FORMATION OF DIFFUSION ZONES IN COATED NI-AL-X TERNARY ALLOYS AND NI-BASED SUPERALLOYS

A. S. Suzuki, G. D. West and R. C. Thomson Loughborough University, Loughborough, LE11 3TU, United Kingdom

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ABSTRACT

Coatings are an essential part of the materials system to protect the turbine blades from oxidation and corrosive attack during service. Inter-diffusion of alloying elements between a turbine blade substrate and their coatings is a potential concern for coated turbine blades at ever increasing operating temperatures because this can cause the formation of undesirable Secondary Reaction Zones (SRZs), which may degrade the mechanical properties of coated Ni-based superalloys. Understanding the effects of each element on the SRZ formation is essential in order to understand both the mechanism and inter-diffusion behaviour between coatings and substrates. In this research, a number of simpler aluminized ternary Ni-Al-X (where X is Co, Cr, Re, Ru or Ta) alloys were investigated in order to elucidate the separate effects of each element on the microstructural evolution, especially at the coating/substrate interface. The aluminized ternary alloys developed distinctive diffusion zones, depending on the third alloy element, 'X'. Specifically, it has been found that both Ni-Al-Re and Ni-Al-Ta alloys developed a continuous SRZ-like diffusion layer. This diffusion zone persisted in the Ni-Al-Re alloys after high temperature exposure, indicating that Re has a stronger effect on SRZ formation than Ta.

INTRODUCTION

Higher operating temperatures of power plant improve thermodynamic efficiency, which in turn leads to a reduction in CO_2 emissions and lower fuel consumption. Ni-based superalloys, used as substrate materials for turbine blades in gas turbines, have excellent high temperature capability. Coatings also have an important role to play: these are frequently applied to the surfaces of the turbine blades to provide additional protection against oxidative and corrosive environments during service.

As the operating temperature increases and the environment becomes more aggressive, the oxidation and corrosion resistance of turbine blade materials becomes more crucial than before. Furthermore, inter-diffusion of alloy elements between a coating and a substrate becomes more important, as this will be very significant at higher temperature, and will accommodate microstructure changes during service, such as the formation of Secondary Reaction Zones (SRZs) [1-6] and Topologically Close-packed (TCP) phases [7]. The term 'SRZ' was suggested by Walston [1], and they were first observed in coated third generation Ni-based superalloys. The SRZ [1] which can form between a coating and a Ni-based superalloy substrate is generally considered to be a detrimental layer for coated turbine blades because it can degrade the mechanical properties of the blades. Sato et al. compared the mechanical properties of various aluminized Ni-based superalloys potentially degrades creep properties. These SRZs typically have been observed in the case of aluminized or Pt-aluminized coated turbine blades, however, SRZs can also appear in other coating systems. In general, SRZs consist of γ , γ'

and TCP phases growing into substrate by the migration of high-angle grain boundaries. The propensity to form such a layer is a sensitive function of composition and surface finish prior to coating. Coatings are an essential part of the materials system to protect the turbine blades from oxidation and corrosion attack during service, and thus it is essential to fully understand the microstructural evolution of SRZs.

Previous studies have shown both positive and negative effects of different alloying elements in the case of Pt-aluminized fourth generation Ni-based superalloys, e.g. Ru encourages SRZ nucleation [5], and Mo is an effective element in impeding SRZ formation [4]. However, these effects have been observed from various multicomponent Ni-based superalloys, with complex alloy compositions, and are not always consistent across alloy systems. Some alloying elements, such as Co shows clear effects in controlling SRZ formation in Pt-aluminized third-generation Ni-based superalloys, whereas this is not the case for Pt-aluminized fourth-generation Ni-based superalloys [6]. This suggests that the effect of some alloy elements on SRZ formation can be overwhelmed by the other elements within Ni-based superalloys.

