

# THE EFFECT OF THE REACTIVE ELEMENT ON THE CHROMOXIDE AND ALUMINIDE LAYERS IN THE HIGH TEMPERATURE CONDITION

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## ABSTRACT

**THE EFFECT OF THE REACTIVE ELEMENT ON THE CHROMOXIDE AND ALUMINIDE LAYERS IN THE HIGH TEMPERATURE CONDITION.** Oxide layers at high temperature condition, as  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , growing act not only as corrosion barrier, but also as a diffusion barrier of aggressive components. MA956 and Ni75Cr25 alloy were studied to observe the effect of Yttrium coating on their oxidation behavior. The influence of these coatings on the oxidation behaviour of the alloy was studied. Thin coatings of Yttrium have been applied to the surface of those alloys by vacuum coating. The growth of the oxide layers under controlled has been investigated in this work by Analytical Transmission Electron Microscope (ATEM) and Scanning Electron Microscopy (SEM). It was found that addition of small amounts of elements such as Yttrium to these alloys greatly increase their oxidation resistance.

## ABSTRAK

**EFEK ELEMEN REAKTIF PADA LAPISAN KROMOKSIDA DAN ALUMINIDA PADA KONDISI TEMPERATUR TINGGI.** Lapisan oksida pada kondisi temperatur tinggi, seperti  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , tumbuh tidak hanya sebagai penahan korosi, tetapi juga sebagai penahan difusi dari komponen-komponen agresif. Paduan MA956 dan Ni75Cr25 dipelajari untuk mengamati efek dari lapisan Yttrium pada sifat oksidasinya. Pengaruh dari lapisan ini pada sifat oksidasi dari paduan telah diteliti. Lapisan tipis dari Yttrium telah dibuat pada permukaan dari paduan melalui pelapisan secara vakum. Pertumbuhan dari lapisan oksida yang terkontrol telah diteliti dalam pekerjaan ini menggunakan Mikroskop Elektron Transmisi Analistik (ATEM) dan Mikroskop Elektron Sapuan (SEM). Telah ditemukan bahwa penambahan sejumlah kecil unsur seperti Yttrium terhadap paduan meningkatkan secara signifikan daya tahan oksidasinya.

## 1. INTRODUCTION

A research and developing program has been founded in order to reduce the oxidation rate by covering the surface with oxidic protective layers, which often consist of  $\text{Cr}_2\text{O}_3$  and/or  $\text{Al}_2\text{O}_3$ . One major limiting factor in the protection is extensive oxide loss from the surface, or oxide spalling under thermal cycling conditions. Oxide layers such as  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  in high temperature condition act not only as corrosion barrier, but also as a diffusion barrier of aggressive components such as S, C, and N. Oxide layers in high temperature reactors (HTR), acts as radioactive permeation barrier of tritium ( $\text{H}^3$ ) and hydrogen ( $\text{H}^1$ ), that permeate through heat exchanger wall. It can be used as corrosion barrier in reactor core fuel element [1-3]. Compact chromia and alumina layers that form on high temperature alloys grow very slowly. Oxide layers preoxidized or in-situ grown in oxidizing atmospheres on high temperature alloys, act as corrosion barrier to protect the base material. Most investigators

have studied the effect of reactive element (RE) additions in alloys on various types of  $\text{Cr}_2\text{O}_3$ -formers and verified the first results. It was found that the coatings did not affect the amount of  $\text{Cr}_2\text{O}_3$  scale, but the alloy had enough chromium. However for  $\text{Al}_2\text{O}_3$ -formers, the influence of this type of coating has never been reported.

The growth of the oxide layers under controlled has been investigated in this work by Analytical Transmission Electron Microscope (ATEM) and Scanning Electron Microscopy (SEM). It was found that addition of small amounts of elements such as Yttrium to these alloys greatly increase their oxidation resistance.

## 2. MATERIALS AND METHODS

The current research was undertaken also to extend the oxidation behaviour of alumina and chromia

former on MA956 and Ni75Cr25 alloy with yttrium coating. The investigated ODS alloy of the type MA 956 were supplied by INCO Alloy International (Hereford, UK) and Ni75Cr25 from powder metallurgy. Specimens were machined to disc geometry in  $45 \text{ } \times 2 \text{ mm}$  and grounded with SiC-320 grid. The chemical composition of the material are listed in Table 1.

