Protective effect of coatings on the corrosion behaviour of Ni based superalloys in gas turbines atmospheres

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Abstract. — The corrosion of Ni based superalloys IN 738, IN 792, UD 720 and MA 6000 in gaseous atmospheres were studied at three temperatures: 800 °C, 950 °C and 1100 °C. The corrosive atmospheres, simulating the composition of combustion gases of turbines, were highly oxidizing (Ar + 10% O₂) and contained low amounts of SO₂. The effect of an anticorrosive coating, of the type MCrAlY, was studied in corrosion tests of coated and uncoated specimens. Weight change measurements, together with SEM analysis were used to determine the extent and morphology of the corrosion. The effect of the MCrAlY coating was to reduce the extent of the corrosion due to the formation of a protective Al₂O₃ layer.

1. Introduction.

The corrosion behaviour of Ni based superalloys has been studied in highly oxidizing gaseous atmospheres containing low amounts of SO₂. This atmosphere simulates the composition of combustion gases of turbines at high temperature in the absence of condensed phases. These gases are highly oxidizing and should promote the formation of protective oxides on the surface. However, they contain some pollutants, such as sulphur that enhance corrosion problems. The Ni superalloys tested are intended for turbine blade applications in advanced gas turbines.

2. Materials.

The development of Ni based superalloys for turbine blades is mainly centered on improving their high temperature creep resistance through changes in alloy composition and microstructure. These changes have not been always accompanied by an increase in the resistance to high temperature corrosion, but sometimes have even resulted in a reduction [1]. As a consequence of the aggressiveness of the environment the resulting corrosion may become the limiting factor for component lifetime. One solution to avoid or reduce the extent of corrosion is to protect the component with a coating.

Most high temperature coatings rely on the formation of a protective oxide scale by interaction with the environment.

The Ni based superalloys tested are: IN 738, IN 792, UD 720 and MA 6000 (ODS alloy). Their compositions are given in table I.

Table I. — *Chemical composition of the alloys (wt%).*

Alloy	Co	Cr	Al	Ti	Mo	W	Ta	Nb	C	B	Zr	Fe	Y ₂ O ₃	Ni
IN 738	8.5	16	3.4	3.4	1.75	2.5	1.75	1	0.17	0.01	0.1			Bal
IN 792	8.9	12.5	3.47	3.9	1.95	4.18	4.14	0.08	0.07	0.01	0.02	0.04		Bal
MA 6000		14.6	4.26	2.34	1.95	4.04	2.01		0.04		0.15	0.66	1.08	Bal
UD 720	14.7	18	2.5	5	3	1.25			0.35	0.03	0.03			Bal

The corrosion tests were carried out on coated and uncoated samples. The anticorrosive coating of a MCrAlY type had the following composition (wt%): Ni 32, Cr 21, Al 8, Y 0.5, Co bal.

The same coating was applied on all the alloys tested by vacuum plasma spray, and it had a thickness of about 250 μm .

The samples to be coated were cylindrical rods with a diameter of 10 mm and a length of 50 mm and they had rounded ends to increase the adherence of the coating. The samples of the base materials were smaller rods with a diameter of 5 mm and a length of 20 mm.

3. Experimental.

The corrosion tests were carried out in a closed loop with three furnaces in parallel operating at three different temperatures: 800 °C, 950 °C, 1100 °C. The corrosive gas circulating in the loop was the same for the three furnaces. A schematic of the installation is shown in figure 1. The composition of the gas was fixed at the beginning of each experiment. During

Fig. 1. — Schematic presentation of the loop used for the corrosion experiments.

the experiment a mass spectrometer controlled the corrosive gas modulating the opening of piezoelectric and solenoid valves to replenish the corrosive species consumed by the corrosion reaction or to add the corrosive mixture in order to maintain a constant working pressure of 1200 mbar. A circulating pump maintained a total gas flow of ~ 25 l/min which corresponds to ~ 8 l/min for each furnace. The specimens were inserted in the furnaces on Al_2O_3 samples holders.

