OXIDATION BEHAVIOR OF POROUS AND NONPOROUS $\gamma$-Ni+$\gamma'$ COMPOSITE COATINGS

Marek KONIECZNY, Bartłomiej SZWED, Igor KARDYNAŁ

Kielce University of Technology, Faculty of Mechatronics and Mechanical Engineering, Kielce, Poland, EU, mkon@interia.pl

Abstract
Composite $\gamma$-Ni+$\gamma'$ coatings on an iron substrate with a nickel interlayer were developed by the conversion of electrodeposited Ni+Al films with dispersed Al particles in Ni matrix. The conversion was made by vacuum annealing at 900 °C for 3 h without and under uniaxial pressure of 1 MPa to obtain porous and full-density coatings, respectively. The cyclic-oxidation resistance of both types of produced coatings at 1000 °C was compared. It was noticed the detrimental effect of porosity on the oxidation resistance of $\gamma$-Ni+$\gamma'$ composite coatings. SEM/EDS and XRD characterisation of nonporous coatings showed that during oxidation a protective continuous Al$_2$O$_3$ layer is formed below a zone of NiAl$_2$O$_4$ spinel. The Al$_2$O$_3$ layer in porous $\gamma$-Ni+$\gamma'$ coatings was identified as discontinuous and therefore not fully-protective. After 100 h at 1000 °C a mass gain for nonporous $\gamma$-Ni+$\gamma'$ coatings was about 7 times lesser than for nickel coating.

Keywords: electroplating, $\gamma$-Ni, $\gamma'$, composite coating, oxidation

1. INTRODUCTION
The intermetallic compound $\gamma'$(Ni$_3$Al) has recently attracted considerable attention because of its great potential for applications as a high-temperature structural material due to its high strength, low density and good oxidation resistance at elevated temperatures [1]. It is also very advantageous that the $\gamma'$ phase shows an anomalous temperature dependence of yield strength and an excellent stability at high temperatures. However, the practical use of the intermetallic is severely restricted by its low-temperature brittleness. One approach to enhancing its fracture resistance is to reinforce it with appropriate volume fractions of ductile nickel [2]. It is very profitable that $\gamma'$ phase (ordered fcc L1$_2$ structure) precipitates coherently in a $\gamma$-Ni (fcc structure) matrix [3]. Nickel and $\gamma'$ have not only a similar structure, but also a modest lattice mismatch (with a lattice constant of 0.3524 nm and 0.3570 nm for Ni and $\gamma'$ phase, respectively). The $\gamma'$ precipitates exhibit a cube-on-cube orientation relationship with the Ni matrix, so that (001)$_{\gamma'}$//(001)$_{\gamma}$ and [100]$_{\gamma'}$//[100]$_{\gamma}$. There is also a low strain energy associated with $\gamma'/\gamma$ interfaces lying on {100} planes. During plastic deformation, dislocations in the Ni matrix prefer to cut through the $\gamma'$ precipitates, rather than bypassing them. Therefore, according to Wang et al. [4] and Meng et al. [5] the $\gamma$-Ni+$\gamma'$ composites can have a high ultimate tensile strength and large elongation and behave as ductile alloys. Recent interests are to adopt electrodeposition to prepare composite Ni+Al [6-8] and subsequently $\gamma$-Ni+$\gamma'$ coatings [9-12]. This is a two-step process including co-deposition of nickel matrix/Al particles composites, and later diffusion treatment to form alloy coatings. There are two types of electrodeposition techniques: conventional electrodeposition (CED), in which the anode and cathode are vertically inserted in the bath and sediment co-deposition (SCD), in which the anode and cathode are set horizontally. In SCD coatings, the Al particles are effectively isolated from each other by the Ni matrix and thus at elevated temperatures, phase formation take places locally around the individual particles. Many investigators [10-12] reported the presence of pores throughout the microstructure in $\gamma$-Ni+$\gamma'$ coatings, which were formed due to local density changes as the Al particles and Ni matrix transform to intermetallic phases. In order to achieve better oxidation resistance in high-temperature regime, it is of great importance to reduce the porosity. The pores and cracks open to the surface of the $\gamma$-Ni+$\gamma'$ coating can be sealed by electroplating of nickel or by applying phosphate-based sealants [13]. To reduce closed pores
inside coatings, the laser re-melting has proved to be a good method [14]. An effective solution to the pore formation problem is applying pressure during the propagation stage of the reaction [11]. The $\gamma'$ phase exhibits excellent oxidation resistance because of its capability to form a continuous $\mathrm{Al}_2\mathrm{O}_3$ layer below an outer layer of NiO and an intermediate layer of NiAl$_2$O$_4$ at high temperatures [15, 16]. Unfortunately, from an oxidation kinetics point of view, $\gamma'$ matrix with the addition of $\gamma$-Ni may reduce the oxidation resistance by promoting the growth of non-protective NiO. The purpose of this work was to investigate the influence of the employed manufacturing method on the oxidation behavior of the porous and nonporous composite $\gamma$-Ni+$\gamma'$ coatings.

