



Cyclic oxidation behavior of uncoated and aluminum-rich nickel aluminide coated Rene-80 superalloy

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ABSTRACT

In this study, aluminide coating was employed to enhance the high-temperature cyclic oxidation of Rene-80 superalloy at 950°C. The microstructural aspects and phase constituents of samples were investigated with scanning electron microscopy (SEM) and x-ray diffraction (XRD) techniques. The result of oxidation tests showed that the weight gain in the uncoated sample was considerably higher than the aluminide coated sample, which indicates the higher rate of oxide formation on the uncoated surface. With the aid of microstructural and XRD analysis, it was confirmed that with the increment of oxidation cycles, the thickness of aluminide coating reduced and the protective β -NiAl phase was converted to alumina scales. According to the EDS results taken from the top coat, it was found that with the increase of oxidation cycles, the content of aluminum in the top layer was drastically decreased and the weight percentage of oxygen was considerably enhanced. Also, in higher oxidation cycles, other protective elements such as Cr and Ti outwardly diffused from the inter-diffusion zone (IDZ) layer which led to reduction in the content of these elements in inner zones of the aluminide coating.

1. INTRODUCTION

Turbine blade materials must be able to work at high temperatures (above 700°C) [1,2]. Accordingly, nickel-based superalloys have been developed to improve the efficiency of turbine engines and their lifetime under the harsh conditions imposed by the turbine environment [3]. However, without using appropriate coatings, Ni-based superalloys cannot perform satisfactorily in the highly oxidizing and corrosive conditions [4]. Thus, diffusion and/or thermal barrier coatings have been used on the surfaces of turbine components [5]. Nowadays, diffusion aluminide coatings are widely employed to protect blades and vanes of gas turbines [6,7]. A wide variety of methods, such as chemical vapor deposition (CVD) [8], pack cementation [9-11], and slurry [12-14] covering are routine diffusion coating ways. Among these methods, pack cementation is one of the economic and most commonly used techniques for applying aluminide

coatings [9, 10, 12]. Generally, aluminide coatings on Ni-based superalloys can be formed with two main mechanisms: (i) Low-temperature high- activity (LTHA) process and (ii) high-temperature low-activity (HTLA) process. The first process is composed of two stages: At the first stage, aluminum inward diffusion from the powder mixture to the substrate is the predominant diffusion direction. Brittle Ni_2Al_3 and Al-rich NiAl phases form at the above mentioned diffusion condition (in the range of 700-850°C) and additional heat treatment at higher temperatures (above 1000°C) is required to convert these phases to the desired β -NiAl phase. In the second stage of LTHA, outward diffusion of Ni atoms from the nickel-based substrate facilitates the diffusional transformation from Ni_2Al_3 and Al-rich NiAl phases to β -NiAl phase [9]. The second process (HTLA) is conducted at a single stage at temperatures above 1000°C for 3-6 h. This process is controlled by the outward diffusion of Ni atoms from the substrate. The required

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aluminum for β -NiAl phase formation is provided from a pack with low Al activity. Existence of β -NiAl in these coatings could facilitate the formation of adherent oxide scales in oxidizing environments which leads to a considerable improvement in the durability of superalloy substrates [9, 12]

Rene-80 is a cast precipitation-strengthened Ni-based superalloy with superior creep resistance which is widely used for fabrication of gas turbine blades. In this superalloy, Cr, Co, Ti, and Al elements are used for gamma prime precipitation. Also, W and Mo elements are added for solid solution strengthening [15]. Due to highly oxidizing environments of turbine blades in operational conditions, these superalloys must be coated with appropriate coatings to enhance their durability. In this paper, pack aluminized high-temperature low activity (HTLA) coating was deposited on Rene-80 superalloy and the coating microstructural aspects and its high-temperature oxidation behavior at 950°C were studied and compared with the uncoated superalloy.