For turbine blade applications, both the alloy and coating compositions can vary significantly, and therefore how each element affects the formation of SRZs in coated turbine blades is key to understanding their nucleation mechanism and predicting their growth behavior. In this research, Ni-Al-X (where X is Co, Cr, Re, Ru or Ta) ternary alloys have been used as substrates in order to simplify the effect of alloying elements on SRZ formation. This paper presents a possible mechanism of diffusion zone formation in aluminized ternary alloys, especially in terms of their microstructural changes during coating preparation and high temperature exposure. It is anticipated that a greater understanding of the formation of SRZs will facilitate the development of materials systems with superior mechanical properties and greater microstructural stability. The results of this study will also act as an indicator of possible problems in terms of microstructural stability when the alloy compositions are varied for future generations of Ni-based superalloys.

EXPERIMENTAL

The ternary alloy compositions used in this study are presented in Table 1. The Ni-Al-Co, Ni-Al-Cr, Ni-Al-Re and Ni-Al-Ru alloys were designed to contain both the γ' and γ phases at 1100 °C from ternary diagrams [9-15], and the Ni-Al-Ta alloy was designed to have γ' phase at elevated temperature using the thermodynamic equilibrium software package, MTDATA [16]. The alloys were prepared via arc melting under an argon atmosphere, followed by an appropriate homogenization heat treatment. Ternary alloys were cut into coupons with a 3 mm thickness. The alloys were grit-blasted and then an aluminizing coating process was applied by a Low Temperature High Activity (LTHA) process, followed by post-production heat treatment (PPHT) at 1100°C for 1 hour under flowing Ar. CMSX-4 was also used as a reference material, and its composition is also listed in Table 1. Isothermal oxidation tests were subsequently conducted at 880°C for up to 500 hours, followed by cooling in air. The resulting microstructures were analysed using scanning electron microscopy (SEM) with a back-scattered detector (BSE), and scanning transmission electron microscopy (STEM) and Transmission Electron Microscopy (TEM) with energy-dispersive X-ray analysis (EDX). Cross-sectional TEM samples were prepared using a dual-beam focused ion beam scanning electron microscope (FIBSEM).

			Table	1. Alloy	, Compo	ositions	(at.%)					
Alloy	Ni	Al	Cr	Re	Та	Co	Mo	W	Ti	Hf	Ru	
Ni-Al-Co	Bal.	20.3				4.4						
Ni-Al-Cr	Bal.	20.0	10.0									
Ni-Al-Re	Bal.	18.0		1.0								
Ni-Al-Ta	Bal.	20.7			3.1							
Ni-Al-Ru	Bal.	20.0									2.1	
CMSX-4	Bal.	12.6	7.6	1.0	2.2	9.3	0.4	2.0	1.3	0.03		

RESULTS

As Aluminized Microstructures

Figure 1 shows cross-sectional microstructures of all of the aluminized ternary alloys. All alloys formed a coating layer within a thickness range of 35 to 70 μ m, and consisted of a β -NiAl phase. The Ni-Al-Cr system consisted of two distinctive coating layers, which are indicated as layers 1 and 2 in Fig. 1. Both layers consisted of the β phase, however, layer 1 was found to contain less than 1.5 at.% of Cr, whereas layer 2 contained approximately 6 at.% of Cr. However, the coating layer in the Ni-Al-Re specimens did not contain Re, suggesting that Re is not incorporated into β -NiAl. The coating layer in Ni-Al-Ta developed a number of discrete particles. EDX analyses also indicated that there was a small amount of Ta content in the coating layer, and therefore it is likely that the discrete particles observed are Ta-rich precipitates. CMSX-4 exhibited typical cross-sectional microstructures of as aluminized Ni-based superalloys [17]. The thicknesses of the coating layer in the specimens were in the order: Cr>Co, Ru>Ta>Re>CMSX-4.

Ni-Al-Co and Ni-Al-Ru alloy did not form any clear diffusion zones after aluminizing at the interface between coating and substrate, however, the other ternary alloys developed continuous diffusion layers with distinct morphologies which depended on the third alloy element, 'X'. The diffusion layer in Ni-Al-Cr in Fig. 1 was approximately 20 μ m thick. In the diffusion zone in Ni-Al-Cr, dark phases were observed which were composed of 30.8Al-10.6Cr-58.7Ni (at.%), whereas bright phases contained 14.9Al-23.1Cr-62.1Ni (at.%). These phase compositions are comparable with the phase composition of the β and γ phases reported in Ni-Al-Cr ternary diagram by Dupin [12], and this means that the diffusion zone in Ni-Al-Cr consists of the β phase surrounded by a matrix γ phase, which was probably formed due to the outward diffusion of Ni during post-production heat treatment. CMSX-4 formed a typical inter-diffusion zone (IDZ) microstructure, consisting of β -NiAl with topologically close-packed (TCP) phases. Except for the TCP phase precipitation in the IDZ, the interfacial morphology between β -NiAl and substrate (γ'/γ phases) formed in CMSX-4 was similar to that in Ni-Al-Cr, and therefore was classified as an inter-diffusion zone.

