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N.B.: When citing this work, cite the original article.

Original Publication:

Kang Yuan, Ru Lin Peng, Xin-Hai Li, Annika Talus, Sten Johansson and Yandong Wang. Hot corrosion of MCrAlY coatings in sulphate and S₂ environment at 900 °C: is SO₂ necessarily bad? 2015, *Surface & Coatings Technology*, 261, 41-53.

<http://dx.doi.org/10.1016/j.surfcoat.2014.11.065>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-111118>

Hot corrosion of MCrAlY coatings in sulphate and SO₂ environment at 900 °C: is SO₂ necessarily bad?

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Abstract

MCrAlY coatings can be corroded due to the basic fluxing (type-I hot corrosion) of the suppose-to-be protective alumina scale in a molten sulphate environment. In this study, two MCrAlY coatings, *coating A* (10 wt.% Al, 20 wt.% Cr) and *coating B* (7 wt.% Al, 28 wt.% Cr), were tested in 48-hour cycles at 900 °C in a sodium-potassium sulphate environment with and without SO₂ (500 ppm). The aim was to study the effect of SO₂ at the typical type-I-hot-corrosion temperature – 900 °C. The results showed that the corrosion behavior of the MCrAlY coatings depended not only on the coating composition but also on the corrosion environment. It was found that in *coating A* alumina scale was more resistant in the sulphate-plus-SO₂ condition than that in the sulphate-only condition. Such phenomenon indicated a beneficial effect of SO₂. On *Coating B*, however, mixed oxide layers, consisting of alumina and other oxides and sulphides, formed after a certain number of cycles in the sulphate environments with or without SO₂ gas. In this coating, the addition of SO₂ in the sulphate environment promoted the formation of non-dense chromia oxides which may form from oxidation of Cr-sulfides.

Keywords: Hot corrosion; Basic fluxing; MCrAlY; SO₂; Alumina

1. Introduction

Hot corrosion of metals or alloys is a type of accelerated damage (comparing with pure oxidation) caused by the deposition of a thin film of molten salts (usually sulphates) on the material surfaces in the temperature interval between 650 and 1000 °C [1-3]. In gas turbines, the formation of corrosive deposits can take place due to a direct shedding of salts from the compressor, by adding fossil fuels for combustion, or by chemical reactions between salts and gases [4,5]. The most common salt present during hot corrosion in gas turbines is sodium sulphate - Na₂SO₄ [1,3-5]. For components experiencing temperatures above 884 °C (the melting temperature of Na₂SO₄), or lower temperatures if other species like K₂SO₄ and NaCl also are present that can decrease the melting point of the salt mixture, the involvement of the molten salts can cause fluxing of the protective oxide scale, resulting in hot corrosion damage of the alloys [2,6-8]. Dependent on the basicity (or acidity) of the molten salts, for instance in Na₂SO₄, an oxide scale like alumina can be dissolved in different ways [2,6-8], like:

The fluxing of the oxide scale (by Eq. 1 or Eq. 2), is controlled by the thermodynamic activity of Na_2O or SO_3 [2,8]. The basic fluxing (Eq. 1) was usually found to occur when the sulphate became a liquid [9], while the acidic fluxing (Eq. 2) occurred in an environment enriched by SO_3 and was typically observed below the melting point of the pure Na_2SO_4 [6,7].

Many researchers have focused on the hot corrosion behavior of MCrAlY coatings (M for Ni and/or Co) in molten-sulphate environments [10-15]. C. Leyens et al. [11] found that the failure of a TBC system (a NiCrAlY coating as the bond coat, and a ceramic as the top coat) was due to the cracking of a non-protective, voluminous, mixed oxide layer forming on the NiCrAlY coating rather than due to the degradation of the ceramic layer in sodium-potassium sulphates at 950 °C. Their another publication [10] showed that the chemistry of the corrosion salts, e.g. K/Na ratio and sulfur ratio, played an important role on the corrosive attack on MCrAlY coatings, indicating that the degradation of coatings in a corrosion environment can be increased or decreased with the change in salt chemistry. The work of Q.M. Wang [12] showed that a catastrophic internal sulfidation of Cr and Ni could take place after the alumina scale lost its protection. The importance of the formation of a protective alumina scale was also strengthened by S. Geng et al. [13] who used a nano-crystalline coating to improve the hot corrosion resistance. The durability of alumina scales on MCrAlY coatings in molten sulphates is also coating-composition dependent [14].