2. MATERIALS METHOD

2.1. Materials and coating preparation

Table 1 displays the nominal chemical composition of Rene-80 superalloy which was used as the substrate in this research. The samples were prepared in disk shape with a diameter of 20 mm and a thickness of 3 mm. The samples were mechanically ground up to 1000-grit (SiC paper) and cleaned in acetone before the coating process.

TABLE 1. Chemical composition of Rene-80 superalloy [16]

Element	Zr	B	C	Al	W	Mo	Ti	Co	Cr	Ni
Wt.%	0.03	0.015	0.17	3.00	4.00	4.00	5.00	9.50	14.00	Bal

A high-temperature low-activity (HTLA) pack aluminizing procedure was utilized in this study. In the HTLA process, the aluminizing temperature was in the range of 1000-1100°C and aluminum content of the pack was lower than that of the substrate. In the pack cementation, samples were embedded in a powder mixture which was composed of 1-3 wt.% pure aluminum, 2-6 wt.% NH_4Cl as an activator, and alumina as the filler. The powder pack with the embedded samples was heated at 1065°C for 3 h in an argon atmosphere to form coatings.

2.2. Cyclic Oxidation test

Cyclic oxidation tests were conducted on three identical samples for each coating type at 950°C in flowing dry air with 0.5 m³/h flow rate for 250 h. During oxidation cycles, samples were placed in the hot section of a heat resistance tube furnace. Each cycle consisted of heating the samples to 950°C, remaining at this temperature for 5 h, and finally cooling down to the room temperature inside the furnace. This cooling procedure was long

enough to cool the specimens to below 30°C. After each cycle, samples were removed from the furnace to determine their weight changes. The weights of samples were measured with an accuracy of 10⁻⁴ g on a digital balance.

2.3. Characterization

Microstructural aspects and chemical analysis of the coatings before and after the oxidation tests were studied by scanning electron microscopy (SEM) (VEGA\TESCAN-LMU), energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD) (D8 advanced Bruker) with monochromatic $\text{Cu K}\alpha$ radiation.

3. RESULTS AND DISCUSSION

3.1. Microstructure of the as-coated HTLA aluminide coating

The microstructure of HTLA aluminide coating on Rene-80 Ni-base superalloy is presented in Fig. 1. The total thickness of the coating was approximately 95 μm . It can be seen that the aluminide coating was consisted of two main regions [9, 17, 18]: zone 1 which mainly comprised of β -NiAl with a low content of substrate precipitates (e.g. point p) and zone 2, interdiffusion zone (IDZ), with a lamellar multiphase inner layer comprising precipitates from substrate elements such as Mo, Cr, W and Ti embedded in β -NiAl. It should be noted that the content of precipitates in zone 2 was considerably higher than that in zone 1.

The XRD spectrum of as-prepared aluminide coating is represented in Fig. 2. It is seen that β -NiAl is the main phase of the coating. The oxidation behavior of the aluminide coating depends on the presence of the β -NiAl phase. In high temperature low activity process in Ni-base superalloys, Ni was the predominant diffusing component that diffuses outward from the substrate to the coating surface and combines with aluminum to form β -NiAl phase in the outer coating area. Also, small amounts of Ni_2Al_3 and Al_2O_3 phases can be found in the microstructure of coating [18]. Alumina scales in the outer layer of the aluminide coating may exist due to partial oxidation or trap of alumina filler particles during the coating process.

3.2. Cyclic oxidation behavior

3.2.1. Uncoated superalloy

Fig. 3 shows the graph of weight changes versus the number of cycles for the uncoated and aluminide coated Rene-80 superalloy. A sharp decrease in uncoated superalloy weight was observed only after 17 cycles of oxidation, which indicates that this superalloy has a very poor oxidation resistance during cyclic oxidation at 950°C. In contrast, it seems that the HTLA coated superalloy exhibited a much better cyclic oxidation

performance. Fig. 3 shows that the cyclic oxidation behavior of uncoated Rene-80 superalloy is composed of two regions [16]: (I) formation of oxide layer up to the seventeenth cycles (oxygen uptake, 0-17 cycles) and (II) rapid destruction of the oxide layer (after the 17th

cycles). As can be seen, after a short period of cyclic oxidation, weight loss in superalloy occurred quickly. Therefore, superalloy without aluminide coating exhibits a very low resistance to cyclic oxidation.