However, both the Ni-Al-Ta and Ni-Al-Re alloys formed a diffusion zone, which was more similar to a SRZ, as in Fig. 1. Ni-Al-Ta formed the narrowest diffusion zone of all the specimens, which was approximately 6 μ m in extent, and consisted of a number of grains with a β phase matrix and Ta-rich precipitates, which grew perpendicular to the substrate with a rod shape and bright contrast in Fig. 1. Earlier work [18] has shown using EDX mapping that the particles precipitated in the diffusion zone of Ni-Al-Ta were rich in Ta, but with an absence of Al.



Figure 2: Bright field images with the selected area diffraction patterns (SADPs) of Ta-rich precipitates in the diffusion zone of as aluminized Ni-Al-Ta: (a) Ni₂AlTa and (b) Ni₂Ta.

Table .	2: TEM	-EDX a	ınalysis	results of the					
preci	pitates j	formed	within	the diffusion					
zone	of alum	inized l	Vi-Al-T	a. (Numbers					
corresponds to Fig. 2.)									
	Al	Ni	Та	Phase					

	7 11	141	14	1 nuse
(1)	15.8	62.1	22.0	Ni ₂ AlTa
(2)	3.0	68.0	29.0	Ni ₂ Ta

Cross-sectional TEM analysis was carried out for the diffusion zone in Ni-Al-Ta. Figure 2 illustrates the bright field images with the corresponding selected area diffraction patterns (SADPs) of Tarich precipitates and TEM-EDX point analysis results (Table 2) respectively. It should be noted that some stacking faults were observed within the precipitates. Fig. 2 indicates that there were differences in the morphologies and size of the

precipitates present: some precipitates exhibited a plate-like morphology, Fig. 2 (a), and others had a more blocky morphology, Fig. 2 (b). According to TEM-EDX analysis and SADPs of the precipitates, the majority were identified as the FCC Ni₂AlTa phase, whereas some of the other precipitates in Fig. 2(b), were identified as the tetragonal structured Ni₂Ta. This suggests that several different phases can coexist within the diffusion layer of as received Ni-Al-Ta.

Microstructural Evolution at 880°C

Aluminized Ni-Al-X ternary alloys and CMSX-4 were exposed at 880°C, and their representative microstructures are shown in Fig. 3 for 20 hours (diffusion zone only) and in Fig. 4 for 500 hours respectively. Due to the relatively low exposure temperature, the microstructural changes in the coating layer after 20 hours were relatively small, and all samples remained in the β -NiAl phase.

However, the diffusion zones started to show some microstructural changes after 20 hours, as shown in Fig. 4. The β phase in the diffusion zone in Ni-Al-Cr showed decreases in both the number and the size of particles. With respect to Ni-Al-Ta, very fine precipitates, having a needle morphology, appeared above the diffusion zone, whereas the size of the Ni₂Ta and Ni₂AlTa precipitated in the diffusion zone decreased. Ni-Al-Ru started to form a layer consisting of very fine precipitates, with a brighter contrast and located just above the substrate. In terms of Ni-Al-Co, Ni-Al-Re and CMSX-4, the microstructural changes in their diffusion zone after 20 hours exposure were less significant than the other alloys.



880°C for 20 hrs.



After 500 hours exposure in Fig. 4, the phase transformation observed in the coating layer was very striking, depending on the third element 'X'. Ni-Al-Co showed the fastest coating layer degradation during the exposure, and the coating layer consisted of the γ' -Ni₃Al and γ phases after

500 hours. Most of the other alloys retained the β phase as matrix phase, however, some transformation from β to γ' phase was observed in Ni-Al-Ru.



