

## THE MICROSTRUCTURE OF THE SCALE FORMED DURING THE HIGH TEMPERATURE OXIDATION OF A FeCrAl ALLOYS

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### ABSTRACT

*FeCrAl alloys have good oxidation resistance at elevated temperature owing to the formation of a continuous Al<sub>2</sub>O<sub>3</sub> surface film, which acts as an oxygen diffusion barrier. The aim of the present study was to investigate the early stages of protective oxide layer formation and its growth on specially prepared commercial FeCrAl alloys, Kanthal AF (K-AF) and Pyromax-C (PX-C), with higher Al and Cr content in the surface layer. Oxidation tests were carried out by annealing at 1200 °C for 24 hours in air atmosphere. Oxidation kinetics was recorded with thermogravimetric analysis, and oxidation products identified by X-ray diffraction and XPS analysis. The surface morphology of the oxide scale was studied by SEM, and the elemental distribution across the scale layer determined by EDS line analysis. The study reveals that higher Al and Cr content in the alloy influenced the oxidation rate at the beginning of the oxidation and promote the early formation of a protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale.*

### 1. INTRODUCTION

FeCrAl – based alloys are well known for their superior oxidation resistance at elevated temperatures. This excellent property relates to the formation of thermodynamically stable

alumina scale on the surface, which protects the bulk material against rapid oxidation. In spite of the superior oxidation properties, the lifetime of the components manufactured from FeCrAl - based alloys can be limited, if the surface of the parts is frequently exposed to thermal cycling at temperatures above 1000 °C. The reason for this is that the major scale-forming element (Al) is consumed in the alloy matrix during thermal cycling, due to repeated thermo-shock cracking and reforming of the alumina scale. If the remaining aluminium content in subsurface area is decreased beneath the critical concentration, the alloy can no longer reform the protective scale, resulting in a catastrophic breakaway oxidation by formation of rapidly growing iron based oxides [1]. The growth rate and adherence of the alumina scale is highly dependent on concentration of minor alloying constituents, including reactive elements RE (Y, Ti, Zr, Hf, etc.). The RE positive effects are: (i) improvement in scale adherence, (ii) selective oxidation of the elements, which form the protective scale, (iii) inhibiting the scale growth, (iv) refining the scale grains and improving its ductility [2]. Yttrium is one of the most commonly used reactive element, but its addition is limited due to its low solubility in the alloy, which lead to the formation of undesired Y-precipitates. In FeCrAl alloys a combination of Y and Hf or Zr may produce the best benefit, while keeping the Y content close to its maximum solubility. It is difficult to determine the optimal concentration of reactive elements, since it also depends on the concentration of other impurities, particularly C and S [3]. The effectiveness of reactive elements also depends on the mode they are added. Namely, they can be added as metallic elements or as metal oxide dispersions. Nychka and Clarke concluded that the rate of oxidation, as well as the ratio between Al outward diffusion and O inward diffusion, depends on the mode of RE addition significantly [4]. Jedlinski and co-workers found out that the best method for alloying is elemental Hf and Y additions, which decrease the scale growth rate and improve its resistance to spalling, while Zr only slightly affects the scale growth rate and moderately improves resistance to spalling [5, 6]. Y blocks outward diffusion of Al because it segregates on grain boundaries [4]. On the other hand Zr rapidly incorporates into the alumina scale, modifying its structure by reducing the oxide grain size as well as forming the Zirconia precipitates and nano-porosity. Hf has a similar effect as Zr with the difference that it more efficiently improves the scale resistance to spalling [7, 5]. Some authors reported that the presence of titanium in FeCrAl alloys could play a role in the transition of alumina to  $\alpha$ -alumina and that minor addition of Ti could cause an acceleration of alumina transformation resulting in the early formation of stable  $\alpha$ -alumina [8].

The scope of this project was an investigation of the oxidation behaviour of two commercial FeCrAl alloys during isothermal annealing at 1200 °C for 24 hours in air atmosphere, with the emphasis on scale growth kinetics and its structure.

