



A new approach for a slurry based coating system for the prevention of high-temperature oxidation

Mesut Aslan, Matthias Wittmar, Henning Bolz and Michael Veith



Introduction

Surface coatings to protect against oxidation extend the service temperature and the service life of basic metals. The commercially used coating systems can be divided into three main groups: first diffusion layers based on Al, Cr or Si which will be converted to corresponding protective oxide phases during the service, second M-Cr-Al-X based overlay coatings where M refers to Ni or Co and X refers to oxygen-active elements such as Y and Hf, third thermal barrier coatings consisting of an overlay coating and a zirconia coating. These coatings are produced mainly by methods like PVD, CVD and plasma spraying [1]. Compared to highly sophisticated commercial coating methods, slurry based oxidation protection coatings for metals are very interesting because of their simple applicability even to complex shaped parts. Pandey et al. report the efficiency of different slurry based coating systems including different phosphate bonded oxides and oxide mixtures with respect to their oxidation protection for carbon steels [2]. Slurries containing a mixture of zirconia and metallic components such as W, Co, Cr and organic binder applied by dipping, painting or spraying were also used for the preparation of oxidation protecting coatings [3]. The reaction bonding of alumina with metallic aluminum to produce near-net-shape bulk ceramics by reaction sintering at moderate temperatures (RBAO) was developed by Claussen et al. [4]. In this method, the metal phase oxidizes to alumina and

the volume expansion occurring during the oxidation partly compensates for the overall shrinkage. The advantage of this RBAO (**R**eaction **B**onded **A**luminum **O**xide) technique concerning the reduced shrinkage is also necessary for the preparation of crack-free/crack-reduced ceramic coatings on rigid substrates. Some work can be found in the literature concerning the use of RBAO technique for oxidation protection and surface sealing [5-7]. Wang et al. describe a coating method by modified electrophoretic deposition with Al containing slurries on Fe-Cr-Al steel substrates, giving no detail about the performance of such coatings. Mechnich et al. use slurries of Al/Al₂O₃ mixtures to coat highly porous ceramic matrix composites with a dense layer to reduce their permeability [6, 7]. However, publications concerning the oxidation protection of carbon steels (which are widely-used and easily oxidized under high-temperature) with RBAO-based coatings could not be found.

Therefore, the aim of the present work was to test a RBAO-based coating system for its ability to prevent high-temperature oxidation of carbon steels. The system consisted of a mixture of alumina and aluminum powders in ethanolic suspensions. To increase the initial packing density powder mixtures of two different particle size ranges were used as alumina source. It is expected that green coatings with higher green densities should result in fired coatings with improved performance.



Experimental

For the preparation of ethanol-based coating slurries the following starting powders were used: alumina (corundum) in two different particle size ranges with specific surface areas of $7.5 \text{ m}^2/\text{g}$ and $1.5 \text{ m}^2/\text{g}$ and metallic aluminum powder with a particle size range of $0\text{-}50 \text{ }\mu\text{m}$ (Al-Sprühgrieb, $0\text{-}50 \text{ }\mu\text{m}$, Possehl Erzkontor, Lübeck). The ratio of fine grained alumina/coarse grained alumina was 38/72 by volume. The aluminum/alumina volume ratio varied between 0.2 and 1.0. Ethanol slurries with a total solid content of 50 wt.% were prepared by attritor milling with alumina balls for 3 h. As a dispersing aid for the slurries an organic acid (trioxadecanoic acid) was used. The all-side coatings on plates from carbon steel (Nr. 1.0330) of different thicknesses were prepared by spraying. The oxidation kinetics of coated and non coated steel samples were characterized by thermogravimetric measurements on samples of dimensions $5 \times 5 \times 1.5 \text{ mm}^3$ (Netzsch, STA 449C). Large size samples of dimensions of $100 \times 100 \times 1.5 \text{ mm}^3$ were annealed at $950 \text{ }^\circ\text{C}$ in air atmosphere (heating rate $10 \text{ K}/\text{min}$, cooling rate $15 \text{ K}/\text{min}$). The degree of oxidation was determined quantitatively by light/electron microscopic examination of polished cross sections of the oxidized samples.