In general, at high temperatures (above about 900 °C) and in gases where the SO_2 or SO_3 partial pressure is low (e.g. less than about 10^{-3} atm), the hot corrosion is driven by the basic fluxing mechanism and metal sulfidation, namely type-I hot corrosion [16]. So far, the research for testing the corrosion behavior of MCrAlY coatings in sulphates at type-I-hot-corrosion temperatures have mainly focused on atmospheres without SO_2 according to authors' literature survey [10-15]. The study of MCrAlY coatings at a type-I-hot-corrosion temperature in sulphate-plus- SO_2 environment was very limited. That could be due to people's general cognition that alumina scale fails mainly due to the high-activity Na_2O in the molten sulphate by the basic fluxing mechanism (Eq. 1).

According to the chemical reaction shown in Eq. 3 [2], the activity of Na_2O and the activity of SO_3 (or the partial pressure of SO_3) can reach a balance in a sulphate environment at a high temperature. This indicates that it is theoretically possible to decrease the activity of Na_2O by simply increasing the activity or the partial pressure of SO_2/SO_3 (in presence of oxygen, SO_2 can (partially) convert to SO_3 [16]). If so, the presence of SO_2 in gas may play a beneficial role for the hot corrosion resistance of MCrAlY coatings, by suppressing the basic fluxing of alumina scales.

For instance, A. K. Mishra's investigation indicated the possibility to decrease the hot corrosion attack on alloys (A.K. Mishra used the alloy U-700) by increasing the SO₂ content in the atmosphere [17,18]. Since there are very few investigations on the hot corrosion behavior of MCrAlY coatings in sulphate-plus-SO₂ environment at type-I-hot-corrosion temperatures, some hot corrosion tests were carried out in this investigation. Two MCrAlY coatings, with different Al and Cr content, will be tested at 900 °C in different corrosion conditions: with sulphate only, with SO₂ gas only, and with sulphate plus SO₂ gas.

2. Experimentals

Two MCrAlY coatings – *coating A* (with higher Al and lower Cr), and *coating B* (with lower Al and higher Cr) whose composition was shown in Table I – were sprayed on a Ni-based superalloy Inconel 792 (Ni-12.5Cr-9Co-4.175W-4.175Ta-3.975Ti-3.375Al-1.9Mo, wt.%) by high-velocity oxy-fuel (HVOF) spraying technique. Before hot corrosion tests, the samples were subjected to heat treatments consisting of solution annealing at 1120 °C for 2 hours in vacuum and ageing at 845 °C for 24 hours in air. Such heat treatment is similar to an industrial practice. The two coatings (*coating A* and *B*), in as-sprayed status, were provided by two manufacturers, showing mainly different substrate-coating interface qualities; *coating B* had a better interface quality with less porosity and less alumina sanding-grits. The quality of the substrate-coating interfaces was greatly improved by applying the annealing and ageing heat treatments.

Three types of corrosion testing were carried out: with salt deposition in air (SD), with salt deposition plus SO₂ in air (SS), and with SO₂ in air (SA), as shown in Table II. The testing was performed in temperature-cyclic furnaces. Each cycle consisted of heating at 900 °C for 48 hours followed by static-lab-air cooling to a temperature at or below 100 °C. The sample surfaces for the SD and SS corrosion, before each 48-hour cycle, were sprayed with a salt blend of (0.8Na,0.2K)₂SO₄ to reach a sulphate deposition of 20-25 µg/(cm²•h). In the SS and SA conditions, 500 ppm SO₂ was added in air.

The sample surfaces after the corrosion were measured by using X-ray diffraction (XRD) technique with Cr-K_α radiation (wavelength = 2.28970 Å). Theta-2theta scanning was carried out in the plane normal to the sample surfaces with a 2theta-angle range between 25° to 95°. The surface morphology of the coatings (without surface clean) was studied in a scanning electron microscope (FEG-SEM) Hitachi SU-70 equipped with energy/wavelength dispersive systems (EDS and WDS). The samples were also cut, mounted and polished for the investigation of the sample cross sections. In the SEM, both secondary-electron (SE) and backscattered-electron (BSE) images were produced. The chemical compositions were measured by using EDS.