## **2. EXPERIMENTAL**

### **2.1. Sample preparation**

The commercial alloys, Kanthal AF (K-AF) and Pyromax-C (PX-C) were used for this investigation. These alloys are ferritic FeCrAl alloys, produced by conventional methods of melting and rolling into 0.7 mm thick sheets. In addition to the main alloying elements (Al, Cr), these alloys also contain small amounts of Si, Mn, C and reactive elements (Y, Mg, Ti, Hf). The Kanthal AF (K-AF) concentration of elements, Zr, Y and Ti is typically 680 ppm, 230 ppm and 600 ppm and for Pyromax-C (PX-C) 2100 ppm Zr, 2600 ppm Ti and 150 ppm

Hf. The content of Al and Cr is higher in Pyromax-C (PX-C) alloy with traces of Hf and Zr reactive elements, while Kanthal AF has traces of Yttrium. The nominal chemical composition of the alloys is shown in the Table 1.

Table 1: Chemical composition of the FeCrAl alloy

	EL.	Cr	Al	Si	Mn	S	Ni	Ti	Mg	Zr	Hf	Y	C	Fe
Kanthal AF	wt.%	22	5.3	0.17	0.18	0.004	0.27	0.06	0.01	0.068	-	0.023	0.03	Ball.
Pyromax-C (PX-C)	wt.%	24.7	6.93	-	0.27	0.001	-	0.26	0	0.21	0.015	-	0.013	Ball.

The investigated materials were in the form of sheet, with dimensions 10 x 20 x 0.7 mm. Prior the oxidation the specimens were ultrasonically cleaned in ethanol. The oxidation process was investigated by thermobalance Netzsch STA 429 during annealing at 1200 °C for 24 h in a laboratory air atmosphere [9]. Samples were heated at a rate of 10 K/min. The surface morphology of alumina scale and its cross-section were studied by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) and by X-ray photoelectron spectroscopy method (XPS). For scale cross-section analysis, the specimens were mounted in epoxy resin before grinding and polishing (with 1 µm diamond suspension).

### 3. RESULTS AND DISCUSSION

#### 3.1. Oxidation kinetics during isothermal annealing at 1200 °C in air atmosphere

Figure 1 shows the mass gain curves obtained by themogravimetric analysis during isothermal annealing at 1200 °C for 24 hours in the air atmosphere. The first two hours of oxidation, when samples were continuously heated up to 1200 °C at a heating rate of 10K/min, were cut off from the diagram due to large background noise and better clarity. During this initial transient stage, the mass gain of PX-C alloy, with higher amount of reactive elements, is much faster than for K-AF alloy. When isothermal annealing is established, oxidation starts to follow the parabolic regime.

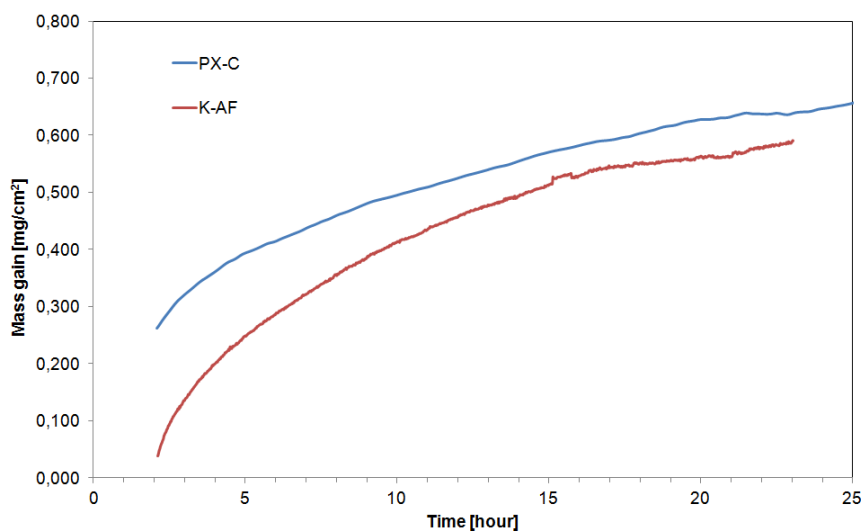


Figure 1: Mass gain as a function of time for Kanthal AF and Pyromax-C alloys; annealed at 1200 °C in air atmosphere.

We have calculated parabolic rate constants  $K_p$  for an oxidation model  $(\Delta m)^2 = K_p \cdot t$ . The parabolic rate constant of PX-C is  $2.2 \pm 0.2 \cdot 10^{-6} \text{ mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$  while for K-AF  $5.1 \pm 0.7 \cdot 10^{-6} \text{ mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$  for first 24 h of oxidation at 1200 °C. The predicted mass gains after 24h isothermal annealing were  $0.68 \text{ mg cm}^{-2}$  for PX-C and  $0.77 \text{ mg cm}^{-2}$  for K-AF alloy, respectively.

