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Effects of a NiFe co-deposited layer on α-Al_2O_3 formation by oxidation of a β-NiAl alloy

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ABSTRACT

Effects of Ni metal, Fe metal or NiFe alloy deposits on the oxidation behavior and oxidation products of a β-NiAl alloy at 1000 °C in air were studied. The surface morphologies of the deposited layers and oxide scales were examined by using field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM). The chemical compositions of the deposited layers were determined before and after oxidation by using energy dispersive X-ray (EDX). The deposited layer and the resultant oxidation products were identified by using X-ray diffractometer (XRD). The chemical composition of the deposited layers was found to affect the morphology of the deposits and the final oxidation products. By oxidation at 1000 °C in air, θ-Al_2O_3 was detected for bare, Ni-coated and Ni-rich coated (Ni17.7 at.%Fe) samples, but was not detected for Fe-coated and Fe-rich coated (Ni72 at.%Fe) samples at all oxidation times. The oxidation mass gain after 100 h on Fe-coated sample was the highest among the coated samples. TEM Cross-sectional images revealed that the grain size of α-Al_2O_3 on both Fe coated and Fe-rich NiFe coated samples were the smallest among the coated samples. XRD and EDX point analysis confirmed the formation of different multilayered oxide scales on oxidized samples, $NiO/NiAl_2O_4/Al_2O_3$ on Ni coated, complex spinel $Ni(Fe)Al_2O_4/Al_2O_3$ on Ni-rich NiFe coated, $Fe_2O_3/(Fe, Ni, Al)_2O_3/\alpha$-$Al_2O_3$ on Fe-rich NiFe coated and Fe_2O_3/α-Al_2O_3 on Fe-coated samples, respectively. Introducing Fe or Fe-rich NiFe coating layer prior to the oxidation of a NiAl alloy resulted in suppression of θ-Al_2O_3 formation and finer grains of α-Al_2O_3, which accelerated the growth rate of α-Al_2O_3 scale. Up to 72 at.% of Fe in NiFe coating was found to be beneficial as an oxidation pretreatment for NiAl alloys to obtain a better high temperature oxidation resistance.

1. Introduction

Oxidation resistance of alumina-forming alloys is promoted by the formation of stable Al_2O_3 scale in which the diffusion of both oxygen and Al is slowed down. Various kinds of Al_2O_3 phases form on these alloys such as metastable γ-, δ- and θ-Al_2O_3 and stable α-Al_2O_3 phases. Among them α-Al_2O_3 oxide scale provides an excellent protective property because of its thermodynamic stability and slow growth rate [1,2]. However, at lower temperature and/or at the early stages of oxidation, metastable alumina phases form first then transform to stable α-Al_2O_3. Because of the rapid growth rates of metastable alumina phases are higher than that of α-Al_2O_3 by about two orders of magnitude [2–4], direct formation of α-Al_2O_3 or rapid transformation of metastable alumina to stable α-Al_2O_3 is required to improve the high temperature oxidation resistance.

Kitajima et al. reported that the deposition of Cr or Fe coating on Al containing alloys suppressed the formation of metastable θ-Al_2O_3 phase by oxidation at 900 °C in air, while Ni coating delayed the transformation of metastable θ-Al_2O_3 to stable α-Al_2O_3 phase [5]. They proposed that the suppression of the θ-Al_2O_3 formation was caused by rapid formation of α-Al_2O_3 phase. The rapid formation of α-Al_2O_3 was attributed to the formation of coated metal oxides, Cr_2O_3 and Fe_2O_3, which have an isomorphous corundum structure with α-Al_2O_3 [5]. These metal oxides may provide a higher density of nucleation sites for α-Al_2O_3. We also investigated the growth rate of Al_2O_3 scales in the oxidation of β-Ni50Al alloy at 1000 °C in air and confirmed that metastable Al_2O_3 phase was not formed on NiAl alloy with Fe or Cr coatings [6].