3. Results

The microstructures of cross sections of the coatings after the solution and ageing heat treatments are shown in Fig. 1. Some pores can be seen in these two HVOF coatings along the splats' interfaces; the porosity level in these coatings was lower than 1 vol. %. The substrate-coating interface became stronger after heat treatments with a decrease in the porosity at the substrate-coating interface comparing with an as-sprayed coating. Fig. 2 and Fig. 3 present EDS maps from the coating cross section near surface. Since the ageing treatment was done in air, some oxidation had occurred at the coating surfaces during the heat treatment, forming a thin alumina scale ($\sim 0.1 \mu\text{m}$). Inside of the coatings, β phase (Ni and Al rich) and γ phase (Co and Cr rich) can be found. In addition, some Cr rich phases also formed in the coatings; in *coating A* the Cr rich phases were mainly α -Cr while in the *coating B* were α -Cr and σ -CrCo. Y was high at the coating splat interfaces, and showed some Y-oxides. In the coatings, Si was dissolved in both β and γ phases (the Si rich "phase" above the coating surface in the mapping results was from the epoxy).

Fig. 4 presents an overview of the corroded coating surfaces. All surfaces remained flat after the hot corrosion tests except for *coating A* in the SS condition. *Coating A* after the SS corrosion showed a heavy edge corrosion, i.e. that the coating edges were drastically attacked by the sulphate acting together with SO_2 . Such edge corrosion was caused by the corrosion of the substrate along the substrate-coating interface which further induced coating bending or deformation, resulting in a heavy break-down of the surface oxide layer and the acceleration of internal sulphidation, oxidation and even nitridation. Since the two coatings (*coating A* and *coating B*) were sprayed by two different manufacturers, the quality of the sub-coat interfaces differed; *coating B* had less porosity and less alumina grinding-grits, therefore, showing a better quality of the sub-coat interface. The edge corrosion behavior cannot fully represent the corrosion resistance of the coatings. The following results and analyses in this study, therefore, will focus on the flat areas of the coatings which were not affected by the edge corrosion.

The XRD spectra measured on the corroded coating surfaces are shown in Fig. 5. The results for "SS-5cyc" and "SS-6cyc" are missing because those two samples were mounted directly for cross-section observation before a XRD measurement. In the results, some peaks from the metallic phases in the MCrAlY coatings are shown, e.g. γ -Ni, β -Ni₃Al and σ -CrCo, while some other peaks represent the corrosion products, e.g. alumina (i.e. α -Al₂O₃), (Co,Ni)Cr₂O₄ spinel (shortened as spinel in this paper) and chromia (i.e. Cr₂O₃). In addition, Na₂SO₄-sulphate was also detected, but only in the SS condition.

The "amounts" of some species like sulphate, chromia, alumina and spinel were calculated by using the approach shown in Fig. 6, in which the areas (i.e. pixels) of the peaks of "k", "l", "m" and "n" were measured. The approach in Fig. 6 can be used for a qualitative comparison of the amount of phases. The results of the comparison are presented in Fig. 7. It shows that the detectable sulphate was only found in the SS condition on both coatings. Chromia was only found in the SS condition and only in *coating B*. On *coating A*, the amounts of alumina and spinels in the SS condition were less than that in the SD condition, while, on *coating B*, more alumina and more or comparable amount of spinels were found in the SS condition than in the

SD condition. Note such approach based on the measurement of the XRD peaks (shown in Fig. 6 and Fig. 7) was highly dependent upon the setting ups of the XRD measurement which, however, may not be well controlled in this study. Therefore, the corresponding results shown in Fig. 7 should be analyzed cooperating with the following microstructure analyses.

The cross-sectional morphology of the surface oxides on the coatings are shown in Fig. 8. The identification of the oxides (alumina, spinels, and chromia) in Fig. 8 was based on the EDS measurement and the BSE imaging contrast. Chromia, formed on *coating B* in the SS condition, showed a plate-like morphology. A continuous alumina layer was shown in all conditions except for the SS condition (5, 6 and 8 cycles) and the SD condition (10 cycles) on *coating B*.