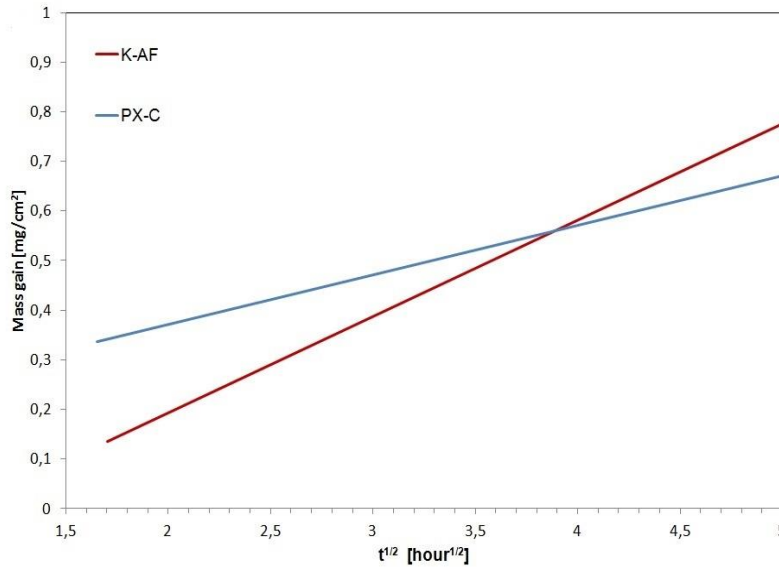


Figure 2: Mass gain as a function of the square root of time for Kanthal-AF and Pyromax-C alloys; annealed at 1200 °C in air atmosphere.

### 3.2. XPS analysis

Figures 3 and 4 show XPS concentration profiles across the surface layer to a depth of 50 nm, recorded after thermogravimetric analysis. As shown in Figure 3 the scale on K-AF is made of Al-oxide ( $\text{Al}_2\text{O}_3$ ) with a significant presence of Mg (4-5 at.% as Mg-oxide). Minor concentration of Zr and Ti (0.3 at.%) were also detected (not shown in the graph for better clarity). XPS analysis of PX-C scale (Figure 4 and Figure 5) reveals the presence of Fe (~2 at.%) and Cr (~ 0,75 at.%) in the scale, which is probably due to the fact that the Al-oxide layer was not completely homogeneous during the transient stage and the Fe-Cr-Al substrate is partially exposed. Also Ti (~ 1.3 at.%) and Zr (~ 1 at.%) elements were found at significantly higher concentrations than in the scale on K-AF samples. On the scale surface of PX-C sample, also traces of elements Na, Ca, Cu and Si (< 0.2 at.%) were detected. We did not find the presence of Mg in the scale on PX-C sample.

