11th Scientific/Research Symposium with International Participation
„Metallic and Nonmetallic Materials“ Zenica, B&H, 21-22. April 2016.

DEPOSITION OF Al THIN FILM ON FeCrAl ALLOY AND CONTINUOUS ELECTRICAL RESISTANCE MEASUREMENT

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Keywords: FeCrAl alloys, PVD, oxidation resistance, in-situ electrical resistanc measurement

ABSTRACT

FeCrAl alloys are used in a wide range of resistance and high-temperature applications such as wire heaters, furnace structure parts, etc. Their oxidation resistance at elevated temperatures relies on the formation of a thin and a continuous Al_2O_3 *layer on the alloy surface. Growth and thickness of the protective* Al_2O_3 *layer depends on Al content in the alloy, especially in the surface layer, where must exceed a critical concentration level. However, such protection is limited when the part is frequently exposed to thermal shocks, due to cracking of the protective layer and further oxidation of the Al depleted surface of the alloy. One of possible ways to improve high temperature oxidation resistance of FeCrAl alloy is to increase the Al concentration in the surface layer by physical vapour deposition (PVD) followed by proper heat treatment to produce the Al diffusion layer. Changes in thin films were studied by electron microscopy (SEM) and in-situ electrical resistivity measurement during heating at 5°C/min in argon gas at atmospheric pressure. After thermal treatment, oxidation tests at 1200 °C for 24h in air were conducted.*

1. INTRODUCTION

FeCrAl – based alloys are well known for their superior oxidation resistance at elevated temperatures. This excellent properties are related to the formation of thermodynamically stable alumina surface scale, which protects the 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 parts are frequently exposed to thermal cycling at temperatures above 1000°C. The reason for this is that the scale forming element, aluminium, is consumed in the alloy matrix due to the repeated thermo-shock cracking and reforming of the alumina scale during thermal cycling. If the remaining aluminium content is decreased beneath a 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].

FeCrAl alloy containing more than 7 wt. % of Al represents an interesting material for the production of components operating at high temperatures. Although a very good protection against oxidation can be achieved for Al concentration higher than 7 wt. %, mechanical properties decrease drastically. Another limitation is that the Al content of this alloy produced by conventional metallurgical methods needs to be lower than 7 wt.% in order to avoid problems related to the formation of intermetallic phases which deteriorates the material ductility [2]. One technological way to extend the lifetime of commercial FeCrAl alloys is to increase the aluminium concentration only in the surface layers of the material [3] and thus increase the available scale forming Al reservoir. Such testing was done by Bennet and colleagues who increase the Al concentration by alloying, aluminising, cladding/plating or preforming an α-Al2O3 protective scale by annealing in oxidizing gas. Increasing the surface Al concentration up to 8 wt.%, increased alloy foil lifetime at 1100°C but prove ineffective at higher temperatures due to higher alloy oxidation rate [4].

The scope of this project was deposition of Al film on to 0,7 mm sheet, followed by various thermal treatments and measurements of the relevant physical properties at various stages of synthetization: composition depth profile, microhardness, phase formation and material changes during heating and oxidation resistance. The in-situ electrical resistivity measurement was used to follow the changes in the material during heating and cooling. The micro hardness measurement of the thin film was not possible because the roughness of the initial sample was too high.

2. EXPERIMENTAL

2.1. Sample preparation

The commercial Kanthal AF alloy was used for this investigation. This material is a ferritic FeCrAl alloy, which is produced by conventional method of melting and rolling into 0,7 mm thick sheet. In addition to the main alloying elements (Al, Cr), this alloy contains small amounts of rare earth metals (REM). The chemical composition of the alloy is in the table 1.

Table 1. Chemical composition of the Kanthal AF alloy

EL.	Cr	Al	Si	Mn	S	Ni	Ti	Zr	Y	C	Fe
Wt.%	22	5,3	0,17	0,18	0,004	0,27	0,06	0,068	0,023	0,03	Ball.