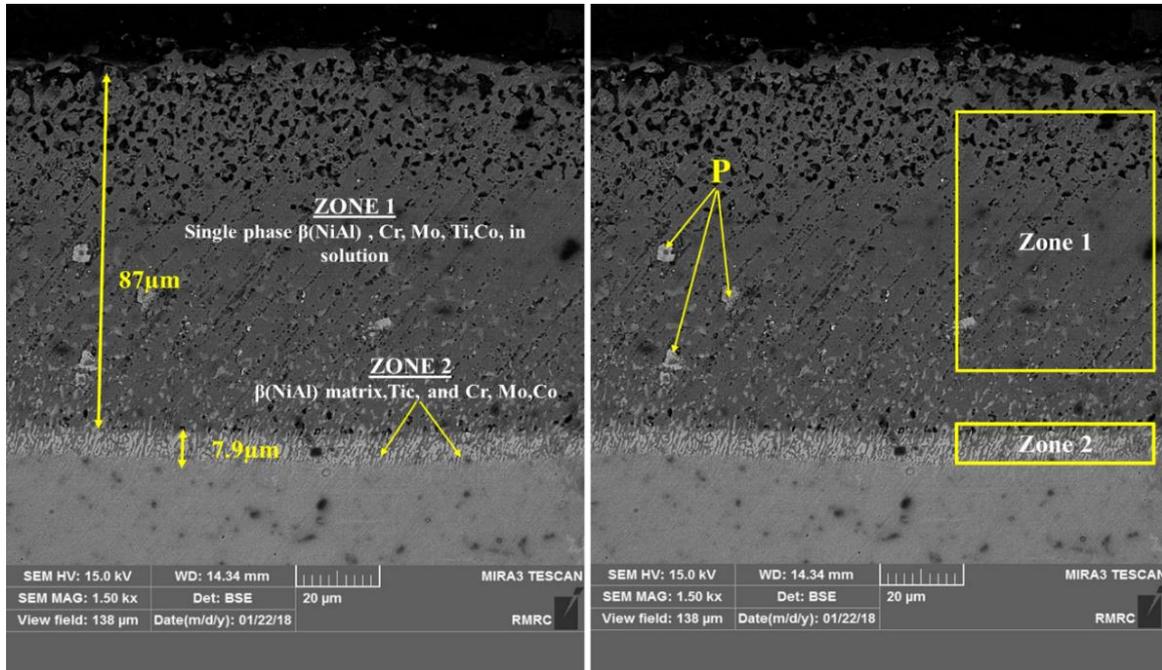


Figure 1. Cross-sectional BSE micrograph of the HTLA NiAl coating on Rene-80 superalloy

Table 2 shows the results of EDS analysis of zone 1 and 2 related to the HTLA aluminide coating. Its comparison with Rene-80 composition (given in Table 1) indicates that the weight percentage of Al increased from 3.0 for the superalloy to 40.1 for the aluminide coating. It is well known that the increment of aluminum content in the composition of Ni-base superalloys negatively affects

mechanical strength, creep resistance, and microstructural stability at high temperatures. However, the enhancement of aluminum (content) in the surfaces of superalloys not only improves corrosion and oxidation resistance but also preserves mechanical strength and creep resistance of Rene-80 superalloy.

