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Preliminary Study of Oxidation Process of Fe-Cr-Al Alloys Using IMA (Report I) †

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Abstract

The oxidation behaviour of Fe-Cr-Al alloys, especially in initial stage at 1000°C, was studied using an iron microanalyzer and the result obtained was compared with that of X-ray diffraction analysis.

In the case of the specimen containing a little chromium and aluminum, protective oxide film considered as Al_2O_3 seems to be partly formed at the surface. For the specimen containing more chromium and constant aluminum, Al_2O_3 layer is formed on the whole surface and Cr_2O_3 is also created in proportion to chromium content. Cr_2O_3 layer becomes to be formed on the outer layer than Al_2O_3 layer with increasing chromium content.

1. Introduction

Last year, the Ministry of International Trade and Industry built energy plan named "Sunshine plan", which contained utilizations of atomic, sunshine energies and terrestrial heat and so on.

Especially, the utilization of atomic energy has been performed with the making of atomic piles. However, the operation of atomic pile has become difficult because of the dangerous radioactive fallout.

On the other hand, large-scale establishment of iron- and steel-making has been difficult because of the problem from environmental viewpoint. The following problems should be considered to develop the use of atomic power for iron- and steel-making.

- 1) It is necessary to take out effective heat at 1300°C for the iron- and steel-making. The problem is outside the limits of use by ordinary steel.
- 2) When helium gas is used as coolant, corrosion at high temperature of metallic materials is introduced with a trace oxygen in helium and carbon from fuel and further the existence of trace water vapor. It is necessary to prevent to be flakes because of the radioactivity. Thus, it is present aim to develop steel which forms adhesive oxide film on the surface.

In this report, the authors treated the oxidation

behavior of iron-chromium-aluminum alloys. When iron-base alloy containing a little aluminum (or chromium) is oxidized at high temperature in air, it is well known that the surface is covered with following four oxide scales; Fe_2O_3 , Fe_3O_4 , FeO and $FeO \cdot Al_2O_3$ ¹⁾ (or $FeO \cdot Cr_2O_3$ ²⁾). With increasing aluminum (or chromium) content, the layer of FeO vanishes and Al_2O_3 (or Cr_2O_3) appears in the inmost layer.^{1,3)} More increasing aluminum (or chromium) content, the only Al_2O_3 (or Cr_2O_3) layer grows and the other oxide layers disappear.¹⁾

In Fe-Cr-Al alloys having a little aluminum and chromium, Fe_2O_3 , Fe_3O_4 , FeO and $FeO \cdot (Cr, Al)_2O_3$ layers are formed on the surface. With increasing aluminum and chromium, Al_2O_3 and Cr_2O_3 layers are formed according to the relative quantity of aluminum and chromium.¹⁾

As above mentioned, the structural contribution of aluminum and chromium in oxide layers has been studied up to date. However, there are only a few studies of oxidation processes in the initial stage. This study will be useful to elucidate the mechanism of oxidation of iron and alloys.

In this paper, the oxidation in the initial stage (at 1000°C for three minutes) of Fe-Cr-Al alloys have been

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studied using an ion micro analyzer (IMA) and a Debye Scherrer method. Up to date, oxidation in initial stage of Fe-Cr-Al alloys have been studied by a transmission electron diffraction method⁴⁾ and weight gain techniques.⁵⁾ However, they have not given the knowledge between the oxide films and the distributions of elements such as iron, chromium, aluminum, oxygen and nitrogen. It is, therefore, thought that IMA is more effective means.

2. Experimental procedures

Specimens used in this study were produced with high frequency induction furnace and followed by homogenizing treatment at 1050°C for 1 hr in argon atmosphere. The chemical compositions of Fe-Cr-Al alloys are shown in Table 1. Each sample is cut and polished mechanically in the forms of a plate. It has surface area of about 10 × 10 mm² and about 0.5 mm thick.

All samples were oxidized at 1000°C for three

Table 1 Composition of Fe-Cr-Al alloys

	Cr (wt%)	Al (wt%)	O (ppm)	N (ppm)
Fe- 3Cr- 3Al	3.240	2.630	116	38
Fe- 7Cr- 3Al	6.717	2.748	56	27
Fe- 13Cr- 3Al	12.98	2.878	176	281

minutes in N₂/20 vol% O₂ mixture purified through a column of silica gel and a magnesium percolator at about 200°C.

The oxide scales were studied by means of an IMA (Hitachi Ltd., IMA-SS type) and a Debye Scherrer camera (Rigaku Denki Co. Ltd., D-3F type). IMA is suitable to analysis of light elements as oxygen, nitrogen and so on, moreover to distribution analysis of elements in thin film.⁶⁾ It is, therefore, expected that IMA is a profitable method to study oxidation mechanism of alloy in the initial stage. IMA, however, has not an ability of sufficient state analysis at present time. On the other hand, Debye Scherrer analysis – in which we can get informations with a little powder sample – compensates such a lack of IMA.