The dimensions of the samples were 10x20x0,7 mm. Deposition of the aluminium layer on the surface of the FeCrAl alloy was conducted by physical vapour deposition technique (PVD) [5,6]. The PVD process was implemented using the device SPUTRON sputtering system (Balzers), which use the low voltage thermionic arc as a source of ions for sputtering. A plasma beam (typically 40V/40A) is produced between the hot filament (Ta wire) and the auxiliary anode around the target. Arrangements of this type are usually referred to as triode or tetrode sputtering system. The particular advantage of this method is that the plasma is formed independently of the sputtering voltage. Targets 60 mm in diameter are interchangeable in situ (up to four different materials), so we may easily produce a multilayered structures. The target-substrate distance is about 225 mm. A planetary drive system, which permits a double rotation of the substrate was also used. The substrates are out of plasma and it is possible to keep the substrate temperature below 100°C. Otherwise, the substrate heating is provided by quartz lamps. The quartz crystal microbalance was used for calibration of deposition rates. Deposition rates and thickness reproducibility were better than 2%. The SPUTRON system is equipped with rotary vane pump, diffusion pump and trap, cooled with liquid nitrogen [7]

Table 2. The deposition parameters of the investigated coatings N°3781 (total thickness: 1,54 µm)

Coating parameters	Al
Target purity	99,95
Background pressure (mbar)	$5x10^{-7}$
Argon pressure (mbar)	$2x10^{-3}$
Target voltage (V)	1700
Target current (A)	0.6
Substrate temperature (°C)	120
Deposition time (min)	150 min
Deposition rate (nm/min)	9

Prior to the deposition, the substrate was cleaned in an ultrasonic bath containing alcohol in order to activate the surface for the deposition process. The thickness of the applied coating was measured with a profilometer (Taylor - Hobson Form Talysurf Series 2), which allows the measurement of the surface profile in one direction of (x, y) plane. Its vertical resolution is 1 nm and lateral resolution 300 nm. The next step was an investigation of the thermal treatment. In-situ measurements of the electrical resistivity as a function of temperature were performed in a tube furnace at a constant heating rate of 5K/min up to 870°C in argon protective atmosphere. Samples were cooled down to the room temperature in the furnace. The measuring system is described elsewhere [8,9]. After determination of the entire temperature range of electrical resistance changes, samples, cut from the same strip, were heated above distinctive temperatures where a non-linear change of electrical resistance occurs. The four-point D.C. electrical resistivity measurement method with tungsten contacts and platinum wires was applied for the measurement of the electrical resistance. The measuring system for in-situ electrical resistivity measurement system (a) and a special holder for samples (b) is shown in Figure 1.

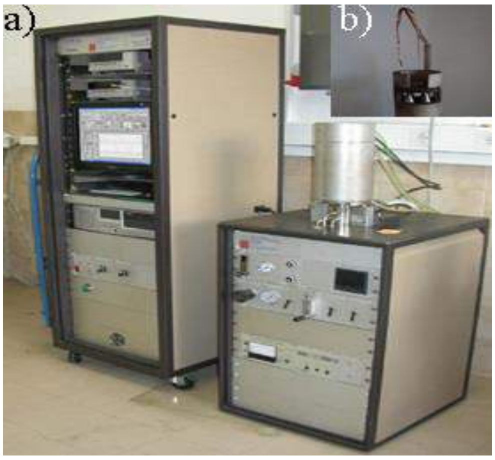

Figure 1: Equipment for in-situ electrical resistivity measurement (a) and a special holder for the samples (b); Faculty of National Sciences and Engineering, Ljubljana [4].

Cross sections for microstructure observations were prepared by cutting the samples with ISOMET precision saw. Optical microscope AXIO CSM 700 and scanning electron microscope Jeol JSM 5610 with EDS were used for microstructure observations. The oxidation resistance of the samples was investigated under isothermal conditions by thermobalance Netzsch STA 429 at1200°C, 24 h in a laboratory air atmosphere.