2. EXPERIMENTAL PROCEDURE

2.1 Specimen preparation

Specimens with the sizes of $20 \times 20 \times 2 \text{ mm}$ were cut from a plate of iron (0.034 wt. % C, 0.038 wt.% Mn, 0.021 wt. % S, 0.01 wt.% P, and balanced Fe) and then ground using SiC papers up to 1200-grit finish. The specimens were coated using the CED technique with a 15 $\mu$m thick film of pure nickel from a Watt's type nickel bath containing 300 g/l NiSO$_4$$\cdot$7H$_2$O, 50 g/l NiCl$_2$$\cdot$6H$_2$O and 35g/l H$_3$BO$_3$. The used operating conditions were: current density 3 A$\cdot$dm$^{-2}$ and temperature 35°C. The anode was a pure electrolytic Ni (>99.9 %) plate. After that, the specimens with as-plated Ni coatings were polished with a 1 $\mu$m diamond suspension and again electrodeposited using the SCD technique. Coatings were deposited on the $20 \times 20 \text{ mm}$ surface whereas the other side of the specimen was isolated using a chemically-resistant glue. The composition of the bath and operating conditions were the same as previous. The bath additionally contained 40g/l of pure spheroidal Al powder with an average particle size of 3 $\mu$m. During SCD, the plating solution was magnetically stirred (250 rpm) in order to keep the particles dispersed and suspended in the electrolyte. The SCD plating time was 3 hours. The as-deposited coatings contained about 25 volume percent of Al particles. The coated samples were then annealed in a special furnace with a vacuum of $10^{-5}$ Pa (Fig. 1).

![Fig. 1](image)

Fig. 1 Equipment used in the present study to form fully-dense composite coatings

Firstly, the specimens were heated to 600 °C and soaked for 2 h for the reaction synthesis. Subsequently, the temperature was increased to 900 °C for rapid development of the structural processes. Some samples were heat treated without and other under uniaxial pressure of 1 MPa that was applied to reduce porosity. The samples were held at 900 °C for 3 h to produce a $\gamma$-Ni+$\gamma'$ coating microstructure and then furnace-cooled naturally to room temperature.
2.2 Cyclic oxidation

Cyclic oxidation tests of as-received porous and nonporous $\gamma$-Ni+$\gamma'$ composite coatings were performed in static air at 1000 °C, which is above the maximum service temperature for $\gamma'$ materials [1]. The as-plated Ni coated specimen was used as a reference. Before the test, all the specimens were polished with a 1 $\mu$m diamond suspension, cleaned using ethanol, and then air-dried. Test samples were held in high-purity alumina boats with one specimen per boat. The test cycle consisted of heating at 20 °C-min$^{-1}$, holding at 1000 °C for 10 h, and furnace-cooling to room temperature. After each of 10 cycles, the boats were removed from the furnace for mass gain measurements. Each specimen was weighted to an accuracy of 0.0001 g together with the boat and any spalled oxide from the coating. Since each $\gamma$-Ni+$\gamma'$ coated specimen has five edge surfaces pure-Ni coated, a correction was made to the measured mass gains on the assumption that the Ni coated surfaces would have the same mass change per unit area as the as-plated Ni coated specimen. After measurements, boats with specimens were returned to the furnace for the next run cycle.

