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# Thermal stability enhancement of hybrid $Ni_2Al_3$/Ni coatings on creep resistant ferritic steels by a mechanism of thermodynamically constrained interdiffusion

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ABSTRACT

Based on the thermodynamic analysis, experimental work is undertaken to investigate the thermal stability of the hybrid $Ni_2Al_3$/Ni coating with a thin inner Ni layer formed on creep resistant ferritic steel. The results showed that once the coating is transformed by interdiffusion to a NiAl/Al-rich-Fe-base-alloy layer structure, thermal stability of the newly formed outer NiAl layer at 650 °C can be enhanced by the constraint imposed on inward Al diffusion by Al activity difference at the outer/inner layer interface. The Fe diffusion into the newly formed outer NiAl layer is restrained by its solubility limit in the newly formed outer NiAl layer.

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## 1. Introduction

Many efforts have been made to increase the creep strength of the 9–12Cr (wt.%) types of ferritic steels at 650 °C by modifying their alloy compositions [1–6]. The aim is to enable them to be used as relatively low-cost structural materials for the construction of new generations of supercritical steam turbine power plants that can be operated at higher steam temperatures and hence with higher thermal efficiencies. At 650 °C, however, the oxidation resistance of these types of steels, which relies on the formation of a $Cr_2O_3$ scale, may be the limiting factor for their application in steam rich environments in which the $Cr_2O_3$ scale either cannot form or losses its long-term protectiveness due to the formation of volatile Cr oxy-hydroxide species [7–10]. Among the three types of protective scales of metal alloys, i.e. $Al_2O_3$, $Cr_2O_3$ and $SiO_2$, the $Al_2O_3$ scale is chemically most stable in high temperature steam. Therefore, the Fe-aluminide coatings capable of forming an $Al_2O_3$ scale have been investigated extensively in recent years in an attempt to assess their long-term oxidation resistance and thermal stability in high temperature steam or water-vapour containing environments [11–15]. It has been evident that the lifetime of such coatings is not determined by the rate of oxidation but by the rate of interdiffusion at the coating/steel substrate interface, which reduces the Al concentration in the coating at an un-desirably fast rate even at 650 °C [12–15]; the growth of the protective $Al_2O_3$ scale cannot be sustained once it drops below a critical level, leading to rapid breakaway oxidation.

Hence, a coating with a hybrid layer structure of the Ni-aluminide/Ni type has been suggested and investigated more recently [16,17]. The outer layer of the coating is Ni-aluminide, which provides oxidation resistance, and the inner layer is Ni, which functions as a diffusion buffer zone to prevent or substantially slow down the Al diffusion towards the steel substrate. The coating with such a hybrid layer structure can be easily produced by electroless or electro Ni plating followed by partial aluminising of the Ni layer at a temperature below 700 °C [16]. It is of critical importance to keep the aluminising temperature sufficiently low to preserve the microstructure and hence the creep strength of the 9–12Cr (wt.%) type of steels. In such a low aluminising temperature range, the aluminised layer obtained is normally $Ni_2Al_3$ [16,17].

There are two interfaces in such a coating; one is between the outer $Ni_2Al_3$ and inner Ni layers and the other is between the inner Ni layer and steel substrate. At both of these interfaces, interdiffusion will take place at elevated service temperatures, which will affect the lifetime of the coating. A phenomenological model has been developed recently to estimate the lifetime of the coating at 650 °C for a case where the inner Ni layer is sufficiently thick such that the inward Al diffusion flux cannot reach the steel substrate and the outward Fe diffusion flux cannot reach the outer Ni-aluminide layer during the lifetime of the coating [18]. In this case, the thickness required of the inner Ni layer will be undesirably large because it has to be thick enough so as not to be totally consumed by interdiffusion at both $Ni_2Al_3$/Ni and Ni/steel interfaces. The interdiffusion at the Ni/steel interface will lead to the formation of an excessively large interdiffusion zone between the inner Ni layer and steel substrate [16]. For instance, it has been observed that the width of this interdiffusion zone reached approximately 117 μm after annealing at 650 °C for 8510 h and it

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can be estimated that, in the required lifetime of 100000 h for the coating in steam turbine applications, this width can grow to nearly 340 μm (Appendix 1).