3. RESULTS AND DISCUSSION

3.1. Microstructure and EDX measurements of the samples after PVD coating

After surface treatment with PVD, samples were characterized by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX). Figure 2. presents an electron micrograph of a cross-section of the PVD aluminium film on a substrate. The thickness of the film measured with a profile-meter was approximately 1,6 µm. Figure 3. presents line analysis (EDX) over the cross section of the deposit coating (marked on fig. 2).

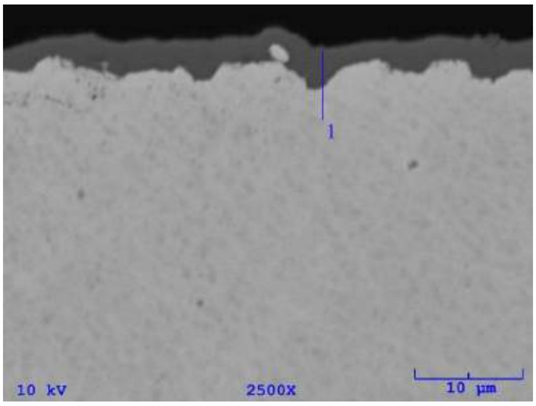

Figure 2. Scanning electron micrograph of a cross section of the PVD Al-layer on a FeCrAl substrate.

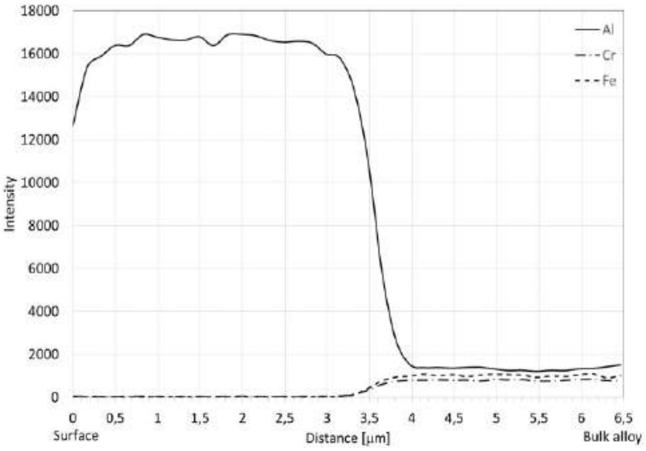

Figure 3. SEM/EDX line concentration profile taken across the PVD Al-layer and FeCrAl substrate boundary.

3.2. In situ electrical resistivity measurements of samples

It has been shown that in-situ electrical resistivity measurements can be a very suitable and precise experimental method for following the microstructural changes and phase transformations in some metallic alloys. The electrical resistance of the material depends on the number of free electrons and their mobility [10]. Any kind of crystal lattice distortion, caused by solute atoms, impurities, dislocations, etc., increases electrical resistivity of the metal due to disturbance of electron mobility. At lower temperatures, FeCrAl alloy samples exhibit practically linear increase of electrical resistance with increasing temperature. At distinctive elevated temperatures, the change of electrical resistivity becomes nonlinear, which is connected with the microstructural transformations in the material matrix. This can be seen more precisely in the electrical resistivity derivative curve ($\frac{dR}{dT}$).

The results of the electrical resistance measurements during heating with constant heating rate are presented in Figures 4. and 5. Two temperature intervals with distinctive temperatures of maximum rate of electrical resistivity change can be seen from the graphs. First one between 520 and 600°C (T_{m1}=558°C) and the second between 750°C and 850°C (T_{m2}=811°C).