Results and discussion

The aluminum powder used for the coating formulations consists of nearly spherical particles ranging from few μm to 20-

$30 \text{ }\mu\text{m}$ (Figure 1a). The morphological changes of this powder as a result of ball milling in ethanol for 3 h are shown in Figure 1b. Obviously a significant plastic deformation of the single aluminum particles took place during this treatment resulting in a plate-like structure (aspect ratio > 3). This plate-like structure was expected to be more adequate for coatings with smooth surfaces, even for systems containing large particles as in the present case. This assumption was proved correct by the observation of the surface morphology of a sprayed coating prepared from slurries with Al: Al_2O_3 ratio of 50:50 by volume as shown in Figure 1c. The coating shows good coverage of the steel substrate and relatively smooth with some rises and dimples. The alumina fraction of the coating seemed to fill the voids between the Al-platelets, as expected.

Oxidation tests of steel samples coated with formulations containing different amounts of metallic aluminum revealed that an aluminum content of around 50 vol.-% was needed to achieve an optimal oxidation protection (Figure 2a). Apparently, formulations with these compositions also result in coatings with optimal density. This can be verified by considering the volume expansion of metallic aluminum during the oxidation reaction. Volume expansion during the oxidation of metallic aluminum amounts to 27.6 % with respect to the initial volume of aluminum. By assuming an initial coating density of 80 % (determined indirectly on slip casted samples from slurries with a Al: Al_2O_3 ratio of 50:50 by

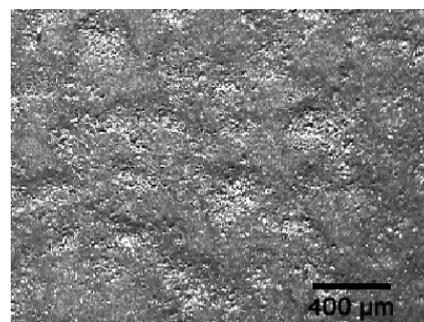
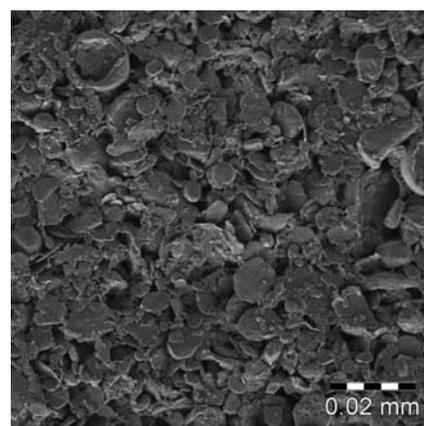
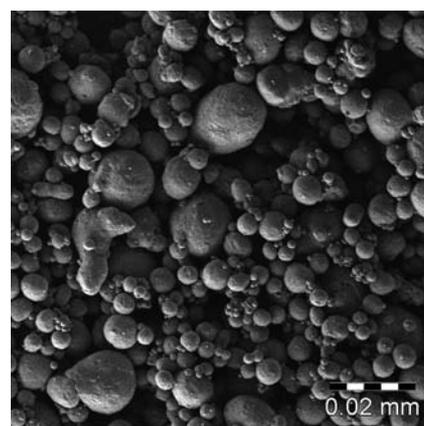


Figure 1: Effect of ball milling on the morphology of aluminum powder and a representative top view of a green coating on steel prepared by spraying. a) (top) SEM picture of as received aluminum powder, b) (middle) the same powder after ball milling for 3 h, c) (bottom) top view of a green coating.

volume) a green coating would densify up to closed density (> 92 vol.-% space filled) by the reaction $2 \text{Al} + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$. Coatings with higher aluminum content would tend to crack thereby reducing their performance with respect to oxidation protection as was seen experimentally (Figure 2a).