TABLE 2. EDS analysis of different zones of aluminide coatings

Coating		Constituent elements							
		Protective elements			Aluminide-former elements		Precipitate-former heavy refractory elements		
		Al	Cr	Ti	Ni	Co	Mo	W	Total
NiAl (Zone 1)	wt.%	40.1	7.5	2.6	38.1	6.3	3.1	2.3	100
IDZ (Zone 1)	wt.%	6.9	27.2	12.0	28.5	8.4	9.1	7.9	100
Point P	wt.%	36.3	10.7	3.9	33.4	7.6	5.0	3.1	100

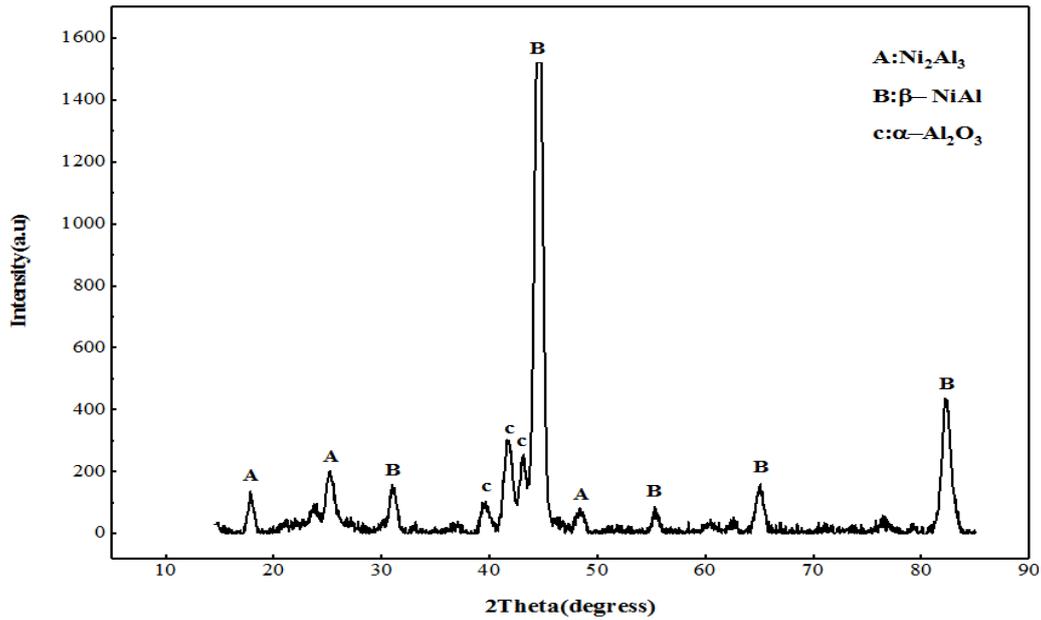


Figure 2. XRD pattern of as-prepared HTLA aluminide coatings

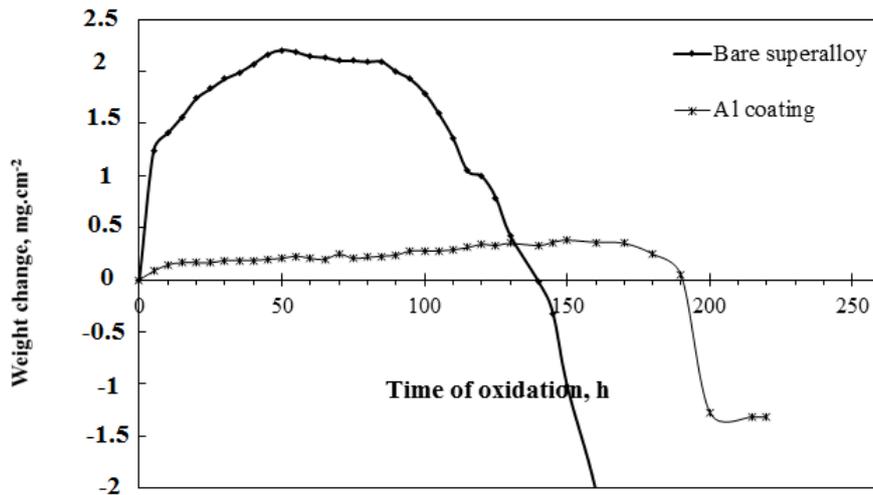


Figure 3. Weight changes of samples versus the oxidation times for the bare and aluminide coated Rene-80 superalloy at 950°C

3.2.2. HTLA aluminide coated superalloy

As shown in Fig. 4, the weight change of the aluminide coated Rene-80 superalloy during cyclic oxidation at 950°C is comprised of three regions [16]:

- I. Formation of oxide layer up to the twenty-fourth cycle (120 hours).
- II. Protection by the oxide scale with minimal weight change from the twenty fourth cycle (120 hours) to thirty-fourth cycle (170 hours).
- III. Continuous weight loss due to peeling after the thirty-fourth cycle (after 170 hours).