These coatings also affected the growth kinetics of Al_2O_3 scale *via* affecting the size of α-Al_2O_3 grains. The α-Al_2O_3 scale that transformed earlier always consisted of smaller grains, whereas the size of grains

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Table 1
Composition of electrodeposition bath [g dm^{-3}].

Bath	Coating	[$NiSO_4 \cdot 6H_2O$]	[$FeSO_4 \cdot 7H_2O$]	[Na_2SO_4]	[H_3BO_3]	H_2SO_4
a)	Ni	15.5	0	35, 50	12.5	0
b)	Ni-Fe	15.5	1.4	35, 50	12.5	0
c)	Ni-Fe	15.5	27.8	35, 50	12.5	0
d)	Fe	0	27.8	35	12.5	0.1 M

increased with delay in the transformation from θ-Al_2O_3 to α-Al_2O_3. Generally the growth rate of alumina scale decreases with increasing the size of Al_2O_3 grain. An Fe coating promoted the rapid formation of α-Al_2O_3 as mentioned above resulting in a small grain size. On the other hand Ni coating was found to delay the transformation and thus enlarged the grain size of α-Al_2O_3 reducing the growth rate of oxide scale compared with the Fe or Cr coatings. From the other viewpoint, however, the rapid transformation of θ-Al_2O_3 to α-Al_2O_3 phase is desirable since the shrinkage of the oxide accompanying the transformation causes stresses and thus cracking of the scales particularly in the cyclic oxidation.

A composition of coatings also affects the oxidation kinetics. Ni coating did not suppress the formation of θ-Al_2O_3 phase while Ni-3.1 at.%Fe_2O_3 nano powder composite coating accelerated the transformation of θ- to α-Al_2O_3 phase resulting in an increased grain size of Al_2O_3 and a decreased growth rate of Al_2O_3 scale. Further addition of Fe_2O_3 of 5.2 and 7.4 at.% to Ni coatings suppressed completely the formation of θ-Al_2O_3 phase or promoted direct formation of α-Al_2O_3 phase resulting in a slow growth rate of scales. However, addition of Fe_2O_3 more than 7.4 at.% did not show any improvement because of agglomeration of Fe_2O_3 particles. Therefore, an Fe/Ni ratio in the NiFe coatings is a meaningful parameter because higher ratio of Fe content corresponds to higher concentration of Fe_2O_3 in the oxide that may affect the oxidation behavior.

The purpose of this study is therefore to investigate a suitable Fe/Ni ratio of the NiFe precoating that may improve the oxidation resistance of a NiAl alloy at 1000 °C in air. For this purpose, NiFe alloy coatings were electrodeposited on a NiAl alloy samples *via* pulsed electrodeposition (PED) prior to the oxidation test. Ni and Fe have different electrodeposition rates [8–12] and thus Fe/Ni ratio can be adjusted by controlling the electrodeposition parameters.

2. Materials and methods

A β-Ni50 at.%Al alloy ingot was prepared from Al and Ni metals (~ 99.99% in purity) by using the Ar-arc melting technique followed by homogenization at 1200 °C for 48 h in vacuum (5×10^{-3} Pa) and was cut into specimens of *ca.* 1 mm thickness. These specimens were ground with SiC paper up to 4000 grit and finished with 3 μm diamond paste to obtain a mirror finish surface and then ultrasonically degreased in acetone for 10 min.

Ni, NiFe or Fe coating was electrodeposited on the NiAl alloy from different baths adjusted to pH 3 listed in Table 1. The pulsed electrodeposition (PED) was conducted by using the following conditions; current density of $i_{cd} = -10$ mA·cm^{-2}, deposition time $t_{on} = 2$ s,