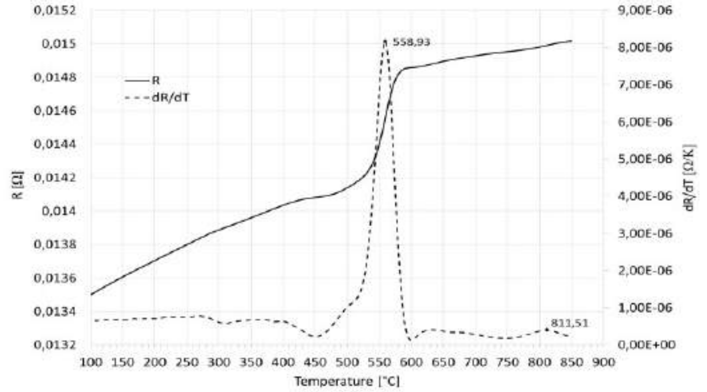

Figure 4. Electrical resistivity and its temperature derivative of FeCrAl sample with PVD Al-layer. Heating at constant heating rate of 5K/min up to 850°C in argon protective atmosphere.

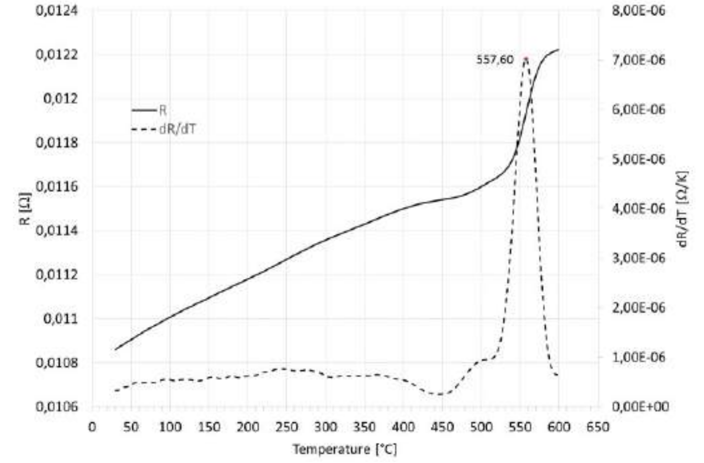

Figure 5. Electrical resistivity and its temperature derivative of FeCrAl sample with PVD Al-layer. Heating at constant heating rate of 5K/min up to 600°C in argon protective atmosphere.

3.3. Microstructure and EDX measurement of the samples after annealing

Figures 6a and b present optical micrographs of the surface of Al - PVD coated samples after heating to 600°C and 850°C respectively. It can be seen from the pictures that at the lower temperature (600°C) Al-layer has not yet completely disintegrate whereas at 850°C vanishes due to Al diffusion into the substrate. This can be seen more precisely on EDX line composition measurement (Figures 7, 8, 9, 10) across the Al-PVD layer and FeCrAl substrate boundary.

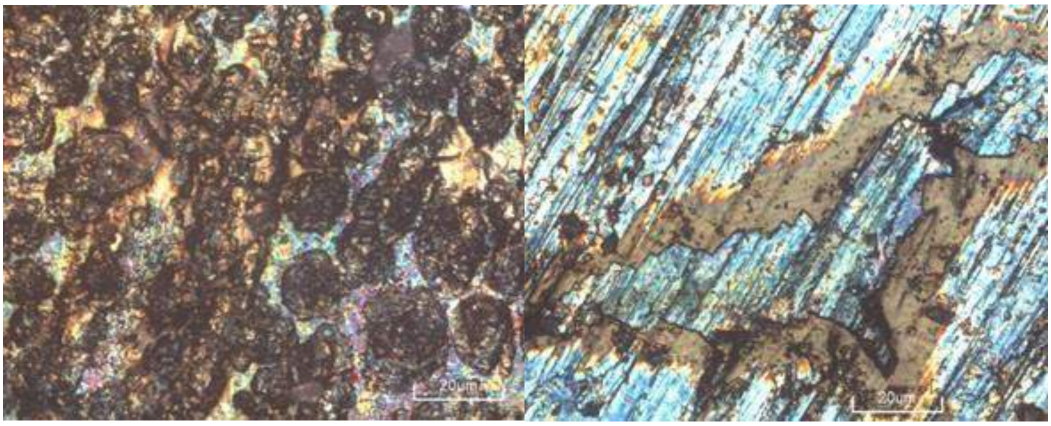

Figure 6. a) Optical micrograph of Al- PVD coated surface after heating (5K/min) up to 600°C, b) Optical micrograph of Al- PVD coated surface after heating (5K/min) up to 850°C