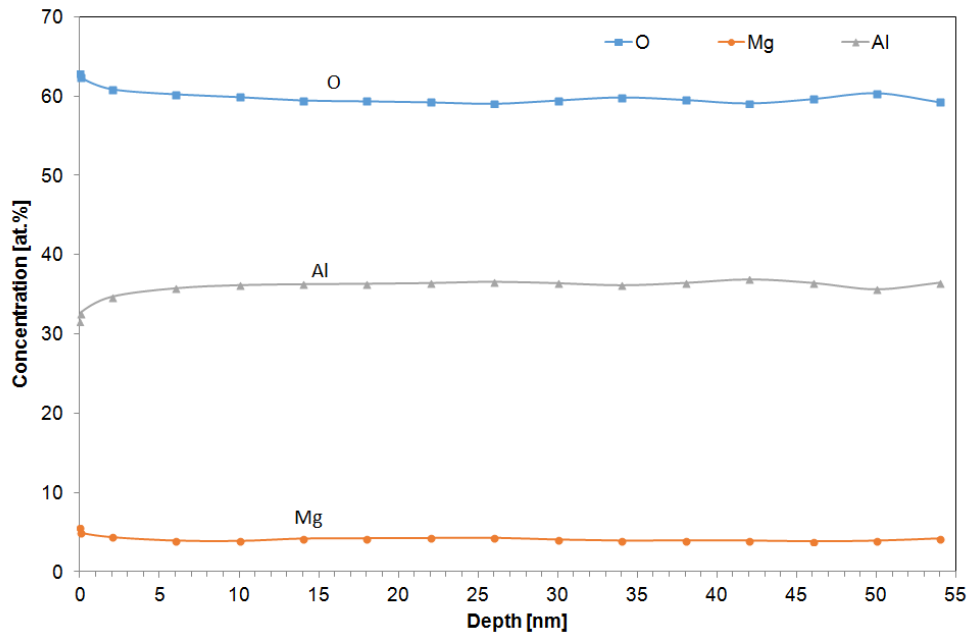


Figure 3: XPS profile of Kanthal AF scale; annealed at 1200 °C/24 h in air atmosphere.

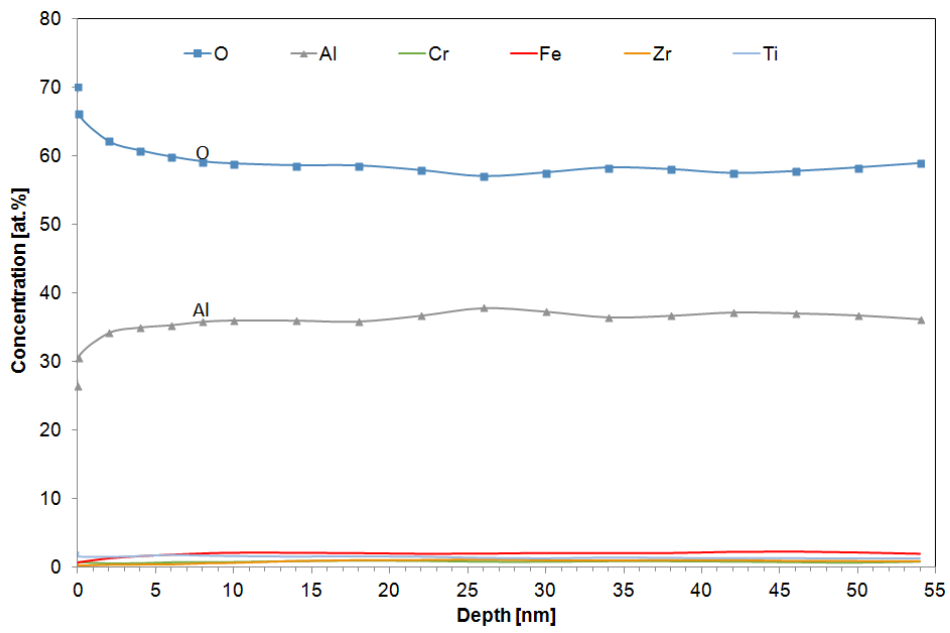


Figure 4: XPS profile of Pyromax-C scale, annealed at 1200 °C/24 h in air atmosphere.

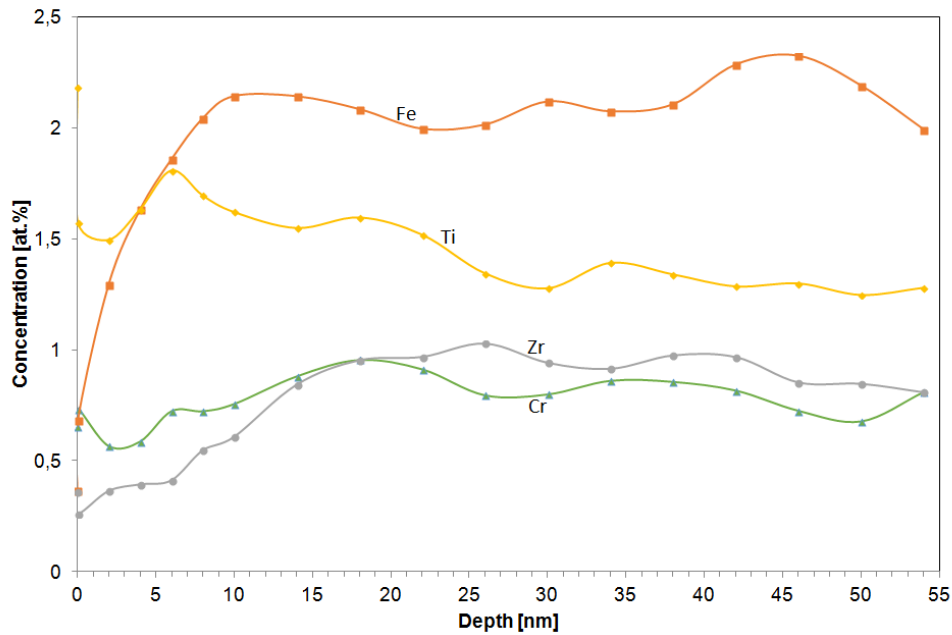


Figure 5: XPS profile of reactive elements; Pyromax-C scale, annealed at 1200 °C/24 h in air atmosphere.

