Optimization of Diffusion Coatings on the Basis of Thermodynamic and Kinetic Considerations

A. Naji, M. Galetz, M. Schütze
e-mail: naji@dechema.de
Funded by: BMWi via AiF
Period: 01.06.2009 - 31.12.2011

Introduction

Materials, which work at high temperatures (1000°C) under oxidizing and water vapor containing atmospheres are severely degraded. Diffusion coatings improve the high temperature corrosion resistance of materials by enriching the substrate with elements that form a protective oxide scale, which is resistant against the conditions mentioned. Single- (Al) and multi-element (Al-Si) diffusion coatings were developed on austenitic 18Cr10Ni and 20Cr31Ni-steels in the form of the pack cementation procedure. In order to determine the most appropriate coating process parameters, thermodynamic and kinetic considerations have been performed. It is shown that the aluminum activity, which arises from the partial pressures of the aluminum chlorides in the powder pack depends on the coating parameters, which can lead to the formation of brittle intermetallic phases, if the Al-activity exceeds a certain value.

Design of Coating Process

The parameters of a diffusion coating process are the coating time, coating temperature and the aluminum and activator amount. By means of the program FactSage thermodynamic phase equilibrium calculations can be done in order to calculate the partial pressures of the aluminum chlorides versus temperature, given by the ratio of Al (master alloy) and NH_4Cl (activator) (Figure 1).
To determine the coating growth, kinetic considerations have to be done, whose basis is Fick's first law:

$$ j = -D \frac{\partial c}{\partial x} $$

By assuming a linearized concentration gradient and a coating growth, which is proportional to the diffusive flux of Al into the substrate, the resulting coating thickness can be written as:

$$ x = \sqrt{2 \frac{D}{k} \Delta c \, t} $$

where k is a constant. Δc is the concentration difference, which also can be written as the difference between the Al-activity of the Al chlorides formed during the coating process and the Al-activity in the intermetallic phases Fe_2Al_5 or FeAl, which are given in [1]. Figure 2 shows the calculated coating growth kinetics at several Al-activities in the pack, caused by varying the Al and NH_4Cl ratio in the powder pack. The process temperature is 1000°C and the coating time is 4 hours. As it can be seen there is an Al-activity limit at a(Al) = 0.128. If the Al-activity in the pack exceeds the amount of the Al-activity in the FeAl phase, Fe_2Al_5 will be formed.
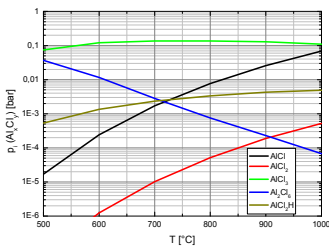
Figure 1: Thermodynamic calculation of the Al chloride partial pressures versus temperature for a given master alloy and activator ratio
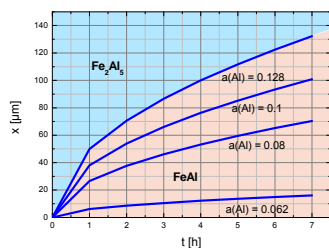
Figure 2: Coating growth kinetics with FeAl and Fe_2Al_5 regimes

Diffusion Coatings

Al single element and Al-Si co-diffusion coatings were developed for austenitic steels via the pack cementation process. The resulting intermetallic phases in both Al and Al-Si coatings depend on whether the coating parameters cause a high or low activity Al coating.
Figure 3 shows cross sections of Al coatings resulting from high and low Al-activity pack procedures on an 18Cr10Ni-steel. The high activity pack leads to a brittle Fe_2Al_5 phase. In the case of Al-Si codiffusion coatings Al and Si were co-deposited into the substrate simultaneously, under the assumption that the Al chlorides of the coating elements (Al and Si) have sufficient partial pressures. By adding another element (e.g. Si) to the master alloy (e.g. Al), the thermodynamic activity of the normally favored element is reduced compared to the single element diffusion process. Both the high and low activity coatings exhibit cracks due to the high coating thickness (Figure 3).
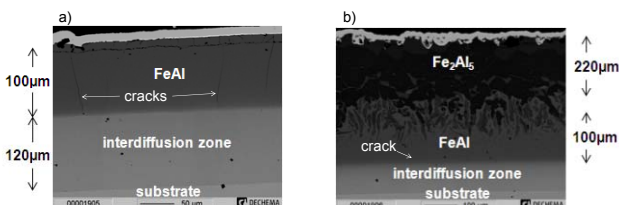
Figure 3: Cross section of a (a) low and (b) high Al-activity coated 18Cr10Ni-steel