Measurements were made under the conditions as follows. In IMA, argon ion beam was focussed on the oxidation surface of a Fe-Cr-Al plate. Therefore oxide scales of a specimen were analyzed in order from outside. The diameter of the beam was about 1 mm and the accelerated voltage was 5KV. In Debye Scherrer analysis, Cr target X ray tube was used. Oxide components in sample were extracted with

10%HCl-90%C₂H₅OH solution.

3. Results

In a Fe-3Cr-3Al alloy, it was observed that the portions oxidized strongly distributed on the surface. The portions probably correspond to nodular scales known as breakaway oxidation⁷⁾ observed in Fe-Al alloys⁸⁾ and austenitic stainless steels.⁹⁾ The reasons for the development of nodules are not yet fully understood. Because in this study it is a purpose to study the oxidation protective film in initial stage, the oxidized portion except for the nodules was especially investigated using IMA. The result is shown in Fig. 1.

In Fe-7Cr-3Al and Fe-13Cr-3Al alloys, the whole surfaces were covered externally with the uniform oxide

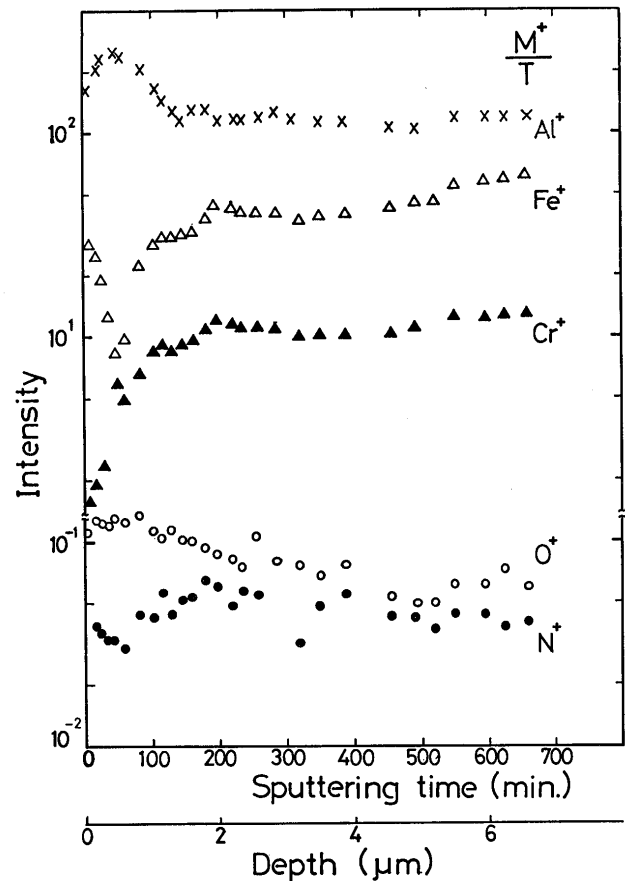


Fig. 1 Distributions of various elements in oxide film and base metal of Fe-3Cr-3Al alloy.

films. The results investigated by IMA are shown in Figs. 2 and 3, respectively. Depth of their abscissas means nominal depth because the sputtering rate depends on the structure of the oxide scales and the base metals.

The Figs. 1, 2 and 3 show following features.

- 1) In all specimens, the oxide scales include less iron than the base metal. Near the middle layer in the oxide scales the quantity becomes minimum.