Table 1. Nominal composition of the alloys  
Nominal Composition in Mass-%

| Alloys   | Fe   | Ni | Cr | Al  | Ti  | Y <sub>2</sub> O <sub>3</sub> |
|----------|------|----|----|-----|-----|-------------------------------|
| MA 956   | Base | -  | 20 | 4.5 | 0.3 | 0.5                           |
| Ni75Cr25 | -    | 75 | 25 | -   | -   | -                             |

The growth of the oxide layers under controlled conditions is studied using an Analytical Transmission Electron Microscope (ATEM) JEOL JEM-2000 FX II and Scanning Electron Microscopy (SEM) JEOL 840C. The behaviour of the oxide layers formed an alloys are investigated with a new technique for preparing the specimens, especially by cross sectional preparation. The specimen should be bounded each other with a special M-Bond 610 on the Messingring ( $\text{ } = 3 \text{ mm}$ ) [4-5].

The MA956 and Ni75Cr25 alloy are, in a special oxidizing procedure, protected by an oxide layer. Here only a short survey of the standard oxidation by Institut für Angewandte Werkstofforschung Jülich. [6-7].:

- Glowing the samples in H<sub>2</sub> atmospheres at the temperatur 950 °C.
- Oxidation in Ar/H<sub>2</sub>O mixing atmospheres at the temperatur 650 °C.
- Oxidation in Ar/H<sub>2</sub>/H<sub>2</sub>O mixing atmospheres at the temperatur 950 °C.
- Cooling down untill the room temperatur

### 3. RESULTS AND DISCUSSION

Fig 1a and 1b presents the TEM cross sectional preparation investigation on Yttrium uncoated MA 956 after standard oxidation process. The Photograph was found at the interface position among the Aluminium oxide layers (Al<sub>2</sub>O<sub>3</sub>) and basic metals. At the interface the void ist found. By EDX analysis, were found Ti<sub>2</sub>O<sub>3</sub> grain and also some sulfur elements, at the interface. At this condition H<sub>2</sub>S molecules flown to the oxide layers through the narrow crack inserted to the interface. The oxide layers consist of Al<sub>2</sub>O<sub>3</sub>. At the surface, the gas phase H<sub>2</sub>S were flown so that the sulfur element inserted to the oxide layer through grainboundary, as atoms and ions [8].

1. Aluminium oxide layer
2. Void
3. Interface between oxide layers and the matrix

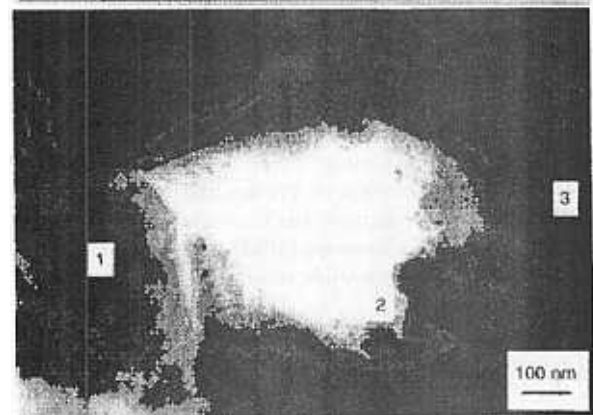
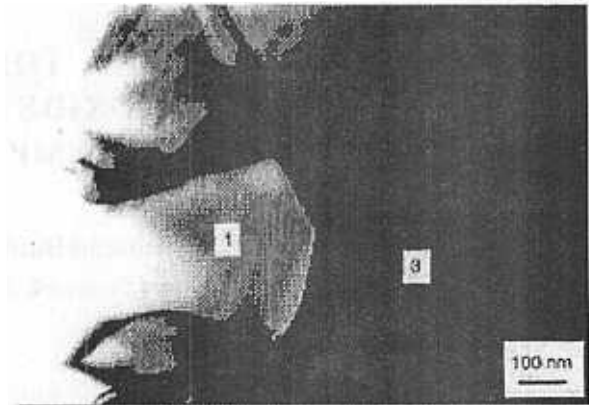


Figure 1a and b: Analytical Transmission Electron Microscopy Micrographs on Yttrium uncoated MA 956