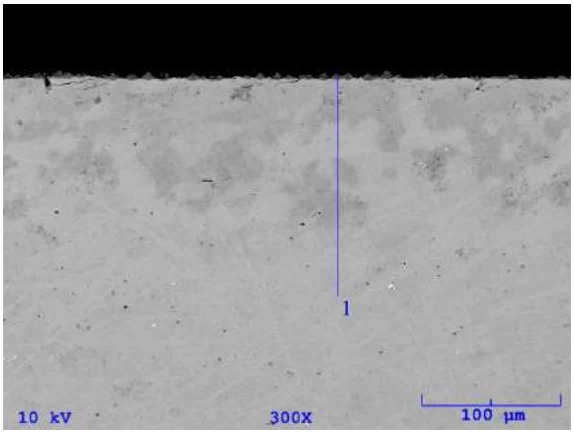

Figure 7. Scanning electron micrograph of a cross section of the PVD Al-layer on the FeCrAl substrate after heating (5K/min) up to 600°C in argon protective atmosphere.

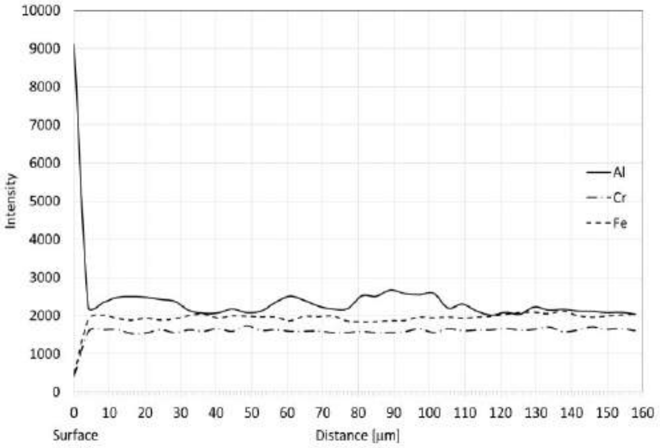

Figure 8. SEM/EDX line concentration profile taken across the boundary of PVD Al-layer and FeCrAl substrate after heating (5K/min) up to 600°C in argon protective atmosphere.

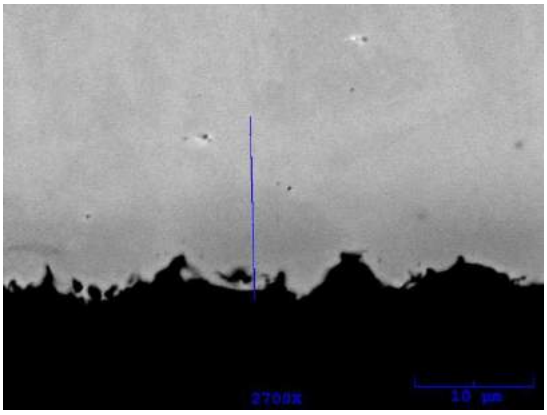

Figure 9. Scanning electron micrograph of a cross section of the PVD Al-layer on the FeCrAl substrate after heating (5K/min) up to 850°C in argon protective atmosphere.