Figure 5: STEM-EDX mapping of the diffusion zone in Ni-Al-Ru at 880°C after 500 hours. (Numbers correspond to Table 3.)

Table 3: STEM-EDX point analysis of diffusion zones of aluminized Ni-Al-Ru at 880°C after 500 hours (at.%).

	Al	Ni	Ru
(1)	27.3	72.7	0.0
(2)	42.4	41.5	16.1
(3)	45.9	35.1	19.0

In terms of the diffusion zone, all alloys showed microstructural changes, with the differences between alloys being more significant than after only 20 hours exposure. The β phase precipitates in Ni-Al-Cr disappeared, and the interface between the coating layer and the substrates became more planar, similar to the interfacial morphology in Ni-Al-Co.

Ni-Al-Re retained the SRZ-like diffusion zone, and some matrix transformation from β to γ' was observed, as shown in Fig. 4. However, the thickness of the diffusion zone in Ni-Al-Re did not change significantly. The very fine needle-like precipitates formed in the diffusion zone of Ni-Al-Ta coarsened, and started to form discrete precipitates along the grain boundaries. Also, under the diffusion zone, some needle-shaped small precipitates, appeared after 500 hours. CMSX-4 demonstrated some TCP phase precipitation underneath the IDZ, which are frequently observed after thermal exposure [17].

In the case of Ni-Al-Ru, the diffusion zones increased in extent. The brightly imaging precipitates shown in Fig.4 became more noticeable, and increased in number with exposure time. The precipitates formed in the diffusion zone of Ni-Al-Ru after thermal exposure were investigated further with STEM. Fig. 5 shows the STEM-EDX mapping results for diffusion zones in Ni-Al-Ru at 880°C for 500 hours, and Table 3 shows the EDX point analysis results. Needle-like precipitates were distributed within the matrix phase (γ' - Ni₃Al). The width of the precipitates was less than 500 nm, but their length varied. The EDX data presented in Fig. 5 demonstrated that the precipitates contained higher concentration of Al and Ru, compared to the matrix phase. Point analysis in Table 3 revealed that the precipitates consist of approximately 35~41 at.% Ni, 43~46 at.% Al, and 16~19 at.% Ru; these compositions are comparable to the NiAl based β_1 phase, which was reported by Chakravory [13,19].

DISCUSSION

In this study, aluminized Ni-Al-X ternary alloys showed a distinctive morphology within the diffusion zone before and after thermal exposure, depending on the third element present. In the LTHA process, Al is the predominant diffusing species, and Al diffuses inwardly to form a coating layer. The coating layer after the aluminizing process typically consists of δ -Ni₂Al₃, and the δ -Ni₂Al₃ in the coating layer transforms to β -NiAl during the post-production heat treatment at 1100°C for 1h. During this process, a diffusion zone is also formed at the interface between the

coating layer and the Ni-based superalloy substrate [20, 21]. During the LTHA process, Al diffuses into γ/γ' phases to form δ -Ni₂Al₃ [22], and Ni moves towards the surface to form β -NiAl during the post-production heat treatment. In Ni-Al-X ternary systems, the formation of diffusion zones after aluminizing depends on the solubility of 'X' elements in the δ -Ni₂Al₃, β -NiAl and γ' Ni₃Al phases. For example, Co and Cr have a large solubility in the β -NiAl phase [9,11,12]. Co can form a complete solid solution in Ni-Al and Ni, and this resulted in no diffusion zone formation after the aluminizing process, as shown in Fig. 2. In terms of Cr, the binary δ -Ni₂Al₃ phase also has approximately 12 at.% of Cr solubility [23]. However, the relatively small solubility of Cr in β -NiAl is responsible for the formation of β phase diffusion zones.

The solubility of both Re and Ta into δ -Ni₂Al₃ and β -NiAl phase is much smaller than that of Cr [10, 24-28]. Specifically, the Re solubility in the β -NiAl phase is 0.53 at.% in the as cast condition [24], and 0.5 at.% in δ -Ni₂Al₃ [28]. Therefore, Re rejected from the β -NiAl and δ -Ni₂Al₃ phases and forms Re-rich phase precipitates, as observed in Fig. 2. Nrita et al. [29] reported that Re has limited diffusion in Ni aluminides. This also suggests that Re in the substrate was rejected from the β -NiAl phase, with segregation occurring at the interface between the coating and substrate.