The formation of such a large interdiffusion zone at the Ni/steel substrate interface may adversely affect the creep strength of the steel substrate. Therefore, it is necessary to minimise such an effect by keeping the inner Ni layer thickness as thin as possible. In such cases, the inner Ni layer will be completely consumed at some stage in service at elevated temperatures by interdiffusion at both $Ni_2Al_3$/Ni and Ni/steel-substrate interfaces. As a consequence, the initial outer $Ni_2Al_3$ layer will be transformed to Ni-aluminide phases with lower Al concentrations, and a thin layer of the steel substrate surface will be aluminised by the inward Al diffusion flux, resulting in the formation of an inner Al-rich-Fe-base-alloy layer at the boundary between the newly formed outer NiAl layer and steel substrate. The present study was undertaken to demonstrate that, when this happens, the newly formed Ni-aluminide outer layer can be stabilised by the interdiffusion constraint imposed by the difference in Al activity between the newly formed outer Ni-aluminide layer and Al-rich-Fe-base-alloy layer at the outer/inner layer interface.

## 2. Basis of the work

The present study considered a case in which the inner Ni layer of the $Ni_2Al_3$/Ni coating is of such a thin thickness that, when it is completely consumed at 650 °C by interdiffusion at both $Ni_2Al_3$/Ni and Ni/steel-substrate interfaces, the outer $Ni_2Al_3$ layer is transformed to NiAl and a thin layer of the steel substrate is aluminised by the inward Al diffusion flux, and an inner Al-rich-Fe-base-alloy layer is formed as a result at the boundary between the newly formed outer NiAl layer and steel substrate.

Much insight may be gained into the factors that may influence the thermal stability of the newly formed outer NiAl phase layer as described above by comparing the Al activities in Ni-Al alloys with those in Fe-Al alloys as it is the activity gradient instead of concentration gradient that determines the direction and rate of diffusion. Although such data are not available at 650 °C, they were measured for higher temperatures by several groups of investigators [19–21], and those reported by Komarek and co-workers [22,23] were the most extensive, which covered temperature range of 900 °C–1127 °C. In a previous study [24], the present authors extrapolated those data to 650 °C with the use of the equation:

$$\log a_{\mathrm{Al}}(T_2) = \log a_{\mathrm{Al}}(T_1) + \frac{\Delta H_{\mathrm{Al}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (1)$$

where $a_{\mathrm{Al}}(T_1)$ and $a_{\mathrm{Al}}(T_2)$ are the activities at temperatures $T_1$ and $T_2$, respectively, $R$ is the gas constant and $\Delta H_{\mathrm{Al}}$ is partial molar enthalpy of Al. Because Al is a solid at 650 °C and the $\Delta H_{\mathrm{Al}}$ values reported by Komarek and co-workers [22,23] were all measured with reference to the liquid Al, a value of 10711 J/mol for the heat of melting of Al [20] needs to be added to their $\Delta H_{\mathrm{Al}}$ values for alloys of respective compositions. The extrapolated Al activity data were re-plotted in Fig. 1 for the convenience of presentation of the analysis to be given below.

On the basis of the results in Fig. 1, a possible stabilising mechanism may be suggested for the newly formed outer NiAl phase layer once the structure of the initial $Ni_2Al_3$/Ni coating is transformed by interdiffusion at 650 °C to the one consisting of an outer NiAl layer and an inner Al-rich-Fe-base-alloy layer.