A more detailed comparison of the microstructures of the oxide layers on the coatings for the SD-10 cycles is shown in Fig. 9. Of course the corrosion attack was non-uniform on the coating surface; however the images in Fig. 9 (as well as for Fig. 10) can represent the morphology in most parts of the oxide layers. One can clearly see that a thicker but purer alumina scale formed on *coating A* (Fig. 9a), while a mixed oxide layer containing alumina, chromia, spinels, and S-rich phases formed on *coating B* (Fig. 9b). The S-rich phases were more or less combined with Cr, being probably Cr_xS_y . Under such less-protective mixed oxide layer, precipitates of Al-nitrides (probably AlN) were also detected in this coating. Note that mixed oxides can also be found in the alumina scale on *coating A* (Fig. 9a); however the amount of the mixed oxides was much less than that on *coating B* (Fig. 9b). Fig. 10 compares the oxides on the two coatings in the SS condition (8 cycles). On *coating A*, a continuous and thin alumina scale formed without forming many spinels or other oxides (Fig. 10a); on *coating B*, however, a mixed oxide layer can be seen, above which chromia plates also formed (Fig. 10b).

Fig. 11 and 12 present EDS mapping results on *coating B* in the SS corrosion. The result in Fig. 11 is mainly aimed to show the formation of Cr-S-rich phases, being probably Cr_xS_y (marked by arrows), in the coating. Fig. 12 shows the distribution of the chemical elements in the mixed oxide layer. According to the results, S was found to be combined by Y under the oxide layer, but was also detected in the mixed oxide layer probably with a formation of some sulfides.

Fig. 13 shows the EDS mapping results at the coating surfaces in the SD and SS conditions. The Al-rich areas represented alumina, the Cr-rich-only areas were chromia, the Cr-Co-rich areas were spinels, the Y-rich areas were Y-oxides, and the S-Na-K-rich areas were sulphates. Based on those mapping results, a summary to describe the corrosion products on the coating surface is given in the Table III. The results show that, for instance, chromia was only formed on *coating B* in the SS condition. In the mapping results, the “S-rich” phase in the SS condition on *coating B* was actually poor of S, according to a WDS measurement on such phase (the S peak used for mapping was close to a Mo peak); this phase contained Y, W, Mo, and Na according to the WDS measurement. By being carefully checked, W and Mo were not from the solution which was used for the sulphate spray or from the as-sprayed coatings, so they probably came from an outward diffusion from the superalloy. The reason for that such Y-W-Mo-Na-phase was not found on the

other coating (i.e. *coating A*) was not clear, but, probably due to that *coating A* got a less hot-corrosion attack on the underlying coating matrix with a denser alumina scale than *coating B* so that W and Mo were not included into the SD corrosion process on *coating A* yet.

The morphology of the coating surfaces under the backscattered-electron detector is shown in Fig. 14 (for *coating A*) and in Fig. 15 (for *coating B*). On *coating A*, some large-size blocky spinels formed in the SD condition, as shown in Fig. 14a and b. Smaller spinels were found in the SS condition as shown in Fig. 14c and d. On *coating B*, large-size and blocky spinels also formed in the SD condition (Fig. 15a and b). The amount of the spinels on *coating B* (Fig. 15b) was higher than that on *coating A* (Fig. 14b), which could be due to the high content of Cr in *coating B*. In Fig. 15b, Y-oxides containing W, Mo and Na were observed on the surface, which corresponded to the Y-Na-rich phases on *coating B* in the SD condition in the mapping results in Fig. 13. In the SS condition (Fig. 15c and d), large blocky spinels were detected on chromia which had a plate-like morphology. The plate-like morphology of the chromia is further shown in Fig. 16b. Among the chromia plates, Na-K sulphates were detected. The morphology of Na-K sulphate on *coating A* is presented in Fig. 16a.

4. Discussion

4.1. Corrosion in the SD condition (sulphate + air)

In a molten sulphate environment, the alumina formed on the MCrAlY coatings could be gradually corroded due to the reactions shown by Eq. 1 or Eq. 2, depending on the acidity of the sulphate [2,6-8]. At 900 °C which was above the melting temperature of the sulphate, the basic fluxing of alumina scales was the dominant mechanism responsible for the failure of the scale [10-15]. Due to the basic fluxing process, a dense alumina scale could become a mixed oxide layer which was less-protective than the pure alumina [11]. The typical morphology of the mixed oxide layer is shown in Fig. 9b. By losing the effective protectiveness of the oxide scale, the scale cannot perform as a barrier against the quick inward diffusion of the atmosphere atoms or molecules (oxygen, nitrogen, sulfur, etc.) and the outward diffusion of the metal atoms or ions (aluminum, chromium, etc). As a result, the growth rate of the oxides (alumina, spinels) increased, internal oxidation or nitridation occurred, and therefore the degradation of the coating can be accelerated.