With respect to Ta, the low solubility in the β phase, which is less than 1 at.% [28], contributed to the formation of discrete particles in the coating layer and diffusion zone. In particular, a variety of precipitates and intermetallic compounds have been reported in the Ni-Al-Ta system [25,30]. It can be considered that the small solubility and variety of possible precipitates in the Ni-Al-Ta system contributed to the formation of an SRZ-like diffusion zone. Ni-Al-Ta contained a number of discrete particles within the coating layer in both as coated and as received conditions. Therefore, it is expected that the lower solubility of a particular 'X' element in β -NiAl and δ -Ni₂Al₃ is strongly associated with diffusion zone formation, as observed in the aluminized condition in this study.

The morphology of the diffusion zones observed in these systems were particularly distinctive (see Fig. 2). Although the matrix phase of the diffusion zone in both Ni-Al-Re and Ni-Al-Ta is β -NiAl, the morphology and the interface between the diffusion zone and substrate is almost identical to the typical SRZ formed in coated Ni-based superalloys [1,2]. Many of the X-rich (X: Re or Ta) precipitates within the diffusion zone also grow perpendicular to the substrate in Fig. 2, and this is a consistent propensity of TCPs growing in SRZ formed in coated Ni-based superalloys [1-4]. However, the interfacial morphology between β -NiAl and the substrate (γ/γ' phases) formed in Ni-Al-Cr was very similar to that in CMSX-4, and therefore was classified as an inter-diffusion zone. It has been noted that the interface morphology between the diffusion zones and the substrates was very different, and therefore the diffusion zone in Ni-Al-Cr is defined as an inter-diffusion zone, whereas the one in Ni-Al-Re and Ni-Al-Ta has been defined to be an SRZ.

The X-rich precipitates (X: Re or Ta) in the diffusion zones were observed to preferentially segregate at grain boundaries [2]. X-rich precipitates may cause the formation of many grains in the diffusion zone during the aluminizing process or post-production heat treatment. A SRZ is generally formed via a phase transformation from β -NiAl to γ' -Ni₃Al in the IDZ during the post-production heat treatment, however, the results from the aluminized ternary alloys have indicated that the SRZ can nucleate before the phase transformation occurs. It is believed that the formation of X-rich precipitates can also act as a nucleation site of a SRZ, and may accelerate the formation of SRZ nuclei during the post-production heat treatment.

The ternary Ni-Al-X alloys demonstrated microstructural changes in both the coating layers and diffusion zones during the exposure at 880°C, however the changes were slower than at 1100°C as expected [18]. In Ni-Al-Co, the coating layer changed to γ and γ' phase, suggesting that all the β -NiAl phase was consumed. This might be due to the inferior oxidation resistance of Co at elevated temperatures [31]. All of the other alloys still contained the β phase after 500 hours exposure, however, Ni-Al-Ru exhibited some transformation from β -NiAl to γ' -Ni₃Al phase near the specimen surface. The effect of Ru on the oxidation resistance of coatings and Ni-based superalloys is the subject of debate [32-35], however, it is clear that Ni-Al-Ru showed slightly faster coating layer degradation than the other samples, except for the Ni-Al-Co.

With respect to the diffusion zones, it must be noted that Ni-Al-Ru exhibited slightly different diffusion zone formation from the other ternary alloy systems. All alloys except for Ni-Al-Ru formed the diffusion zones before exposure, however Ni-Al-Ru developed the diffusion zones consisting of very fine Ru-rich precipitates during exposure. This is likely to be associated with the solubility of 'X' elements into the various Ni-Al phases. In the case of Ru, there is complete solid solubility between the NiAl and RuAl phases at 800°C and a high amount of Ru solubility in NiAl at 1000°C [9]. However the solubility reduced as Al receded. This suggests that Ru remained within the NiAl phase during the aluminizing process, and it was gradually rejected and appeared as precipitates during the exposure, due to the Al loss during exposure. The matrix phase around the Ru-rich precipitates was the Ni₃Al phase, with a very limited solubility for Re, which explains the formation of Ru-rich precipitates during the exposure. Although the formation of the diffusion zones was observed in Ni-Al-Ru during the exposure, all of the other ternary alloys exhibited microstructural degradation of diffusion zones in respect of di diffusion zone thickness and precipitate morphology.