### 3.3. Oxide scale morphology

The scale's composition has high impact on its surface morphology [8]. Figures 6a and 6b show the surface of the scale on K-AF and Figures 7a and 7b surface of the scale on PX-C alloy after oxidation at 1200 °C for 24 hours in air atmosphere. K-AF alloy scale is composed of fine equiaxed oxide grains with a diameter of about 1 μm. Additionally, RE-rich oxide particles with a typical size of 2-3 μm are visible. The surface is quite flat and without cavities. Because of the presence of Y, the Al<sub>2</sub>O<sub>3</sub> scale grows only by inward diffusion of oxygen, while suppressed Al<sup>3+</sup> cation diffusion hinders the scale's lateral growth and results in flat surface morphology [2]. The scale of the PX - C sample differs from K-AF considerably. Outer surface layer of the scale is wrinkled and composed from small oxide grains with a diameter of about 2 μm.

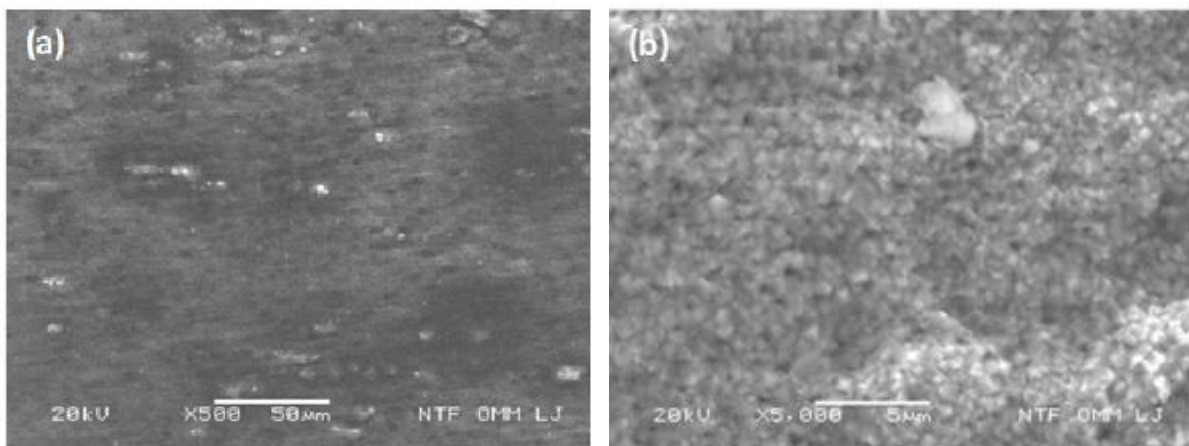


Figure 6: Surface morphology of Kanthal AF scale; annealed at 1200 °C/24 h in air atmosphere.