It can be seen in Fig. 1 that, in the range of 44.0–55.6 at.% Al, which is a range where the NiAl phase can remain stable at 650 °C [25], the Al activity is always lower in the NiAl phase than in Fe-Al alloys, and more importantly, as the Al concentration decreases, the Al activity decreases far more rapidly in the NiAl phase than in Fe-Al alloys. This difference in Al activity and in its dependence on Al concentration at the interface between the newly formed outer NiAl phase layer and inner Al-rich-Fe-base-alloy layer will set up an Al activity constraint that would restrict further inward Al diffusion and hence act to stabilise the newly formed outer NiAl layer.

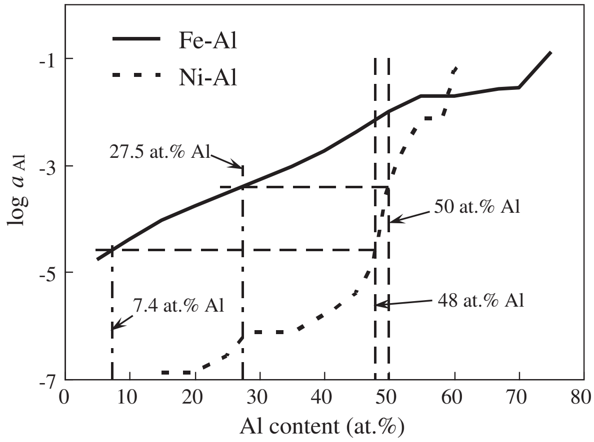

**Fig. 1.** Al Activities as a function of Al concentration in Ni-Al and Fe-Al alloys at 650 °C.

For instance, when the Al concentration in the outer NiAl layer is 50 at.%, the Al concentration in the inner Fe-Al alloy layer would have to be below 27.5 at.% for Al to diffuse into it from the outer NiAl layer. And for the Al concentration in the outer NiAl layer to drop further from 50 at.% to 48 at.%, the Al concentration in the inner Fe-Al layer would have to be reduced to a level below 7.4 at.% before the Al atoms in the outer NiAl layer can diffuse into it. In other words, the newly formed outer NiAl phase layer can be self-stabilised once the inner Ni layer of the $Ni_2Al_3$/Ni coating is completely consumed and the coating layer structure is transformed by the interdiffusion from $Ni_2Al_3$/Ni to NiAl/Al-rich-Fe-base-alloy at 650 °C. The experimental work described below was undertaken to validate such analyses.

## 3. Experimental work

The substrate used was the P92 alloy steel with a nominal composition of Fe-9Cr-1.8W-0.5Mo-0.1C (wt.%). Specimens of approximately 20 × 10 × 2 mm were manually ground using SiC abrasive paper to a 600-grade finish. The same procedures as the ones reported previously were used to prepared the hybrid $Ni_2Al_3$/Ni coatings [16–18]. They firstly were electroplated with a Ni layer and the Ni layer was then partially aluminised using pack cementation process in a powder mixture of Al, $Al_2O_3$ and $AlCl_3$ at 650 °C. The amount of $AlCl_3$ used was 2 wt.% in all cases but the amount of Al added and the length of aluminising time used were adjusted to give two coatings with different inner Ni layer thicknesses.

The aluminised specimens were then annealed at 650 °C in a tube furnace under the Ar atmosphere. They were taken out of the furnace at different intervals, and a small section was sliced out from each of them using a precision cutting wheel, which was then ground and polished by following normal metallographic preparation procedures.

The cross-sectional microstructure and depth profiles of alloy elements in all the coating specimens were analysed by means of scanning electron microscopy (SEM) (FEI Quanta200) and energy dispersive X-ray spectroscopy (EDS) (Oxford INCA). The phases of the coating in the outmost surface layer were analysed from the specimen surfaces by X-ray diffraction (XRD) ((PHILIPS X'Pert PRO MPD diffractometer with Cu-$K_\alpha$ source radiation).

## 4. Microstructure of the coatings investigated

Two coatings were prepared, designated as coating A and coating B, respectively. The cross-sectional SEM image and depth profiles of

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