase).

5) The plate-like structure is built of the pure θ-Al_2O_3 phase.

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