Protective high temperature coatings with intrinsic depletion sensor

Krasimir Aleksandrov [a,*], Mathias C. Galetz [a], Gerald Schmidt [a], Francesco Depentori [a], Michael Schütze [a], Iulian Teliban [b], Eckhard Quandt [b]

[a] Dechema-Forschungsinstitut, Frankfurt am Main, Germany
[b] Christian-Albrechts-Universität zu Kiel, Kiel, Germany

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ABSTRACT

A novel approach for non-destructive residual life-time estimation of coatings for high temperature applications is presented. Coatings of ferromagnetic Cr-doped AlN are applied on a paramagnetic metallic substrate (Ni-base alloy) using a diffusion treatment. The Cr-content in AlN achieved by this procedure is about 2 at.%. Applied on a metallic plant component (turbine blade, chemical reactor, boiler tubes etc.) these coatings serve simultaneously two functions. On the one hand they deliver protection against high temperature corrosion because they act as a reservoir phase for alumina and chromia scale formation, while on the other hand due to their magnetic properties they can be used as a depletion sensor for the reservoir of the protective elements. Knowledge about the oxidation kinetics combined with monitoring of the coating's magnetic moment before and after oxidation can allow prediction of its residual life-time. Magnetic investigations of the coating indicate soft ferromagnetic behaviour. The ferromagnetic domains are visualised with the help of magnetic force microscopy (MFM). During oxidation of the coating a change in the microstructure of the alloy subsurface zone takes place. This is characterised by a gradual decrease of the amount of the ferromagnetic Al(Cr)N-phase and by the formation of new ferromagnetic precipitates of Ni and Fe throughout the diffusion zone. Their influence on the net magnetic moment of the coating–alloy system is discussed.

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1. Introduction

High temperature corrosion of metallic components in process and power generation plants is a serious issue. It is caused by the presence of different gaseous species in the environments common for these industries.

Simultaneous optimisation of the corrosion resistance and mechanical strength of the alloy used is difficult. Frequently, improved corrosion resistance compromises the mechanical properties of the alloy and vice versa. Surface modification by the application of Al- and/or Cr-rich metallic or intermetallic coatings allows increased corrosion resistance with virtually no change in the mechanical properties of the alloy. Protection against high temperature corrosion is achieved by the formation of a dense scale of Al_2O_3 and/or Cr_2O_3, which serves as a barrier between the environment and the metal. However, progressive scale formation as well as interdiffusion between the coating and the substrate during long operating periods depletes the subsurface in the scale-forming elements, Al and Cr. If their concentrations drop below a critical value the coating is no longer able to deliver corrosion protection [1–6]. Usually increased corrosion attack and rapid failure of the component follow. At present the depletion process of the coating can be recorded only by *destructive* methods.

In this paper the attempt to develop a new high temperature protective coating with sensor properties made of ferromagnetic Cr-doped AlN is reported. Doping of AlN with small amounts of Cr (2–7 at.%) alters the magnetic behaviour of this phase from para- to soft ferromagnetic, with a Curie temperature as high as 1000 K [7–11].

Monitoring the change of the coating's magnetic moment before and during operation under corrosive attack can enable *non-destructive* measurement of the depletion process. As substrates, paramagnetic alloys (austenitic steels, Ni-base alloys) have to be used. A detailed description of the concept is given elsewhere [12].

2. Experimental

The coatings were applied to Alloy 602 CA (Table 1) using a two-step diffusion treatment (pack cementation) in an inert atmosphere (argon). A detailed general description of the pack cementation principle is given in Ref. [13].

Prior to pack cementation the alloy samples ($15 \times 10 \times 4$ mm) were ground on SiC paper down to 1000 grit and then ultrasonically cleaned in ethanol. Afterwards the samples were embedded in the "pack" – a powder mixture containing the coating element Al and/or Cr (master alloy), NH_4Cl (activator) and Al_2O_3 – and placed in an alumina crucible, and then into a tube furnace. The activator serves to transfer the master alloy into the gas phase, while Al_2O_3 prevents the pack from sintering. In the first stage Al was applied, while application of Cr and N_2 took place in

Table 1
Average composition in wt.% of Alloy 602 CA.

Element	Ni	Cr	Fe	Al	Si	Ti	Mn	C	Cu	Y	Zr
Alloy 602 CA	60.0	26.0	11.0	2.1	0.5	0.2	0.1	0.25	0.1	0.12	0.1

the second stage. The parameters of the diffusion treatment are listed in Table 2.

To estimate oxidation resistance, coating degradation and magnetic moment change under oxidation conditions, coated Alloy 602 CA was exposed to air at 600 °C up to 1000 h. The morphology and thickness of the coatings were determined from metallographic cross-sections using light microscopy and SEM. The chemical composition of the coatings was determined by means of energy dispersive (EDX) and wavelength dispersive (EPMA) X-ray analyses. Magnetic characterisation was performed using VSM (vibrating sample magnetometer) and magnetic force microscopy (MFM).

By VSM the sample which is fixed to the sample holder vibrates with a given frequency and amplitude (60 Hz and 1 mm, respectively). It is centred between the two magnet pole pieces of an electromagnet that generates a DC magnetic field with high homogeneity (Fig. 1) [14].

Field strengths of several Tesla are commonly possible with laboratory VSM systems. Stationary pickup coils are mounted on the poles of the electromagnet. Their symmetry centre coincides with the magnetic centre of the sample. The oscillatory motion of the magnetized sample induces a voltage in the detection coils. The induced voltage is proportional to the sample's magnetization, which can be varied by changing the DC magnetic field produced by the electromagnet. In graphical form either the magnetic moment or the magnetization of the sample are plotted as a function of the applied magnetic filed.