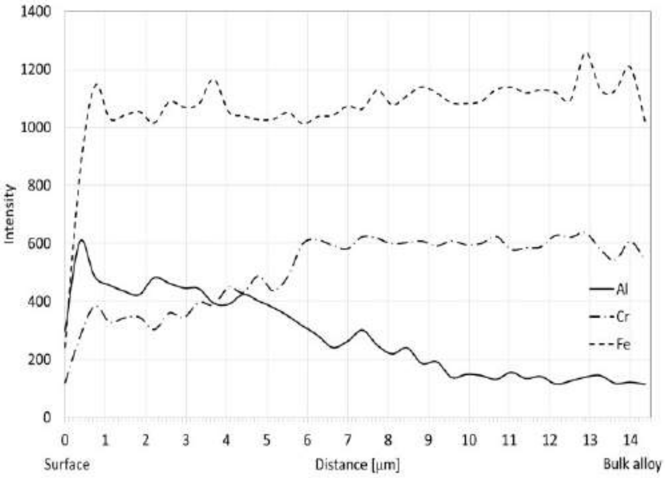

Figure 10. SEM/EDX line concentration profile taken across the boundary of PVD Al-layer and FeCrAl substrate after heating (5K/min) up to 850°C in argon protective atmosphere.

3.4. Oxidation testing

The effectiveness of PVD coating and annealing processes at different temperatures was evaluated by the oxidation testing under isothermal conditions (thermo-balance Netzsch STA 429 [11]) at 1200°C/24h in a laboratory air atmosphere. The results are presented by the relative mass gain versus time chart (Figure 11).

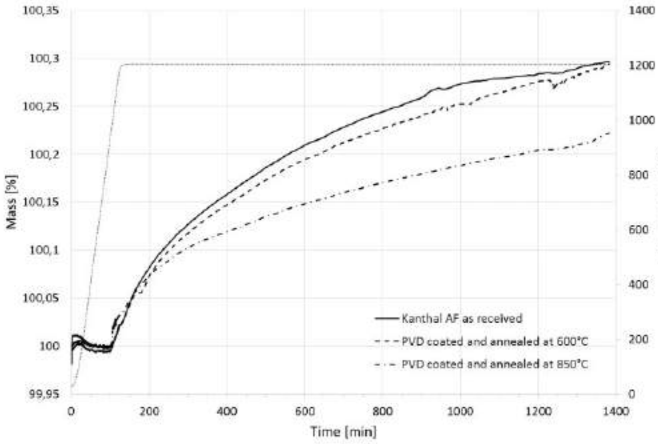

Figure 11: Relative mass gain as a function of oxidation time in air at 1200°C (heating rate 10K/min)

The lowest mass gain was achieved with the PVD Al-coated samples annealed at 850°C and the highest mass gain in the commercial alloy Kanthal AF (without PVD Al-layer). The oxidation resistance of PVD Al-coated sample annealed at 600°C was also improved in comparison to commercial Kanthal AF sample, indicating that diffusion of aluminium into the substrate has already began.

4. CONCLUSIONS

It is well known that high temperature oxidation resistance of FeCrAl alloys originates from a formation of thin and continuous Al_2O_3 layer on the alloy surface. Growth and thickness of the protective Al_2O_3 layer depend on Al content in the alloy, especially in the subsurface layer, where must exceed a critical concentration level. In order to avoid technological problems of foil production at higher (>7%) aluminium content in the alloy, one possible way to improve high temperature oxidation resistance is to increase the Al concentration only in the subsurface layer by physical vapour deposition (PVD), followed by proper heat treatment. The in-situ electrical measurement was used to study the decomposition kinetics of thin film structure. During heating at constant rate of 5 K/min, two temperature intervals of microstructural transformations were detected. First one indicate the start of Al-layer decomposition and diffusion of Al into the substrate. The second one is probably related to some minor phase formation, but we couldn’t provide evidence for that assumption. Because thickness of the Al diffusion layer depends on temperature and time of annealing, further investigations will be focused on longer annealing times at lower temperatures. The potential of this procedure will be also confirmed using the real – life components.

5. REFERENCES

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