According to the oxide morphology (Fig. 8 and 9), a thick but purer alumina formed on *coating A* (Fig. 9a), while on *coating B* with a lower Al content (7.5 wt.%), a less protective mixed oxide layer formed (Fig. 9b). One good criterion to judge the protectiveness of the oxide layer is the amount of spinels formed on the surface. With a less protectiveness of the oxide layer, the outwards diffusion rate of the alloying elements, like Cr, Co, and Ni from the coating to the surface, would be accelerated, to form more spinels. The surface morphology in Fig. 14b and Fig.

15b clearly shows the higher-percentage coverage of spinels on *coating B* than *coating A*, supporting the conclusion that *coating A* was more resistant against the SD corrosion.

4.2. Corrosion in the SA condition (SO₂ + air)

The degradation of the coatings in the SA condition was very limited according to the results in Fig. 7 and microstructures in Fig. 8. The alumina scale formed was very thin (< 0.5 μm) and seem-to-be adhesive at the coating surface (Fig. 8). In such SO₂-including atmosphere, no internal sulfidation or oxidation was found in both coatings up to 6 cycles.

4.3. Corrosion in the SS condition (sulphate + SO₂ + air)

Coating A and *B* showed totally different corrosion behavior in the SS condition. On *coating A*, a thin and dense alumina scale formed, above which some small spinels were also found (Fig. 10a and Fig. 14c,d). While on *coating B*, a mixed oxide layer formed, above which large blocky spinels and plate-like chromia were observed (Fig. 10b and Fig. 15c,d). The result in Fig. 7 (“alumina on *coating B*”) also indicates that *coating B* failed to provide sufficient aluminum to the surface to support the formation and growth of the alumina scale. Furthermore, *coating B* had a higher Cr content (28 wt.%), which could be the reason for the formation of chromia in the SS condition (see “chromia on *coating B*” in Fig. 7, and oxide morphology in Fig. 10b).

Based on the results and the analyses above, there were still two questions that remained to be answered: 1) on *coating A*, why the alumina in the SS condition was not as corroded as in the SD situation, 2) on *coating B*, why chromia can form in the SS condition while no or limited chromia could be found in the SD and SA situations. To answer those questions, the effect of SO₂ in the sulphate environment should be clarified.

4.4. SO₂ effect

4.4.1. In *coating A* (10 wt.% Al, 20 wt.% Cr)

In *coating A*, the SS condition gave less corrosion attack (slower growth of alumina and spinels) than the SD condition (Fig. 7). Up to 8 cycles in the SS condition, the alumina scale was still thin and dense (Fig. 10a). The explanation for that, as put forward at the beginning of this paper, probably can be a beneficial effect of SO₂. The alumina scale should have been corroded by the basic fluxing mechanism (Eq. 1). But the reaction was somewhat inhibited in the SS condition due to the increased partial pressure of SO₂ (SO₂ was (partially) converted to SO₃ [16]), which resulted in the decrease of activity of Na₂O. According to Eq. 3, a decrease of the Na₂O activity would give less basic fluxing of alumina scale. Since the alumina scale in the SS condition (up to 8 cycles, Fig. 10a) kept a dense and thin morphology, the acidic fluxing (e.g. by Eq. 2) appeared not to occur, at least with such SO₂ partial pressure in this study. Furthermore, as a result of the inhibition of the reaction in Eq. 1 (from left side to the right side in the equation), many Na-K-sulphates, probably still keeping in the formation of (0.8Na,0.2K)₂SO₄, were observed at the

coating surface in the SS condition (see Fig. 13). As a contrast, in the SD condition where SO₂ gas was not added, Na-K-sulphates were not detected.