Results of experiments with coatings with equal amounts of Al and Al_2O_3 (50:50 composition), but different thicknesses show that the optimal coating thickness seems to be approximately 40 μm (Figure 2b), which relates to the upper limit of the particle size range of the deformed metallic aluminum powder used for the coating formulations.

Following the optimization of the composition and coating thickness the influence of the coatings with these optimized parameters (Al: Al_2O_3 ratio 50:50, coating thickness around 40 μm) on the oxidation kinetics of steel substrates was investigated. The related experiments were carried out on small samples by thermogravimetric (TG) measurements as well as by furnace annealing of large sized samples on which cross sections were observed with respect to oxidation propagation (Figure 3). The plot in Figure 3a shows the TG curves obtained on samples of non-coated steel, steel coated with Al: Al_2O_3 and steel coated only with alumina (to demonstrate the exhibit of metallic aluminum addition), respectively. Non-coated samples and samples coated with alumina mixtures show similar oxidation character, indicating a strong weight gain at the beginning of isothermal holding at 950 °C which decreases with time

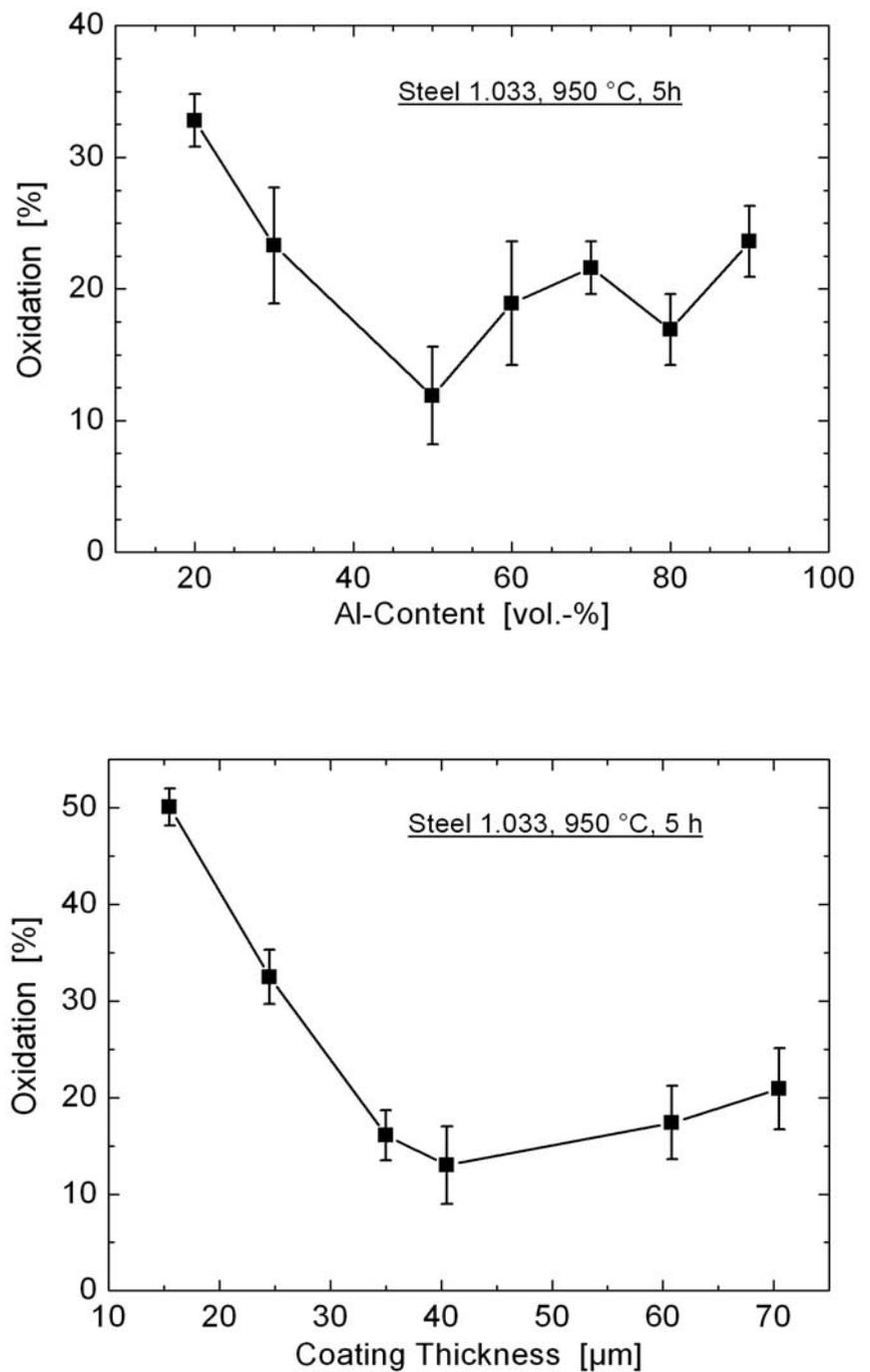


Figure 2: Optimization of the coating formulation with respect to aluminum content and coating thickness. a) (top) Oxidation vs. aluminum content, b) (bottom) oxidation vs. coating thickness.



and becomes almost linear after 60 min. The coatings with an alumina mixture effect only a minor decrease of weight gain compared to the non-coated samples and thus, seem to be not effective for oxidation protection. The reason is that alumina and even alumina mixtures can not form a dense protecting layer at temperatures of 950 °C due to low sintering activities. In contrast, samples coated with Al:Al₂O₃ show from the beginning of the isothermal holding a nearly continuously decreasing weight gain