2.3 Characterization

For characterization, the specimens were sectioned and mounted in a cold setting resin. Grinding was conducted with successively finer silicon carbide papers up to 1200 grit. The polishing step with a 1 $\mu$m diamond suspension was performed using a Struers polishing machine. The microstructural observations were conducted using a JEOL JMS-5400 scanning electron microscope (SEM) and a Carl Zeiss NEOPHOT 2 optical microscope. The chemical analysis was performed using an Oxford Instruments ISIS-300 energy dispersive X-ray spectrometer (EDX). The phase structure of the coatings was determined using X-ray diffraction (XRD), which was performed on a D/max RAPID II-R Rigaku diffractometer with the Cu K$_{\alpha}$ incident radiation.

3. RESULTS AND DISCUSSION

3.1 Coating microstructures

Typical porous and nonporous $\gamma$-Ni+$\gamma'$ composite coatings are shown in Fig. 2. Both coatings are uniform in their thickness, which was controlled to be about 15 $\mu$m for the Ni interlayer and about 100 $\mu$m for the composite $\gamma$-Ni+$\gamma'$ layers.

![Fig. 2 Microstructure of $\gamma$-Ni+$\gamma'$ coatings heat treated without pressure (a), and under pressure (b)](image-url)
Details of the reaction synthesis of $\gamma$-Ni+$\gamma'$ composite coatings during heat treatment at 900 °C were discussed in detail in previous work [11]. It was shown that due to density changes as the Al particles and Ni matrix transform to intermetallics in bulk reaction synthesis, porosity is always found in the resultant microstructure (Fig. 2a). A significant amount of small pores within $\gamma$-Ni+$\gamma'$ composite coatings have been also reported by Liu [6] and Susan [10]. An effective solution to the pore formation problem is applying pressure during the propagation stage of the reaction (Fig. 2b). The composite coatings after heat treatment consist of a two-phase mixture and a nickel sublayer neighboring to the iron substrate. Using X-ray microanalysis, it was found that the dark-gray single phase is the $\gamma'$ containing 75.44 at. % Ni and 24.56 at. % Al. The lightly shaded region surrounding the $\gamma'$ particles is the $\gamma$-Ni solid solution consisting of 92.47 at. % Ni and 7.53 at. % Al. The XRD analysis confirmed the results.

3.2 Oxidation resistance

Fig. 3 provides the mass changes of as-plated Ni, fully-dense $\gamma$-Ni+$\gamma'$ and porous $\gamma$-Ni+$\gamma'$ coatings prepared during cyclic oxidation at 1000 °C for the periods of up to 100 h.