Beneficial effects by adding or increasing the content of SO₂ in corrosion processes have been recognized by many other researchers. For instance, in an alkali-chloride-induced corrosion situation, the presence of SO₂ can dramatically reduce the corrosion rate of some steels by transferring the corrosive chlorides to less-corrosive sulphates in a temperature between about 500 to 700 °C [19,20]; in this case, the sulphates were less corrosive than the chlorides. The researches by A. K. Mishra [17,18] showed that a higher SO₂/SO₃ partial pressure could decrease the corrosion attack (decreasing mass gain of the samples) on the alloy U-700 rather than a lower partial pressure of SO₂/SO₃. Of course, the content of SO₂ should be well controlled otherwise sulfur-induced acidic corrosion would take place [19]. In those studies, SO₂ was added to change the reaction direction and therefore changed the corrosion attack on alloys. Such strategy was similar to the idea being put forward in this study, i.e. that SO₂ may perform a beneficial role on the hot corrosion process if the aggressive corrosion reaction can be inhibited due to the addition of SO₂.

4.4.2. In *coating B* (7.5 wt.% Al, 28 wt.% Cr)

The addition of SO₂, similar to the case in *coating A*, also inhibited the reaction in Eq. 1 (from left side to the right side) in *coating B*, i.e. inhibiting the basic fluxing of alumina by decreasing the activity of Na₂O. The results in Fig. 13 demonstrate that fact (i.e. the existence of sulphates). However, the increased SO₂ partial pressure in the SS condition, comparing with that in the SD condition, brought heavy corrosion attack by introducing a different corrosion mechanism on *coating B* through, probably, the sulphidation of Cr.

At an early stage of the SS corrosion, the high activity of SO₂/SO₃ within the molten sulphate promoted the formation of phases like Cr_xS_y in the coating. The Cr_xS_y can be quickly oxidized to convert to chromia, forming the outmost chromia layer at surface where the oxygen partial pressure was high. Such processes can be described by the following reactions (Eq. 4 and 5). The reaction in Eq. 4 can continuously take place near the oxide-coating interface, since a continuous and dense alumina scale was not formed on the coating (Fig. 10b).

The increased acidity of the salt may also promote the occurrence of the acidic fluxing of alumina in this coating (e.g. through Eq. 2). The S-Al-rich phases in the oxide layer in Fig. 12 can probably be the result of that. When diffusing into the coating, S was captured by Y as shown in Fig. 12 (the S-Y-rich particles under the oxide layer). Ni-S-rich or Co-S-rich phase was not detected, therefore Ni and Co may just be oxidized directly to form spinels without any pre-sulfidation process as Cr.

4.5. Summary of corrosion mechanisms

The hot corrosion behavior of the MCrAlY coatings at 900 °C up to 480 hours is schematically summarized in Fig. 17. The SA condition (500 ppm SO₂ + air) gives limited attack on both MCrAlY coatings, since the SO₂/SO₃ gas alone (without sulphate) cannot corrode the continuous and dense alumina scale. The alumina scale on *coating A* grows thicker due to the basic fluxing of alumina in the SD condition (sulphate + air) than in the SA condition. Since *coating A* (high-Al content) can effectively support the growth and healing of the alumina scale, the oxide layer can stay intact as, almost, a pure alumina. However, in *coating B* the Al content is low and the Cr content is high so the oxide layer becomes a mixture containing various phases like alumina, chromia, spinels and Cr-S-rich phase. The amount of the large spinels on the mixed oxide layer in *coating B* is higher than that in *coating A*, due to the outward diffusion and the oxidation of Co, Ni and Cr from the coatings. When adding SO₂ in the sulphate-containing environment (the SS condition), the corrosion attack on *coating A* decreases significantly comparing with that in the SD corrosion. This is due to the decreased activity of Na₂O and therefore a decreased basic fluxing rate of alumina scale, because of the increased SO₂/SO₃ partial pressure. However, in *coating B* with low Al and high Cr, the sulfidation of Cr (forming Cr_xS_y) within the acidic sulphate probably becomes dominant which is responsible for the early hot corrosion of the coating. The Cr_xS_y can be oxidized to convert to chromia at the oxygen-pressure high position, e.g. at gas-contacting surface. The chromia shows plate-like morphology. Without forming a continuous alumina scale, *coating B* only forms a non-protective mixed oxide layer in the SS condition where the sulfidation (for Cr) and acidic fluxing (for Al) may play a key role on the continued corrosion process.

The analyses and conclusions in this paper are based on the results of the corrosion testing up to 480 hours. However, the corrosion behavior of the coatings may probably be changed with longer time. For instance, the chromia layer on *coating B* in the SS condition, if becoming a denser layer due to a sintering effect in a longer corrosion process, could perform a durable resistance against the corrosion according to the “fluxing theory” [2,8]. That would be an interesting topic for future work.