The matrix phase of the diffusion zones transformed into the γ' -Ni₃Al phase, in particular in Ni-Al-Re and Ni-Al-Ta, and the some precipitates were reduced their numbers, and integrated into other precipitates in both Ni-Al-Re alloys and Ni-Al-Ta, with the progress of interdiffusion of alloying elements. Also, Ni-Al-Ta exhibited a greater reduction in precipitates than those in Ni-Al-Re. At 900°C, the diffusion coefficient of Ta in Ni is approximately 8×10^{-17} - 2×10^{-16} m²/s and that of Re is $4-5 \times 10^{-17}$ m²/s respectively [36], with Ta clearly having a faster diffusion rate than Re. It is expected that part of the Ni₂Ta/Ni₂Al₂Ta phase was consumed into the γ' -Ni₃Al phase during the phase transformation of matrix phase in the diffusion zone, resulting in a reduced density of the precipitates in Ni-Al-Ta after the exposure.

In this study, both as aluminized Ni-Al-Ta and Ni-Al-Re alloys formed distinctive diffusion zones which were defined to be SRZs, indicating that both Ta and Re are prone to SRZ formation at an early stage. Comparing the microstructural degradation of the diffusion zone between Ni-Al-Re and Ni-Al-Ta, Re maintained a clear layer and the effect of Re for SRZ formation is persistent after the exposure. It should therefore be concluded that both Re and Ta promote SRZ formation, and the effect of Re is stronger than that of Ta. Ni-Al-Ru did not show any diffusion zone formation after aluminizing, however β_1 precipitates appeared after the exposure. Due to the formation to Re and Ta. On the other hand, it can be concluded that Ni-Al-Co and Ni-Al-Cr have no clear negative effect on the diffusion zone formation. Ni-Al-Cr formed a precipitate-free diffusion zone, and Ni-Al-Co did not show any diffusion zones. The solubility of 'X' elements into δ - Ni₂Al₃, β -NiAl, γ '-Ni₃Al and γ phases, and the diffusion coefficients of 'X' element in Ni are contributing factors to the change in diffusion zone thickness and their morphology.

CONCLUSIONS

Ni-Al-X ternary alloys designed to contain γ and γ' phase were aluminized, and their microstructural evolution, especially in terms of diffusion zones, was investigated. The following conclusions can be drawn from this research:

- Aluminized ternary alloys developed distinctive diffusion layers depending on the third elements: Ni-Al-Cr alloys formed a layer consisting of both γ and β phases, which is more similar to a traditional inter-diffusion zone in coated Ni-based superalloys, whereas Ni-Al-Re and Ni-Al-Ta formed a continuous layer consisting of β phase and Re-rich/Ni₂Ta or Ni₂AlTa precipitates with high-angle grain boundaries present.
- Ni-Al-Ru did not form a diffusion zone after aluminizing, however, the microstructure developed to contain γ' -Ni₃Al phase and NiAl based β_1 precipitates.
- The matrix phase of the diffusion layer formed in Ni-Al-Re and Ni-Al-Ta alloys comprised the β phase, however, this layer can be defined to be a secondary reaction zone, because the layer also consisted of many grains and Re or Ni₂Ta/Ni₂AlTa precipitates with high-angle grain boundaries between the layer and substrate.
- After exposure at 880°C for 500 hours, the diffusion layer disappeared in the Ni-Al-Cr system, and the diffusion layer in Ni-Al-Re and Ni-Al-Ta demonstrated a loss of Rerich/Ni₂Ta and Ni₂AlTa precipitates and phase transformations in the matrix phase.
- Both Re and Ta can promote the formation of SRZs. The effect of Re is persistent after thermal exposure, and it is concluded that Re has the stronger effect than Ta.

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