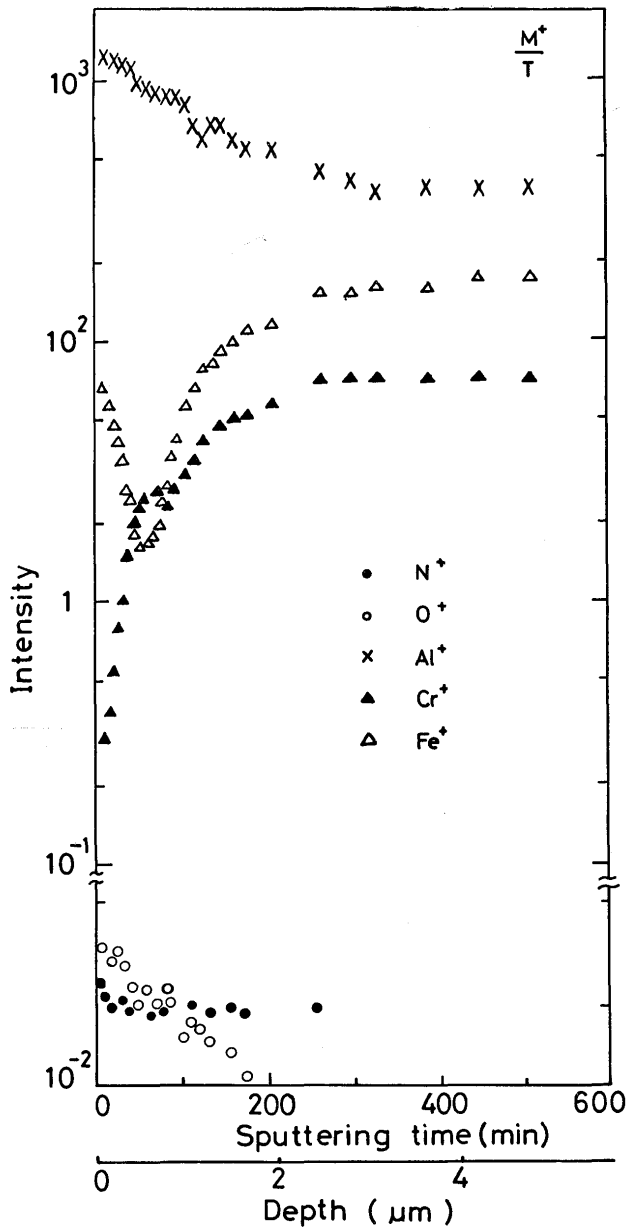


Fig. 2 Distributions of various elements in oxide film and base metal of Fe-7Cr-3Al alloy.

2) More aluminum in oxide scales are included than in base metal. The layer including the maximum aluminum exists on the comparatively outer side in the oxide scales.

3) In the specimens including less chromium, a little chromium distributes in oxide scales. On the other hand, in most chromium content alloys (Fe-13Cr-3Al) oxide scales include more chromium and the layer including the maximum chromium exist on outer than that including the most aluminum.

4) Oxygen increases monotonously from base metal to outer layers. For nitrogen obvious changes are not observed.

In Debye Scherrer analysis, diffraction lines due to the compounds shown in Table 2 were observed. In

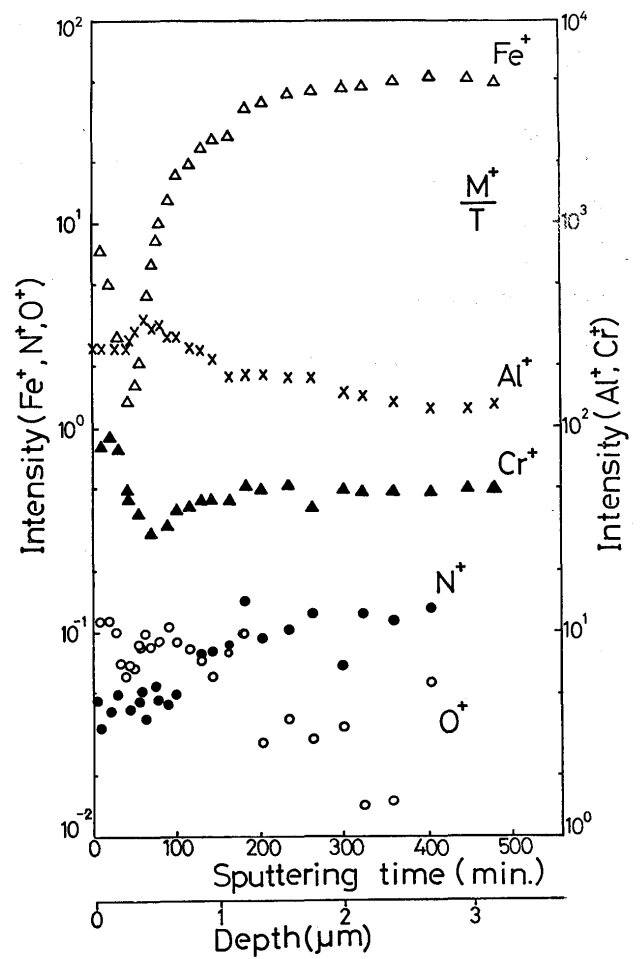


Fig. 3 Distributions of various elements in oxide film and base metal of Fe-13Cr-3Al alloy.

Table 2 Compounds observed by X-ray diffraction analysis

Sample	Observed compounds
Fe- 3Cr- 3Al	(Fe,Cr,Al) ₂ O ₃ , FeO(Fe,Cr,Al) ₂ O ₃ , AlN
Fe- 7Cr- 3Al	αAl ₂ O ₃
Fe- 13Cr- 3Al	Cr ₂ O ₃ , αAl ₂ O ₃

Fe-3Cr-3Al, nitrogen is considered to be introduced from atmosphere through nodules and combine with aluminum as AlN in base metal. The other compounds are assumed to be almost included in nodules. Any informations for the protective oxide film such as Al₂O₃ measured by IMA were not given due to a little quantity. In Fe-7Cr-3Al and Fe-13Cr-3Al, only protective oxide films were observed and the knowledges for iron in oxide scales were not accepted in spite of the detection by IMA. It is probably attributed that little iron oxide was formed.

The comparison of the results of IMA with those of Debye Scherrer analysis will lead to following conclusions. For the specimens containing a little chromium and aluminum, protective oxide film considered to be mainly Al_2O_3 is formed only on the portion of the surface. For the specimens containing more chromium under the condition of constant aluminum content, the protective oxide films consisting of Al_2O_3 and Cr_2O_3 are created on the surface of the specimens. With increasing chromium content, Cr_2O_3 layer becomes to be formed on the outer layer than that of Al_2O_3 .

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