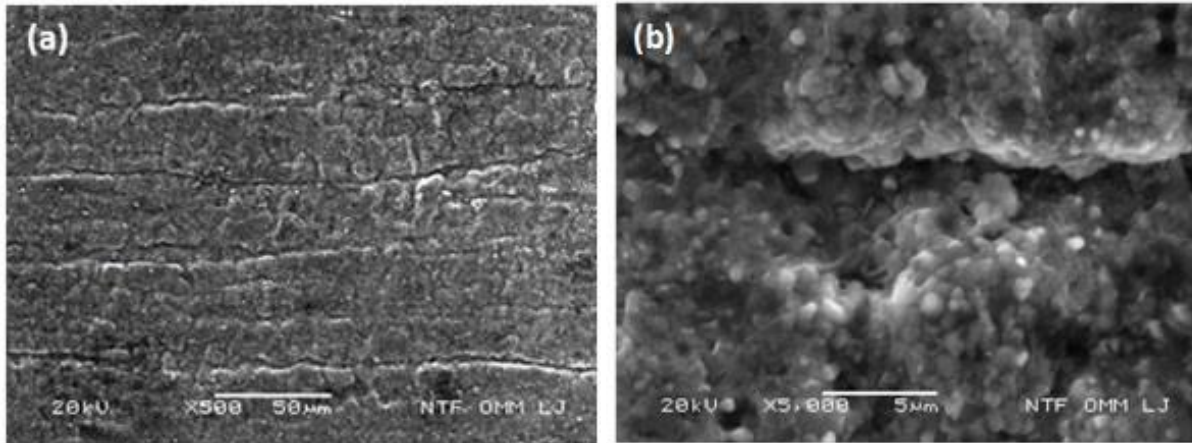


Figure 7: Surface morphology of Pyromax-C scale; annealed at 1200 °C/24 h in air atmosphere.

### 3.4. SEM cross-section and EDS analysis

The SEM observation and EDX line and spot concentration measurements (Figures 8, 9, 10, 11) of the sample surface cross sections reveal that Al diffuse from the bulk material towards the alloy-scale interface while oxygen diffuses from the other direction into the subsurface area of the bulk material. Cr diffusion of the bulk material is significantly slower than oxygen and aluminium diffusion and Cr concentration gradually depletes in the subsurface area. Oxide layer formed on the K-AF is thicker than on PX-C alloy. The thickness of the oxide layer formed on the Kanthal AF is about 3.7 μm (Figure 12a) and on Pyromax-C approximately 2.3 μm (Figure 12b), which is in good correlation with the mass gain measurements that indicate higher mass gain after 24 h oxidation for the K-AF alloy.

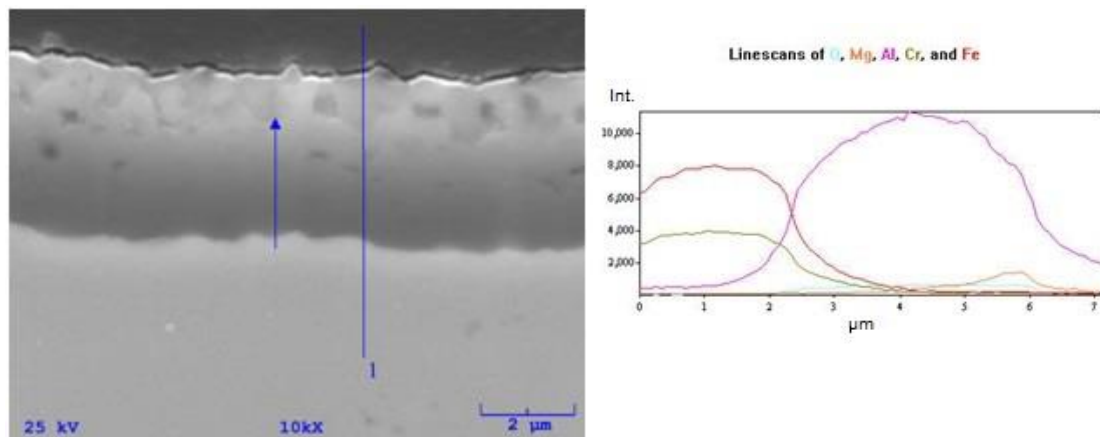


Figure 8: SEM/EDX line concentration profile taken across the scale on Kanthal AF.