At 1000 °C, the nickel coating, as well as, the porous and nonporous $\gamma$-Ni+$\gamma'$ coatings obey the parabolic rate law, which implies that oxidation is bulk-diffusion controlled. On the basis of measurement, relationships between the mass change per area ($d$ - expressed in g/cm²) of the oxidized specimens and the holding time ($t$ - expressed in hours) have been determined and they are $0.0007 \cdot t^{0.55}$, $0.0002 \cdot t^{0.4}$ and $0.00018 \cdot t^{0.4}$ for Ni, porous $\gamma$-Ni+$\gamma'$ and nonporous $\gamma$-Ni+$\gamma'$ coatings, respectively (Fig. 3). A high mass gain for nickel and about 7 times lesser for $\gamma$-Ni+$\gamma'$ coatings are found after 100 hours at 1000 °C. The results correspond well to previous studies of nickel and $\gamma$-Ni+$\gamma'$ oxidation at moderate to high temperatures [9, 10, 12]. EDS analysis (in combination with XRD) showed that the surface scale was composed of non-protective NiO for Ni and mainly NiAl₂O₄ spinel for $\gamma$-Ni+$\gamma'$ coatings. Below the NiAl₂O₄ zone, a continuous Al₂O₃ layer was formed in nonporous $\gamma$-Ni+$\gamma'$ coatings and discontinuous one in porous coatings. The nonporous $\gamma$-Ni+$\gamma'$ coatings are capable of forming continuous protective alumina scales below an outer NiAl₂O₄ layer because the Al concentration in the coatings is high enough and the diffusion rate is fast enough to supply Al to the surface in order to maintain Al₂O₃ scale growth. The detrimental effect of porosity on the oxidation behavior of $\gamma$-Ni+$\gamma'$...
coating can be easily explained. In the early stage of oxidation, when the coating surface and the internal surfaces of open pores are oxidized, the compressive stress is developed in the oxide scale and the tensile stress in the $\gamma$-Ni+$\gamma'$ coating [16]. The oxidized pores in the coating matrix act as the stress enhancers and can magnify the tensile stress at sharp tips of those pores. The plastic deformation that may happen at the tips results in the formation of dislocation pipes. The internal oxygen diffusion following through these pipes can connect the neighboring pores and accelerate the oxidation. The oxide growth is characterized with the dominant outward diffusion of Al and the depletion of Al below the oxidation/coating interface. If the Al content drops below a critical level, it is not possible to form a continuous surface alumina layer [9]. Owning to differences in the diffusion rates of Al and Ni, the Kirkendall effect occurs in the Ni-Al system [17]. The inward diffusion of Ni in the Al-depleted region leads to a number of Kirkendall vacancies, which are condensed as another pores at the grain boundaries in the coating. Therefore, the higher the porosity in the $\gamma$-Ni+$\gamma'$ coating, the easier the formation of interconnected oxidized pores and the more severe the oxidation of the coating. When specimens are exposed to 1000 °C, depletion of the $\gamma'$ phase occurs just below the external oxide layers near the coating surface. The coating was initially fully $\gamma$-Ni+$\gamma'$ (Fig. 2b), but after 20 h at 1000 °C, a $\gamma'$ depletion zone (containing $\gamma$-Ni and oxides) has developed about 15 $\mu$m wide near the coating surface (Fig. 4a). The width of the depletion zone continues to increase with time (Fig. 4b), and after 100 h at 1000 °C it reaches about 30 $\mu$m.

![Fig. 4 Cross-sectional morphology of nonporous $\gamma$-Ni+$\gamma'$ coating after 20 h (a) and 100 h oxidation (b)](image)

According to Susan’s analysis [10] the depletion onset time for 150 $\mu$m wide $\gamma$-Ni+$\gamma'$ coating increases with decreasing temperature and may last 500 h at 1000 °C, 2000 h at 900 °C, 8000 h at 800 °C, and even 80000 h at 700 °C. Therefore, for long-term diffusion at high temperatures, it is possible to obtain these coatings as single-phase $\gamma$-Ni layers.

4. **CONCLUSIONS**

Composite $\gamma$-Ni+$\gamma'$ coatings on an iron substrate with a nickel interlayer can be easily developed via three-step technology: conventional electrodeposition of nickel interlayer, sediment co-deposition of Ni+Al composite coating and subsequent vacuum annealing. The coatings heat treated without external pressure are porous due to local density changes as the Al particles and Ni matrix transform to intermetallic phases. The coatings heat treated under uniaxial pressure of 1 MPa are fully-dense and nonporous. At 1000 °C, as-plated nickel and $\gamma$-Ni+$\gamma'$ coatings follow parabolic oxidation kinetics, which implies that oxidation is bulk-diffusion controlled. A non-protective NiO layer forms during oxidation of nickel. During oxidation of nonporous $\gamma$-Ni+$\gamma'$ coatings a thin protective continuous Al$_2$O$_3$ layer forms below a zone of NiAl$_2$O$_4$ spinel. A high volume fraction of pores in the $\gamma$-Ni+$\gamma'$ coatings decreases oxidation resistance by forming oxidized
channels between the pores. It results in dropping of the Al content in the reaction zone below a critical level. Therefore, the Al2O3 layer in porous $\gamma$-Ni+$\gamma'$ coatings is discontinuous and not fully-protective. The results show that after 100 h at 1000 °C a mass gain for the nonporous $\gamma$-Ni+$\gamma'$ coating is the smallest of all investigated materials. Hence, the employed manufacturing method allowing to obtain fully-dense $\gamma$-Ni+$\gamma'$ layers can be practically used to improve the oxidation behavior of the composite coatings.

**LITERATURE**