High Temperature Corrosion Tests

Cyclic oxidation tests were performed on coated (Al, Al-Si) and uncoated specimen of 18Cr10Ni and 20Cr31Ni-steel and compared with an uncoated Ni23CrFe alloy. The specimens were exposed for 250 x 4h cycles at 1000°C in a combustion atmosphere (51.6% N_2, 31.9% H_2O, 13.3% CO_2, 3.2% O_2). The cooling procedure was at room temperature for 1 hour in synthetic air.
The recorded mass gain per unit area (Figure 4) shows that diffusion coatings improve the high temperature corrosion resistance of the coated materials significantly. The mass change curves have a low slope.
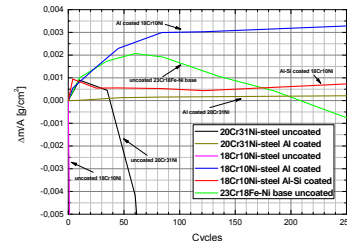
Figure 4: Mass gain per unit area of exposed specimens

Al coatings promoted the formation of an aluminum oxide layer on the exposed steels. However, cracks and spallations occurred in the diffusion layer. This is due to the cracks which were formed during the coating process. In the case of high activity Al coatings the Fe_2Al_5 phase promotes the extension of the cracks during cyclic oxidation, due to its brittleness and the mismatch of thermal expansion coefficient between Fe_2Al_5 and austenitic steels. Furthermore, during exposure Fe_2Al_5 transforms to FeAl. Later Al diffuses even further into the substrate to form a solid solution as shown in Figure 5a. The Al-Si coating enhanced a closed oxide scale without cracks (Figure 5b). Besides promoting the formation of the FeAl phase in the coating procedure, it is expected that Si increases the ductility of the coating [2] and the adherence of the Al_2O_3 scale to the substrate [3]. In some cases of the Al-Si-coated 18Cr10Ni-steel large nodules consisting of iron oxide were generated. The reason is that the Al in the coating is consumed during exposure and consequently cannot protect the substrate any more.
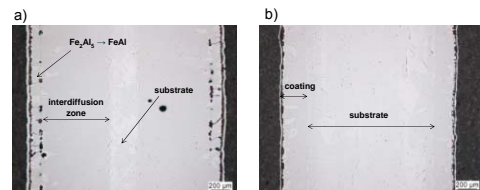
Figure 5: Cross section of a (a) high activity Al coated and a (b) low activity Al-Si coated specimen of 10Cr18Ni-steel after 1000h exposure

Next Steps

- Detailed design of the coating process
- Development of low activity coatings without cracks
- Optimization of the Al-Si diffusion coating by increasing the Al reservoir
- Lifetime estimation of the coating for exposure

Project Partners

- O. Pasdag, Zentrum für Brennstoffzellen Technik GmbH, Duisburg
- T. Ebersbach, Institut für Fügetechnik und Werkstoffprüfung GmbH, Jena

Acknowledgment

References

- [1] P. D. Desai, J. Phys. Chem. Ref. Data, Vol. 16, No. 1, 1987
- [2] E. Fitzer et al., Thin Solid Films, 64 (1979) 305 – 319
- [3] H. Arabi et al., Intern. Journ. of Eng. Science, Vol. 19, No.5-1, 2008, Page 39-44