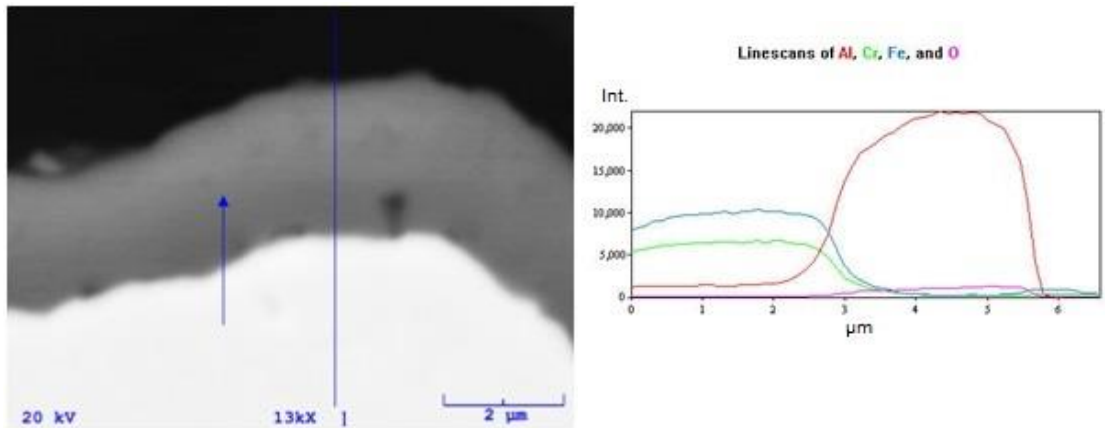
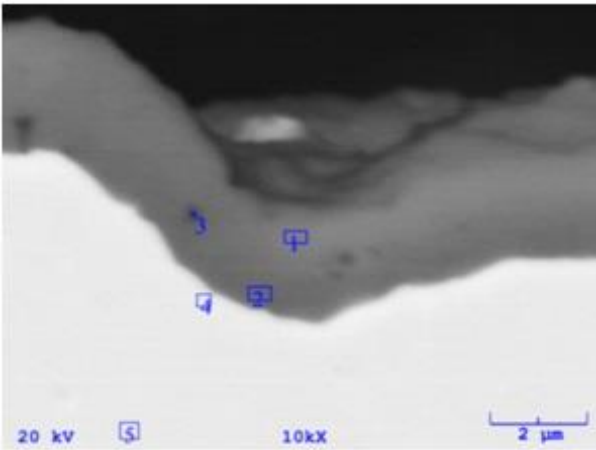
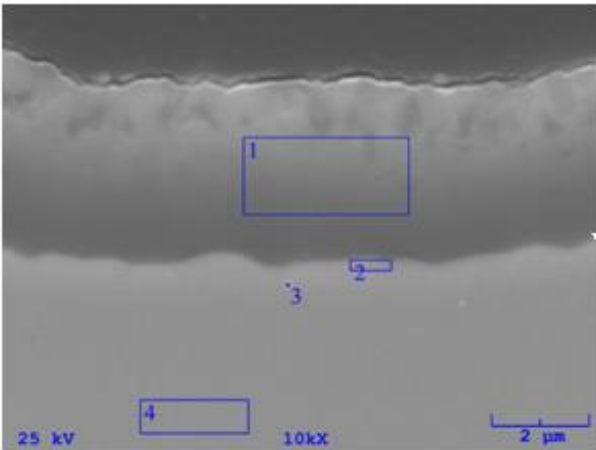


Figure 9: SEM/EDX line concentration profile taken across the scale on Pyromax-C.



	1	2	3	4	5
O	17.2	7.2	13.8	2	
Al	78.5	65.3	77.0	30.8	5.2
Si			1.5		
Ti				0.3	0.2
Cr	1.1	8.7	2.5	18.5	26
Fe	3.1	18.5	5.2	48.5	68.4
Ni		0.4			0.3

Figure 10: SEM micrographs and EDS elemental analysis of scale perpendicular cross section; Pyromax-C; annealing at 1200 °C/24 h.



	1	2	3	4
O	19.1	2.6	0.9	
Mg	1.61	0.35		
Al	72.8	28.9	11.4	3.4
Si				0.2
Cr	1.9	15.2	19.2	21.4
Fe	4.4	52.9	68.5	74.9

Figure 11: SEM micrographs and EDS elemental analysis of scale perpendicular cross section; Kanthal AF alloy; annealing at 1200 °C/24 h.