The life span of samples during oxidation is determined by the number of cycles in which the curve of weight

changes conflues with the X-axis. Therefore, the life span of the aluminide coated Rene-80 superalloy at this cyclic oxidation test condition is about 190 hours. According to Fig. 4, the applied aluminide coating on this superalloy is stable during oxidation at 950°C up to 34 cycles. After 34 cycles of oxidation, a continuous weight loss due to degradation of oxide scale was observed which indicates that the minimum amount of aluminum required for the protection of the surface after 34 cycles has been consumed.

The phase changes of the aluminide coating during the oxidation cycles were investigated by the XRD analysis (Fig. 5) and the results were used to interpret the

oxidation behavior. It is seen that with the increase of oxidation cycles from 0 to 45, the intensity of β -NiAl phase gradually decreases and the intensities of alumina peaks increase. The calculated values for the ratio of main peaks of alumina and β -NiAl ($\frac{I_{\max \beta-NiAl}}{I_{\max alumina}}$) before oxidation was about 0.16 which reaches to about 0.36 after 25 cycles, 0.49 after 40 cycles, and 1.63 after 45 cycles. During oxidation cycles, aluminum from β -NiAl phase of the coating, penetrates the surface and forms an alumina oxide scale that protects the samples against oxidation [19]. Due to the important role of β -NiAl phase as a protective layer during high-temperature oxidation, it is anticipated that reduction in the content of this phase reduces the oxidation resistance of the coating [19].

To study the degradation of the coating more precisely during cyclic oxidation, the metallographic examination of each of the specimen was conducted to observe the structural changes and degradation after different oxidation cycles. SEM-BSE cross-sectional images of the aluminide coatings at 25th, 40th, and 45th oxidation cycles are represented in Fig. 6. It can be seen that after 25 cycles of oxidation (Fig. 6(a)), the microstructure of coating did not considerably change and it was similar to the microstructure of coating before oxidation cycles. However, by applying 40 oxidation cycles (Fig. 6(b)), a thick alumina scale evolved at the top layer of this coating. With the increment of oxidation cycles to 45 (Fig. 6(c)), the thickness of Al_2O_3 layer increased more and the total thickness of the aluminide coating decreased which confirm the occurrence of degradation of this coating after 45 cycles. Also, the degradation was noticed in the IDZ layers of aluminide coatings [19].

The results of EDS analysis taken from the top layer (zone 1) and IDZ layer (zone 2) of the sample coated with aluminide coating after oxidation for 45 cycles are

provided in Table 3 and 4, respectively. According to the EDS results of the top coat, it was found that with the increment of oxidation cycles, the content of aluminum in the top layer was drastically decreased and the weight percentage of oxygen was considerably enhanced [20]. These findings confirm the XRD results and microstructural observation of oxidized samples. Also, it is seen that after 45 oxidation cycles, other protective elements such as Cr and Ti outwardly diffused from IDZ layer which led to the reduction in the content of these elements in inner zones of the aluminide coating.

CONCLUSIONS

The results of these experiments and the subsequent discussion support the following conclusions:

1. The Al-rich nickel-aluminide coating considerably increased the cyclic oxidation resistance of Rene-80 superalloy at 950°C.
2. The uncoated Rene-80 faced rapid oxide formation before a catastrophic failure, while the coated sample showed a slow rate of oxide formation up to the end of the coating lifetime.
3. The morphology of cross-section of the oxidized coating showed that the major part of the coating thickness was lost after the whole cyclic oxidation testing. This result was in accordance with a lifetime of about 190 hours that has been determined from the weight changes-time curve for the coating under the conditions used in the oxidation test.