5. Conclusions

This paper studied the hot corrosion behavior of two MCrAlY coatings, *coating A* (10 wt.% Al, 20 wt. % Cr) and *coating B* (7.5 wt.% Al, 28 wt. % Cr), in a (K_a,K)₂SO₄ environment with and without SO₂ gas (500 ppm) in air at a typical type-I-hot-corrosion temperature 900 °C up to 480 hours. The main remarks are as follows:

- In the environment with sulphate and without SO₂ gas, both *coating A* and *coating B* were attacked by the typical basic fluxing corrosion on alumina scale. *Coating A* had higher

corrosion resistance due to its higher ability to support the growth and healing of the alumina scale.

- In the environment with both sulphate and SO₂ gas, *coating A* got very limited corrosion attack. (K_a,K)₂SO₄ was detected on the coating surface, indicating SO₂ could decrease the Na₂O activity and inhibit the basic fluxing of the oxide scale.
- However, for *coating B* (with lower Al content and higher Cr content), sulfidation of Cr became a dominant corrosion process in the sulphate-plus-SO₂ environment, resulting in the formation of an out layer of porous chromium oxides which were probably converted from the oxidation of sulfides of Cr.

Acknowledgement

The Siemens Industrial Turbomachinery AB (Finspång, Sweden) and Swedish Energy Agency through KME consortium – ELFORSK are greatly acknowledged for their financial support, 60% and 40% respectively, in this research. The Swerea KIMAB is appreciated for the corrosion testing in SO₂-including environment. The research school of Agora Materials and Strategic Faculty Grant AFM in Linköping University are also acknowledged for their support on this research.

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Tables

Table I. Alloying compositions of MCrAlY coatings.

	Ni	Co	Cr	Al	Y	Si	Ta	Ru
<i>Coating A</i>	30	Bal.	20	10	0.6	0.5	0.5	0.5
<i>Coating B</i>	30	Bal.	28	7.5	0.6	0.6	-	-

Table II. Corrosion testing.

Condition	Temperature	(0.8Na,0.2K) ₂ SO ₄ deposition	Gas	Cycles
Salt Deposition (SD)	900 °C	~ 20 µg/(cm ² •cycle)	air	2, 6, 10
Salt deposition and SO ₂ (SS)	900 °C	25 ± 6 µg/(cm ² •cycle)	SO ₂ , 500 ppm + air	5, 6, 8
SO ₂ and Air (SA)	900 °C	-	SO ₂ , 500 ppm + air	6

Table III. Summary on the corrosion products from the top-view of the coatings. Note such summary only represents the results from Fig. 10.

	On <i>coating A</i>		On <i>coating B</i>	
	SD, 10 cycles	SS, 8 cycles	SD, 10 cycles	SS, 8 cycles
Alumina	Less dominant*	Dominant*	Less dominant	Not detected
Chromia	Not detected	Not detected	Not detected	Dominant
Spinel	Dominant, large and blocky	Dominant, small size	Dominant, large and blocky	Dominant, large and blocky
Y-oxides	Detected, rich of Na	Limited detected	Detected, rich of Na	Limited detected
S-Na-K sulphates	Not detected	Highly detected	Not detected	Highly detected

* “dominant” means highly covering the surface (> 30-40% coverage), “less dominant” means covering small parts of the surface (< 30% coverage).

List of figure captions

Figure 1. Cross sections of the coatings after the solution and aging heat treatment. (a) *coating A*, (b) *coating B*.

Figure 2. EDS maps on *coating A* near the coating surface (the square in Fig. 1a). Note the Si rich particles are not in the coating but some Si rich stuffs from the epoxy.

Figure 3. EDS maps on *coating B* near the coating surface (the square in Fig. 1b). Note the Si rich particles are not in the coating but some Si rich stuffs from the epoxy.

Figure 4. Overview of the corroded surfaces of the coatings. The heavy spallation of coatings from edges of the samples in the SS condition was due to the corrosion of the substrate along the substrate-coating interface and the catastrophic deformation of the coatings. Such heavily-damaged area from the sample edges can not represent the corrosion resistance of the coatings.