4. Corrosion tests.

The corrosion tests had a duration of 1000 hours with periodical interruptions to allow weight change measurements. After 100 and 500 hours some samples were withdrawn for microscopical examinations. Two gaseous mixtures were used based on Ar as carrier gas + 10 vol% O_2 with an addition of SO_2 at the levels of 0.1 and 0.3 vol%.

4.1 RESULTS.

4.1.1 Corrosion experiment in 0.1 vol% SO_2 containing atmosphere. — The materials tested were: IN 738 at 800 °C, IN 738 at 950 °C, UD 720 at 1100 °C.

Figure 2 presents the gravimetric results obtained on specimens exposed in this experiment. The reproducibility between specimens was very good, and the weight changes for coated specimens were very low for the three temperatures. It was apparent that a significant weight change had been observed for uncoated alloys particularly at 950 °C and 1100 °C. Cross sectional metallographic examinations of uncoated specimens after 1000 hours of exposure are presented in figure 4.

- The alloy IN 738 at 800 °C had only a few microns of internal penetration and a thin corrosion layer, but at 950 °C the internal penetration is more than 50 μm with a slightly thicker surface layer.
- The alloy UD 720 corroded at 1100 °C had a very deep internal corrosion (~ 120 μm) and a friable thicker corrosion layer.

SEM X-ray maps of specimens corroded at 950 °C and 1100 °C (Fig. 5) showed the presence of Cr in the outer part of the scale leaving a Cr depleted zone beneath the scale where Al_2O_3 precipitates are present. No sulphur was found in the corroded zones.

Coated samples showed a good corrosion resistance at the three temperatures tested. SEM X-ray maps of cross sections of the specimens showed the formation of a thin layer of Al_2O_3 on the surface (Fig. 6). Only one specimen, corroded at 1100 °C, showed a few points of corrosion where the Al_2O_3 layer was not continuous. Following an accurate inquiry, it was concluded that small coating defects were at the origin of this phenomenon.

4.1.2 Corrosion experiment in 0.3 vol% SO_2 containing atmosphere. — The materials tested were: IN 738 at 800 °C, IN 792 at 950 °C, MA 6000 at 1100 °C.

The gravimetric measurements obtained on specimens exposed in this experiment are reported in figure 3. Smaller weight changes are measured on coated samples compared with specimens of the base alloys.

- The alloy IN 738 at 800 °C showed the same corrosion behaviour as in the previous experiment (Fig. 7).
- The alloy IN 792 at 950 °C showed an internal corrosion with a penetration of ~ 80 μm in some points and a friable surface layer (Fig. 7). From SEM X-ray maps it appeared that Cr and Ti are concentrated in the corrosion layer whereas Al was present in the internal precipitates.

Fig. 2. — Weight change measurements for the alloys and coatings exposed to Ar, 10% O₂, 0,1% SO₂ gaseous mixture.

- On alloy MA 6000 at 1100 °C after 100 hours of exposure a corrosion layer was observed which disappeared after 500 and 1000 hours leaving the surface covered with an Al₂O₃ layer (Fig. 8).
- Coated samples, showed the formation of a thin layer of Al₂O₃ with the resulting protective effect (Fig. 9).

As in the previous experiment, no sulphur was detected in the corrosion zones.

Fig. 3. — Weight change measurements for the alloys and coatings exposed to Ar, 10% O₂, 0.3% SO₂ gaseous mixture.

5. Discussion.

The gaseous mixtures selected for the corrosion experiments have attempted to simulate the composition of combustion gases of turbines. The concentration of 0.1 vol% of SO₂ corresponds to the level present in a combustion gas resulting from burning residual oil with 2 wt% of sulphur [2]. These mixtures are highly oxidizing and the partial pressure of sulphur is too low for the formation of sulphides on the surface of alloys, therefore only oxides are formed.