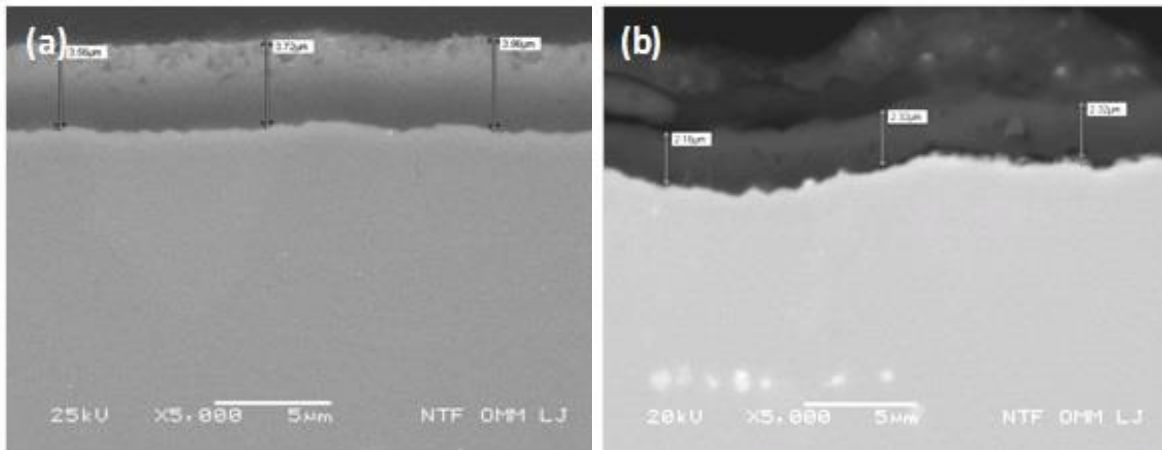


Figure 12: Scale thickness measurements (SEM); Kanthal AF (a) and Pyromax-C (b).

#### 4. CONCLUSIONS

It is well known that high temperature oxidation resistance of FeCrAl alloys originates from a formation of thin and continuous  $\text{Al}_2\text{O}_3$  layer on the alloy surface. Oxidation of two commercial FeCrAl-based alloys was studied during annealing at 1200 °C for 24 hours in air atmosphere. Growth and thickness of the protective  $\text{Al}_2\text{O}_3$  scale depend on Al content and the concentration of reactive elements in the alloys.

- The scale formation in the initial stage is faster on the Pyromax-C alloy than on the Kanthal AF alloy due to higher amount of Al, Cr and reactive elements in comparison to Kanthal AF alloy.
- When sufficiently thick layer of scale is formed, higher concentration of Zr and Ti with a combination of small addition of Hf in Pyromax-C produce  $\text{Al}_2\text{O}_3$  scale with lower growth rate at 1200 °C than small additions of Y, Mg, Ti and Zr in Kanthal-AF alloy.
- Further investigations will be focused on the long-term isothermal annealing and cycling tests in order to determine the resistance against spalling of the oxide layer and prolonged alloy lifetime.

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#### 5. REFERENCES

- [1] Gurrappa I., Weinbruch S., Naumenko D. and Quadackers W. J.: Factors governing breakaway oxidation of FeCrAl-based alloys. *Materials and Corrosion*, 51, pp. 224-235, 2000.,
- [2] Grabke H. J., Siegers M., Tolpygo V. K.: Oxidation of Fe-Cr-Al and Fe-Cr-Al-Y Single Crystals. Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str.1, 40237 Düsseldorf, Germany, *Z. Naturforsch.* 50a, pp. 217-227, 1995.,
- [3] Pint B. A.: Progress in Understanding the Reactive Element Effect Since the Whittle and Stringer Literature Review, Metals and Ceramics Division Oak Ridge National Laboratory Oak Ridge, TN pp. 37831-6156, 2003.,
- [4] Jedlinski J., Borchardt G. and Mrowec S.: The influence of reactive elements on the degradation of commercial Fe-23Cr-5Al alloys at high temperatures. *Werkstoffe und Korrosion* 41, pp. 701-709, 1990.,
- [5] Pint B. A. Optimization of reactive-element addition to improve oxidation performance of alumina-forming alloys. *J. Am. Ceram. Soc.*, Vol. 86., Issue 4, pp. 686-696, 2003.,
- [6] Nychka J. A. and Clarke D. R.: Quantification of aluminium outward diffusion during oxidation of FeCrAl Alloys. *Oxidation of metals*, Vol. 63, Nos. 5/6, pp. 325-351, 2005.,

- [7] Kochubey V., Al-Badairy H., Tatlock G., Le-Coze J., Naumenko D., Quadackers W.J.: Effect of minor addition and impurities on oxidation behaviour of FeCrAl alloys. Development of novel surface coatings compositions. *Materials and corrosion*, 56, No. 12, pp. 848-853, 2005.,
- [8] Cuff R., Buscail H., Caudron E., Issartel C., Riffard F.: Oxidation behaviour of Kanthal A1 and Kanthal AF at 1173 K: effect of Yttrium alloying addition, *Applied Surface Science* 207, pp.246-254, 2003.,
- [9] [http://www.ssfs.si/download/Mehanika\\_kontakta/V4\\_Merilne%20metode.pdf](http://www.ssfs.si/download/Mehanika_kontakta/V4_Merilne%20metode.pdf).