Figure 5. XRD spectra showing the identification of metallic phases from the coatings and corrosion products on the coating surfaces. Peak “a” in “*coating B*, SD-10cyc” in Fig. 2b, which was not recognized using the XRD database, was probably due to the Y-Na-W-Mo rich oxides which were observed on *coating B* in the SD condition for 10 cycles (the Y-Na-W-Mo rich oxides were shown in Fig. 12).

Figure 6. A part of XRD spectrum (*coating B*, SS, 8 cycles). The shade areas “k”, “l”, “m” and “n” (“k” for a sulphate peak, “l” for a chromia peak, “m” for an alumina peak, and “n” for a (Co,Ni)Cr₂O₄-spinel peak) will be used for a semi-quantitative comparison of the amount of the sulphates or oxides formed on different coatings and in different corrosion conditions, the results of which are shown in Fig. 4.

Figure 7. Comparison of the amount of (Na,K)₂SO₄ sulphate, chromia, alumina and spinels on coating surfaces in different corrosion conditions. The Y-axes are pixels in the shade areas of “k”, “l”, “m” and “n” peaks in Fig. 3, corresponding to the amount of the corresponding species. The dot-dash lines mark the level of “HT” samples; “HT” stands for the heat-treatment status of the coatings before any corrosion testing.

Figure 8. Overview of the cross sections of surface oxides (BSE images). “1” for alumina, “2” for spinels, “3” for chromia, and “4” for the coating material. Above the oxide layer is epoxy, under the layer is the coating.

Figure 9. Part of the oxide layer on (a) *coating A* (BSE image) and (b) *coating B* (BSE image) after the SD corrosion for 10 cycles. The mixed layer in (b) contains various species of Al-rich, Cr-rich, Co-Ni-Cr-rich and S-rich phases. The morphology shown in these two images is mostly representative for the oxide layer on the coatings.

Figure 10. Part of oxide layer on (a) *coating A* (SE image) and (b) *coating B* (BSE image) after the SS corrosion for 8 cycles. The mixed layer in figure (b) contains various species of Al-rich, Cr-rich, Co-Ni-Cr-rich and S-rich phases. The morphology shown in these two images is mostly representative for the oxide layer on the coatings.

Figure 11. EDS maps on a part of the cross section of *coating B* in the SS corrosion for 6 cycles. The arrows point the Cr-S-rich products along a splats' interface.

Figure 12. EDS maps on a part of the cross section of *coating B* in the SS corrosion for 8 cycles. In the oxide layer, the Al-rich phases were alumina, the Cr-rich phase were chromia, the Co-rich phase were spinels, the S-rich phases in the oxide layer were in rich of Al or Cr. The Y-S-rich phases below the oxide layer could be Y-sulfides.

Figure 13. EDS maps on the corroded surfaces of the coatings in the SD condition for 10 cycles or in the SS condition for 8 cycles. The samples were directly put into the SEM after the corrosion testing and without any surface clean. The brightness of the images reflects the richness of the elements. Note that the "enrichment" of S in "low-Al coating, SD-10cyc" condition is due to the existence of Mo in Y-Na-Mo-W-oxides; no S was found by WDS checking in those oxides.

Figure 14. Corrosion surfaces of *coating A* (BSE images): (a) SD, 6 cycles, (b) SD, 10 cycles, (c) SS, 6 cycles, (d) SS, 8 cycles. The bright areas are spinels marked as "2" while the grey matrix is alumina scale marked as "1".

Figure 15. Corrosion surfaces of *coating B* (BSE images): (a) SD, 6 cycles, (b) SD, 10 cycles, (c) SS, 6 cycles, (d) SS, 8 cycles. "1" for alumina scale, "2" for spinels, "3" for Y-Na-Mo-W-oxides, "4" for chromia.

Figure 16. Local part of coating surface in SS condition for 8 cycles (SE images): (a) *coating A*, (b) *coating B*. "I" marks the areas rich of $(\text{Na,K})_2\text{SO}_4$, "II" marks alumina scale plus spinel islands (wide arrows for the spinels), "III" marks chromia plates.

Figure 17. A schematic illustration of the corrosion behavior of *coating A* and *coating B* in different corrosion environments.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Coating A

Figure 8.

Figure 8. (continued)

Coating A

Figure 8. (continued)

Coating B

Figure 8. (continued)

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 13. (continued)

Figure 14.

Figure 15.

Figure 16.

Figure 17.