which indicates diffusion controlled oxidation through dense protecting layers (total weight gain after 120 min isothermal holding, 110 µg/mm² for Al:Al₂O₃ coated samples, 350 µg/mm² for non-coated samples, respectively). The effect of long term air annealing on the oxidation propagation of coated and non-coated steel samples is shown in Figure 3b. It can be clearly seen that Al:Al₂O₃ coatings are very effective for oxidation protection. After 10 h holding at 950 °C in air only 20 % of the initial thickness of the steel samples is lost if they are coated. In case of non coating almost 85 % will be lost. In contrast, coatings from phosphate bonded oxide mixtures allow under similar conditions only an oxidation protection of around 50 % as reported by Pandey et al. [2].

Quantitative and qualitative microstructural analysis were carried out on polished cross sections of the samples by SEM and EDX analysis, respectively (Figure 4). Figure 4a shows a SEM picture of a coated sample which was heated to 950 °C and cooled down to room temperature after 1 min holding time. The coating seems

to be dense (closed porosity) with some large pores inside the coating. The cross section clearly shows crack formation along the phase boundary between metal and coating. Therefore, the scales formed is easily removable. The coating seems to consist of different phases. A closer look by EDX reveals that aluminum, iron and oxygen are detectable over the coating indicating alumina and iron oxide phases might be present. No metallic aluminum cluster could be found by EDX. But, in samples which were annealed at 950 °C for 1 min metallic aluminum could be detected by XRD measurements. The results of EDX analysis on locations labeled as 1-8 on the SEM picture in Figure 4a are shown in Table 1.

Location	Intensity [counts]		
	Fe	Al	O
1	3423	0	0
2	3258	0	0
3	2212	0	0
4	333	4188	1972
5	120	4284	1798
6	0	4805	1705
7	403	2591	1597
8	901	386	1269

Table 1: Results of EDX analyses on sample in Figure 4a.