By the MFM method a 2-dimensional map of the ferromagnetic domains is charted. By this technique, which is a variant of AFM (atomic force microscopy) a flexible cantilever with a magnetized tip, coated with a ferromagnetic coating of approximately 10–250 nm, is scanned over the surface. This is done by a two-pass measurement. In the first pass, the topography is recorded via intermediate contact mode (tapping mode). The topography data is then saved and the cantilever is lifted above the sample at a distance usually smaller than 100 nm (lift mode) and is subsequently oscillated with a fixed frequency (the same resonance frequency used for the tapping mode) at constant distance from the sample surface to record the magnetic data (Fig. 2a). The magnetized tip interacts with the sample's local magnetic stray fields. This causes a phase shift between the excitation oscillation and the cantilever oscillation, which is then recorded. The larger the phase shift, the bigger the magnetic interaction. The phase shift can be recorded via the oscillation of a laser which is reflected from the back of the cantilever into a photo detector. This shift is transmitted further to a computer, where a 2D map of the stray magnetic field (magnetic forces) of the investigated sample is generated. Since magnetic forces appear in the presence of magnetic domains, the resulting image shows their distribution throughout the investigated sample. The latter are distinguished as

Table 2
Pack cementation parameters.

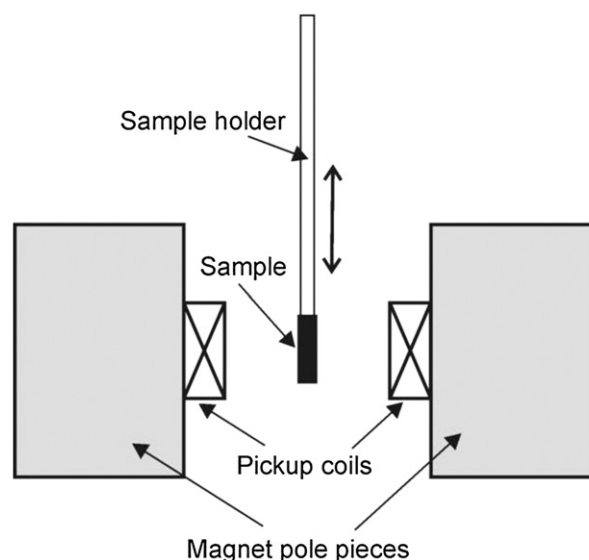| Pack cementation	Stage 1	Stage 2
Pack content (powders)	Al, 10 wt.% (99.5%, <160 μm, Carl Roth) NH_4Cl, 1 wt.% (>99%, Alfa Aesar) Al_2O_3, 89 wt.% (98%, Riedel-de-Haën)	Cr, 10 wt.% (99%, −325 mesh, Alfa Aesar) NH_4Cl, 1 wt.% (>99%, Alfa Aesar) Al_2O_3, 89 wt.% (98%, Riedel-de-Haën)
Temperature	1000 °C	1000 °C
Duration	5 h	5 h
Process gas	Ar + 5% H_2	N_2

Fig. 1. Schematic representation of VSM basic principle.

areas of different contrast (brighter or darker), while the rest of the picture (paramagnetic areas) shows no change in contrast (Fig. 2b).

For MFM measurements, a Bruker Multimode VIII with Nanoscope V controller was used. The tips were Co/Cr coated MESP (Bruker).

3. Results and discussion

Fig. 3a shows a cross-section image of coated Alloy 602 CA using two-stage pack cementation as described above. At the top of the diffusion zone a thin layer of Cr-doped AlN i.e. $Al_{1-x}Cr_xN$ is found. The Cr amount established by SEM (Fig. 1b) and EPMA averages 2 at.%. Some CrN that formed in the course of the diffusion treatment also observed at the top.

Furthermore, $Al_{0.98}Cr_{0.02}N$ dispersed in the metal matrix is found up to a depth of 50 μm throughout the diffusion zone. Some cracks in the $Al_{0.98}Cr_{0.02}N$ layer are observed. These can be caused by the difference in the coefficients of thermal expansion of the substrate and of $Al_{0.98}Cr_{0.02}N$. The bottom part of the diffusion layer mainly contains AlN and Al_2O_3.

The magnetization curve of the coated substrate (Fig. 4a) shows pronounced ferromagnetic character, which is due to the application of the coating. The uncoated substrate shows paramagnetic properties up to 8000 G (Fig. 4b).

The coated substrates indicate an obvious change of the magnetic moment by oxidation. Fig. 5 shows the change of the magnetic moment by oxidation at 600 °C up to 1000 h. A non-linear behaviour can be seen with a high increase of the moment during the first hours of oxidation followed by a strong decrease with the lowest value of the moment after around 300 h of oxidation. Further on, the magnetic moment increases monotonically with the oxidation time.

The largest changes in the magnetic behaviour (magnetic moment change) occur after 30 h and 300 h of oxidation (points in red circles, Fig. 5), which indicate a major change in the chemical composition of the diffusion layer. After 30 h the top of the diffusion zone still consists mainly of $Al_{0.98}Cr_{0.02}N$ (Fig. 6). Since Cr_2O_3 is found at the very top of the layer this suggests that CrN found in the as coated state is fully oxidised. However, Cr_2O_3 is not ferromagnetic. Thus, its formation is obviously not responsible for the magnetic moment value increase.

An interesting observation is the appearance of metallic precipitates (Ni, Fe, from the substrate) through the diffusion zone along with $Al_{0.98}Cr_{0.02}N$ (range marked with rectangular). These can be responsible for the increased magnetic moment. By VSM the net magnetic moment