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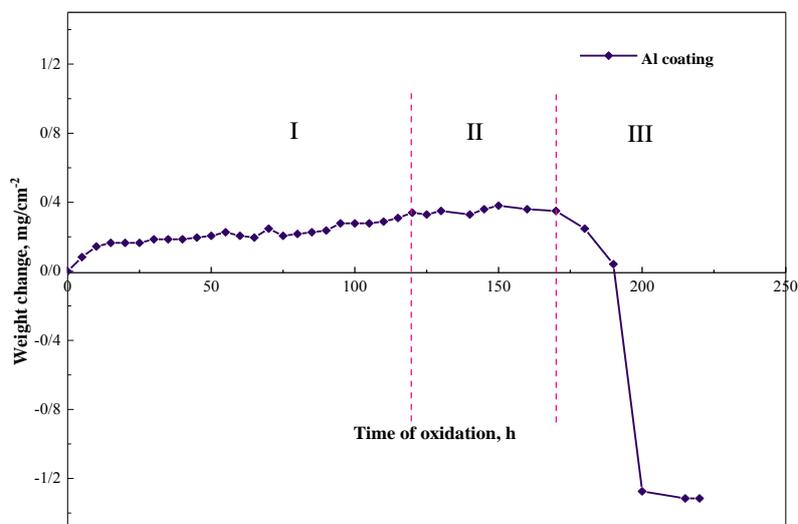