After a long time exposure to air at 950 °C for 5 h a formation of FeO_x scale takes place, not only between the Al:Al₂O₃ coating and metal substrate, but also above this coating as outer layer. This behavior indicates that the Al:Al₂O₃ coating must be partly permeable for Fe and

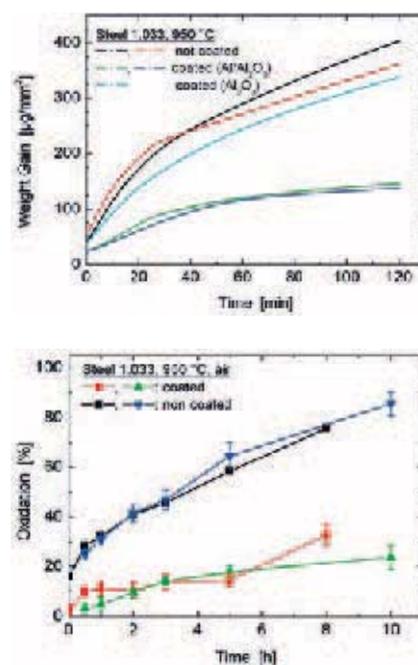


Figure 3: Oxidation behavior of samples during isothermal holding at 950 °C in air. a) (top) TG plot, b) (bottom) furnace annealing.

also for O with local permeability differences (Figure 4b).

Summary and conclusions

Coatings containing Al and Al_2O_3 binary mixtures with an Al content of 50 vol.-% and a thickness of 40 μm result in a significant reduction of the oxidation of steel at high temperatures. The scale formed can be easily removed due to crack formation along the phase boundaries of metal and coating. Thus, this coating system can be used as temporary coating to reduce scaling loss. There is an additional potential for the further improvement of the coating properties to be used as permanent protective coatings by reducing/preventing the crack formation through optimization of the processing and the starting powders, especially metallic aluminum.

References

- [1] J.R. Nicholls, JOM Journal of the Minerals, Metals and Materials Society, 52, 1, (2000), 28-35.
- [2] J.L. Pandey, M. K. Banerjee, Anti-Corrosion Methods and Materials, 44, 6, (1997), 368-375.
- [3] L. Kamo, M. Greathouse, R. Kamo, Proc. Int. Thermal Spraying Conf., & Exposition, Orlando, Florida, USA, 28 May-5 Juni 1992.
- [4] N. Claussen, S. Wu, D. Holz, J. Am. Ceram. Soc., 76, (1993), 970-980.
- [5] Z. Wang, P. Xiao, J. Shemilt, J. European Ceram. Soc., 20, (2000), 1469-1473.
- [6] P. Mechnich, W. Braue, H. Schneider, Int. J. Appl. Ceram. Technol., 1(4), (2004), 343-350.
- [7] W. Braue, P. Mechnich, Mat. -wiss. u. Werkstofftech. 38(9), (2007), 690-697.

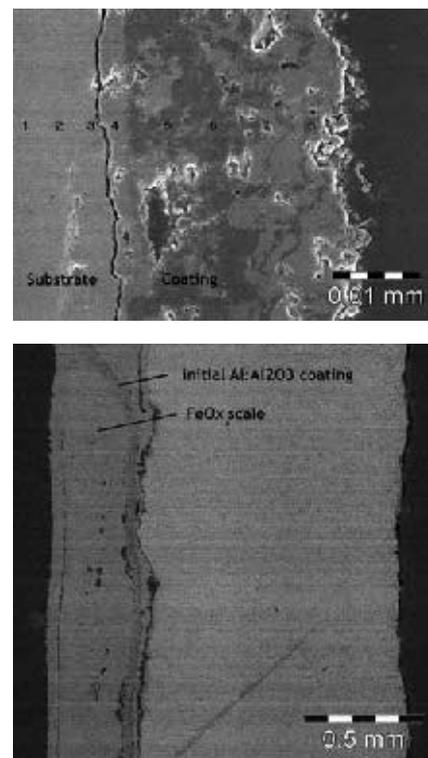


Figure 4: SEM pictures of Al:Al₂O₃ coatings after annealing at 950 °C in air. a) (top) SE picture, 950 °C, 1 min, b) (bottom) BSE picture 950 °C, 5 h.