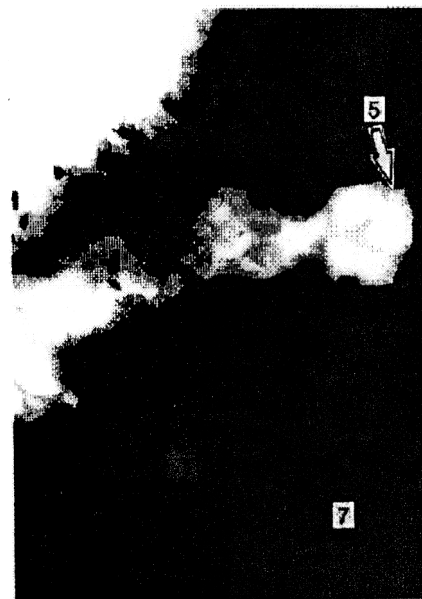


Figure 2: Analytical Transmission Electron Microscopy Micrographs on Yttrium uncoated Ni75Cr25 alloy

Fig. 2 present TEM-cross section investigation on Yttrium uncoated Ni75Cr25 alloys after standard oxidation process. The photograph was found at the interface, under the interface were found voids formed the

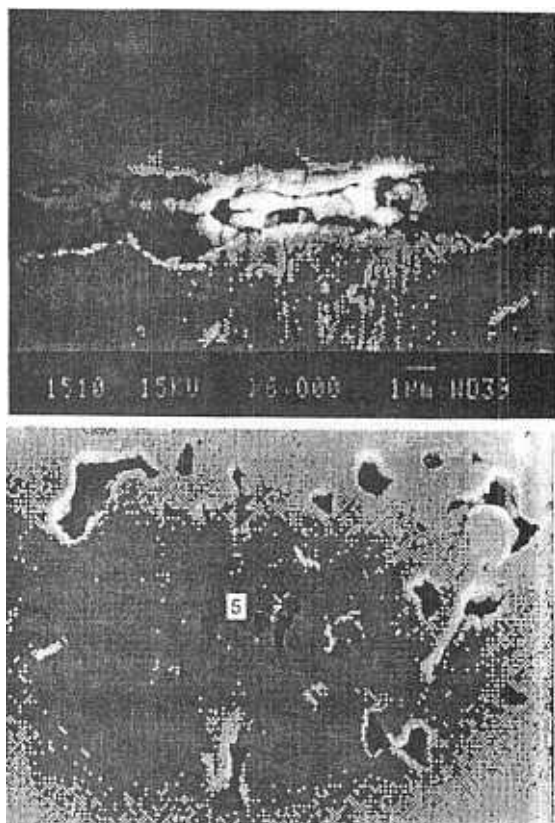


Figure 3a and 3b: Cross section SEM micrographs of oxides formed after standard oxidation on Yttrium uncoated Ni75Cr25 alloy

channel like. By EDX analysis, at the interface were found some sulfur elements. According to Smialek [9] and Lees [10], at high temperature the sulfur was able to destroy the oxide layer stick from the matrix, due to sulfur segregation at the interface layer.

Fig. 3 present SEM-cross section investigation on Yttrium uncoated Ni75Cr25 alloys after standard oxidation process at the the oxide layer (Fig 3a) and interface position (Fig. 3 b). The defects were found at the oxide layer and at the interface as voids.

If there metal cation like  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Cr^{3+}$  transport over, the holes will be formed and condens to form the voids [11-13]. It can be concluded that by increase the oxidation rate and so will increase the metal cation diffusion or transportation. The void easier to transport the sulfur inserted to the matrix. An decrease in the oxidation rate with reactive element coating (Yttrium) was observed by HUSSEY et.al. [14]. Compact chromia and alumina scales that form on high temperature alloys grow very slowly and generally provide very good resistance to high temperature oxidation. With reactive element coating (Yttrium) so will decrease the metal cation diffusion and greatly improves the oxidation resistance of the alloys. The Yttrium content on MA 956 side is lower than 10% wt. Yttrium coating on Y- containing MA 956 alloy had

no significant effect in the oxidation by IAW-standard process [15].

#### 4. CONCLUSION

From the microstructure investigation it can be concluded that:

- After standard oxidation on Yttrium uncoated MA 956 and Ni75Cr25 were found the voids at interface between the oxide layer and the matrix, that decrease their oxidation resistance. Contrary to alloying addition of reactive elements in the form of a Yttrium showed compact chromia and alumina oxide layer.
- The cross sectional microstructural was investigated by TEM, can be given more information for characterization corrosion layer at high temperature alloys, especially at the grain boundary, at the metal-oxide interface.

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