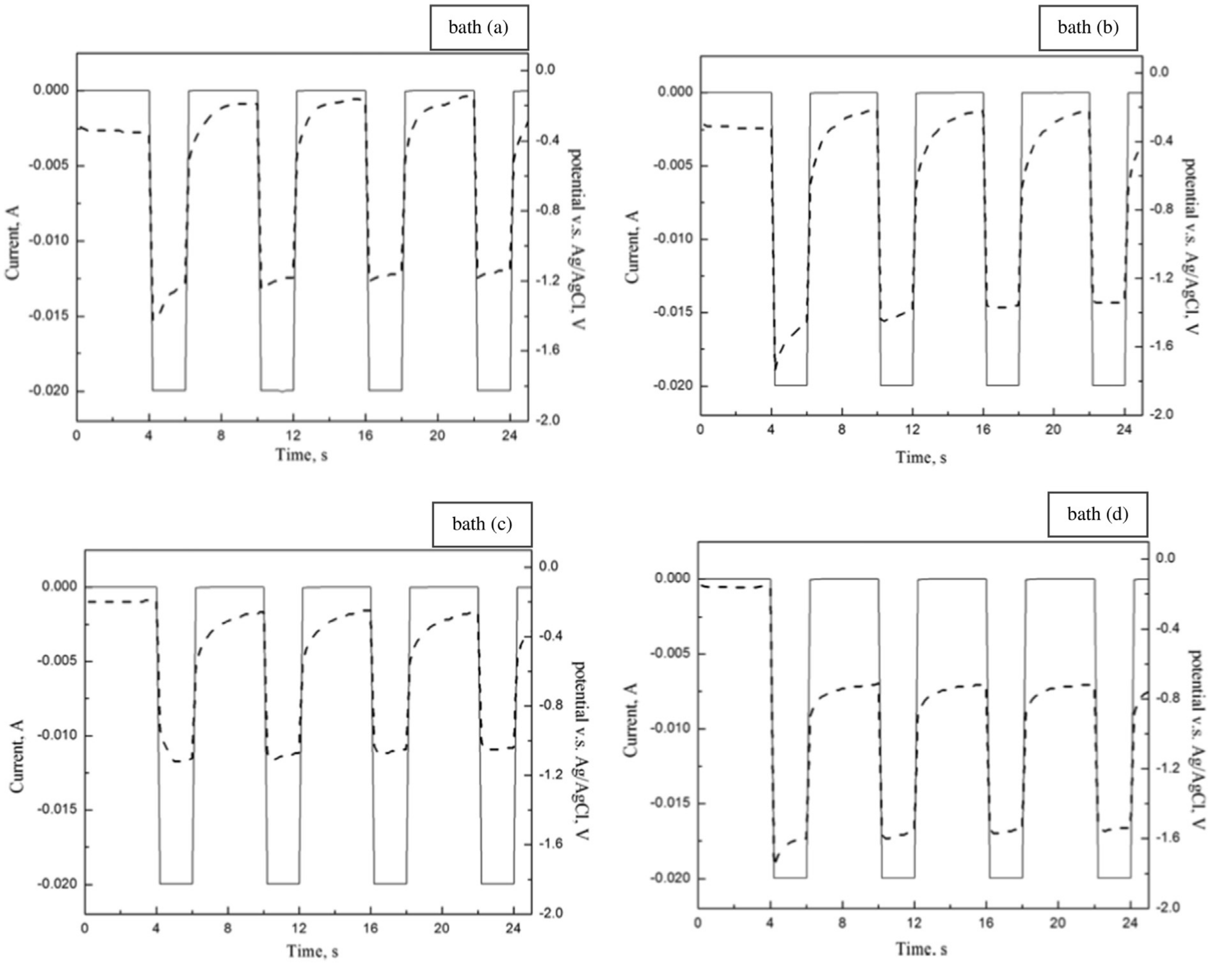

Fig. 1. Current waveform for galvanostatic PED and potential response measured for electrodeposition of coatings on Ni50Al samples at $i_{cd} = -10$ mA·cm^{-2}, $t_{on} = 2$ s, $t_{off} = 4$ s and $T = 25$ °C, pH 3, for 600 s in the baths (a)–(d) listed in Table 1 with agitation at 400 rpm.