Fig. 4. — Metallographic cross sections of IN 738 at 800 °C and 950 °C, and UD 720 at 1100 °C, after 1000 hours exposure in 0.1% SO₂ gaseous mixture.

Fig. 5. — SEM X-ray maps of cross sections after 1000 hours exposure in 0,1% SO₂ gaseous mixture: A) IN 738 at 950 °C; B) UD 720 at 1100 °C.

However other authors have observed sulphidation under the oxide layer even if the sulphur content was very low [3-6]. The limiting value of sulphur dioxide partial pressure required to promote sulphide formation at metal scale interface is too low to be avoided by fuel purification [4, 5]. The results of our tests did not reveal the presence of sulphides in the internal precipitates found in the uncoated alloys. This does not exclude the possibility of sulphides formation over longer time periods, because gas transport through the scale may be very slow, since it depends heavily on kinetic factors and morphology of the oxide layer [4]. The

Fig. 6. — SEM X-ray maps of cross sections of coated samples after 1000 hours exposure in 0.1% SO_2 gaseous mixture: A) IN 738 at 950 °C; B) UD 720 at 1100 °C.

Fig. 7. — Metallographic cross sections of IN 738 at 800 °C and IN 792 at 950 °C, after 1000 hours exposure in 0,3% SO_2 gaseous mixture.

corrosion undergone by the alloys tested is an oxidation process with the formation of friable mixed oxides on the surface giving rise to spalling.

At the high temperatures, attained in our experiments, materials rely on the formation of an Al_2O_3 layer on the surface to ensure oxidation resistance, because Cr forms volatile oxides (CrO_3) [7, 8]. The huge weight loss measured at 1100 °C on UD 720 material, may be attributed mainly to CrO_3 volatilization.

Fig. 8. — SEM X-ray maps of cross sections of MA 6000 samples exposed at 1100 °C in the 0.3% SO₂ gaseous mixture: A) After 100 h; B) After 1000 h.

The alloy MA 6000 tested at 1100 °C showed that during the initial stages of attack the formation of a surface scale of mixed oxides occurred, which evaporated and spalled away leaving a thin layer of apparently protective Al₂O₃ (Fig. 8). This mechanism is in agreement with the weight change curve.

If we consider the chemical composition of the materials tested (Tab. I), it appears that alloy MA 6000 has a higher Al content compared with other alloys and contains yttria dispersions. The good corrosion resistance of the MCrAlY coating in all the conditions tested is apparently due to the formation of a thin layer of Al₂O₃ on the surface (Figs. 6 and 9).

Although in the present work the presence of yttrium-containing phases was not detected in the oxide scales of ODS alloy MA 6000 and MCrAlY coating, the results obtained strongly support the assumption that yttria may change the scale growth mechanism resulting in a better oxidation resistance [9].

6. Concluding remarks.

- The Ni superalloys tested IN 738, UD 720, IN 792 showed the formation of a non protective scale with precipitation of oxides in the alloy substrate. The corrosive attack increased with the temperature.

Fig. 9. — SEM X-ray maps of cross sections of coated samples after 1000 hours exposure in the 0,3% SO₂ gaseous mixture: A) IN 792 at 950 °C; B) MA 6000 at 1100 °C.

- The ODS alloy MA 6000 at 1100 °C formed a corrosion scale of mixed oxides during the initial period of the test. Subsequently a thin Al₂O₃ layer appeared on the surface.
- The MCrAlY anticorrosive coating applied on the surface of the alloys showed good corrosion resistance in all the conditions tested.
- The lack of condensed phases in the tests conditions, does not exclude the possibility of sulphides formation [4, 10] over longer time periods.

Acknowledgements.

Thanks are due to Mr. A. Grossi for experimental assistance and to Mrs. M. Romor for metallography.

The work described in this paper is in the frame of the research programme of ENEL-CRTN, Milano - Italy.

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