Figure 4. Cyclic oxidation curve of the HTLA aluminide coating at 950°C

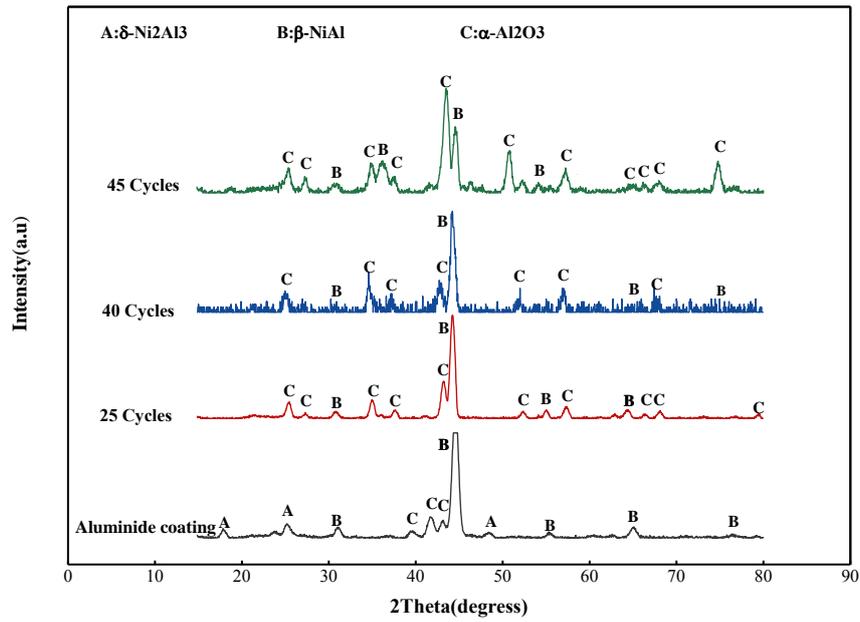


Figure 5. XRD patterns of the aluminide coatings at various oxidation cycles

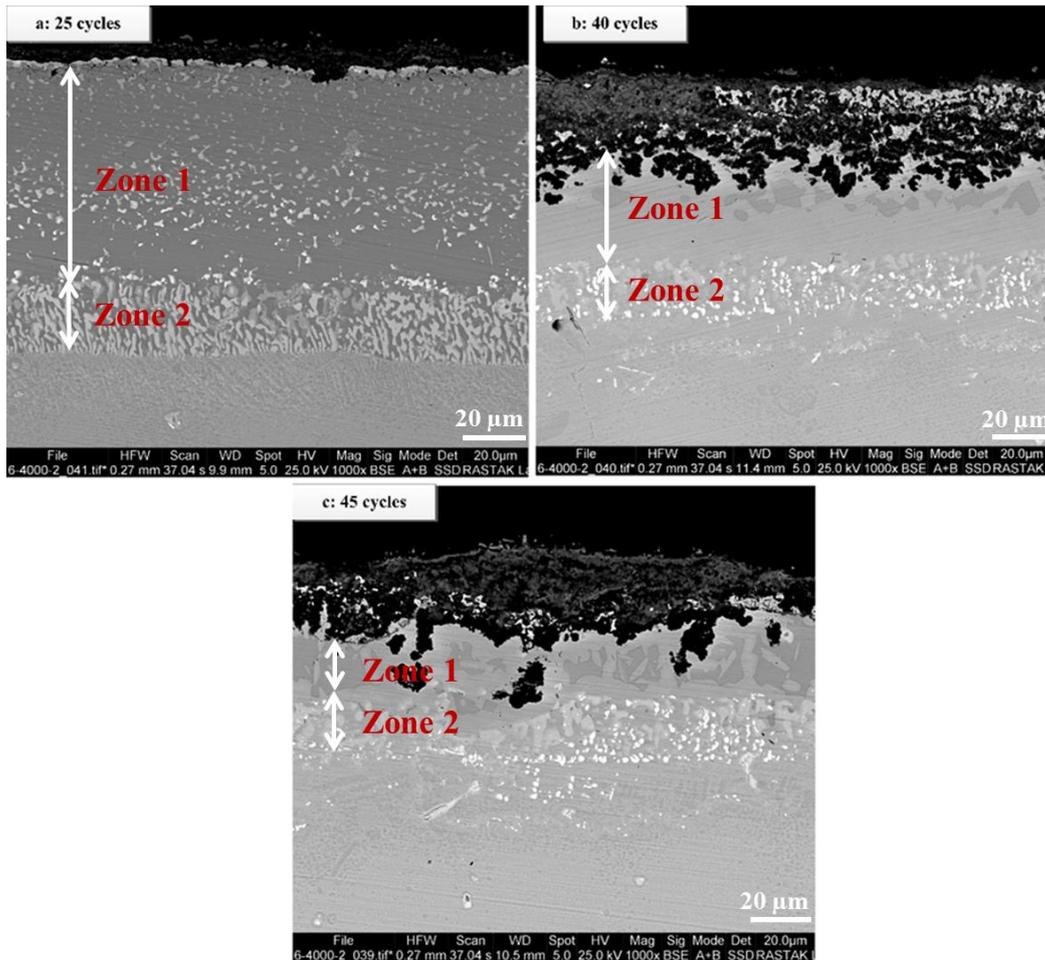


Figure 6. Cross-sectional SEM-BSE micrographs of the HTLA aluminide coatings on Rene-80 superalloy after various exposure times: (a) 25 cycles, (b) 40 cycles, and (c) 45 cycles

TABLE 3. EDS analysis of the aluminide coating before and after oxidation cycles

Coating		Constituent elements							Oxidation
		Protective elements			Aluminide-former elements		Precipitate-former heavy refractory elements		
		Al	Cr	Ti	Ni	Co	Mo	W	
0 Cycles	wt.%	40.1	7.5	2.6	38.1	6.3	3.1	2.3	-
45 Cycles	wt.%	22.6	15.2	5.7	32.7	5.4	2.2	2.1	14.1

TABLE 4. EDS analysis of the IDZ layer before and after oxidation cycles

IDZ		Constituent elements						
		Protective elements			Aluminide-former elements		Precipitate-former heavy refractory elements	
		Al	Cr	Ti	Ni	Co	Mo	W
0 Cycles	wt.%	6.9	27.2	12.0	28.5	8.4	9.1	7.9
45 Cycles	wt.%	5.6	24.5	1.9	45.0	9.3	6.0	7.7

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