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COMPOSITES THEORY AND PRACTICE

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PROPERTIES OF γ-Ni+γ' COMPOSITE COATINGS TRANSFORMED FROM Ni+Al ELECTRODEPOSITS

Composite γ-Ni+γ' coatings on an iron substrate were developed by the conversion of Ni+Al electrodeposits with dispersed Al particles in an Ni matrix. The conversion was made by vacuum annealing at 900°C for 3 h under a uniaxial pressure of 1 MPa and full-density composite coatings were obtained. A nickel interlayer was successfully employed to block the mutual diffusion between the iron substrate and aluminium and therefore hard and brittle Fe-Al intermetallics were not formed. The oxidation resistance of as-plated Ni and γ-Ni+γ' composite coatings at 1000°C was compared. After 100 hours at 1000°C, a mass gain of oxides for the γ-Ni+γ' coating was about 7 times less than for the nickel coating. The γ-Ni+γ' coating follows parabolic oxidation kinetics, which implies that oxidation is bulk-diffusion controlled. SEM/EDS and XRD characterisation showed that during oxidation, a thin continuous Al_2O_3 layer is formed below the matrix of an $NiAl_2O_4$ spinel. The wear mass loss of the γ-Ni+γ' coatings was found to be about 3 times smaller than the as-plated Ni and Ni+Al coatings. Moreover, the γ-Ni+γ' coatings oxidised for 20 h, containing very hard and wear-resistant Al_2O_3 particles, show the smallest wear mass loss of all the tested materials.

Keywords: γ-Ni+γ' composite coating, oxidation resistance, wear behaviour

WŁAŚCIWOŚCI WARSTW KOMPOZYTOWYCH γ-Ni+γ' WYTWARZANYCH NA DRODZE TRANSFORMACJI GALWANICZNYCH POWŁOK Ni+Al

Warstwy kompozytowe γ-Ni+γ' na podłożu żelaza zostały wytworzone na drodze przekształcenia galwanicznych powłok Ni+Al. Konwersji dokonano poprzez wygrzewanie w próżni w temperaturze 900°C przez 3 godziny pod naciskiem. Uzyskano nieporowate powłoki kompozytowe. Zastosowana warstwa niklu skutecznie zablokowała dyfuzję pomiędzy podłożem z żelaza oraz cząstkami aluminium i dlatego w badanych próbkach nie stwierdzono występowania kruchych faz z układu Fe-Al. Porównano odporność na utlenianie w temperaturze 1000°C galwanicznej powłoki niklowej oraz powłoki kompozytowej γ-Ni+γ'. Stwierdzono, iż przyrost masy tlenków dla warstwy kompozytowej był około 7-krotnie mniejszy niż dla powłoki niklowej. Określono także kinetykę przyrostu masy tlenków. Badania z wykorzystaniem metod SEM/EDS oraz XRD pozwoliły scharakteryzować powstałe podczas utleniania produkty. Stwierdzono, że na niklu powstawały warstwy NiO, a warstwy tlenków na kompozycie γ-Ni+γ' składały się z $NiAl_2O_4$, pod którymi występowały ciągłe warstewki Al_2O_3. Testy trybologiczne wykazały, że ubytek masy warstw kompozytowych γ-Ni+γ' był około trzy razy mniejszy niż galwanicznych warstw niklowych oraz kompozytowych warstw Ni+Al. Ponadto stwierdzono, że utleniane przez 20 h warstwy γ-Ni+γ' miały najmniejszy ubytek masy podczas prób ścierania spośród wszystkich badanych materiałów. Efekt ten pojawiał się po czasie badania dłuższym niż 25 minut, gdy zostały odsłonięte w warstwie twarde i odporne na ścieranie cząstki Al_2O_3.

Słowa kluczowe: warstwa kompozytowa γ-Ni+γ', odporność na utlenianie, zużycie ścierne

INTRODUCTION

In recent years, intermetallic phase γ'(Ni_3Al) has attracted appreciable attention because of its great potential for applications in the aerospace and power industries as a high-temperature structural material due to its low density, high strength and good oxidation resistance at elevated temperatures [1]. Unfortunately, the γ' phase shows extreme brittleness at room temperature. One approach to enhancing its fracture resistance is to reinforce it with appropriate volume fractions of ductile nickel, which is used as a major component of many alloys used for high-temperature applications [2].

Nickel, solid solution γ-Ni and γ' phase have not only a similar structure, but also a modest lattice mismatch (the misfit of γ-Ni/γ' is below 1.3%) [3]. The γ' precipitates exhibit a cube-on-cube orientation relationship with the γ-Ni matrix. During plastic deformation, dislocations in the γ-Ni matrix prefer to cut through the γ' precipitates. Therefore, according to Wang et al. [4] and Meng et al. [5], γ-Ni+γ' composites can behave as ductile alloys with a high ultimate tensile strength and large elongation. Presently, many different coating techniques such as magnetron sputtering [5], physical vapour deposition [6] and thermal spraying [7] have been employed to produce γ' intermetallic coatings on various substrates. Unfortunately, the techniques are sophisticated and usually very costly. On the other hand, electrodeposition is a very simple and cost-efficient practical method. There are two main types of electrodeposition techniques: one with a cathode vertically inserted in the bath and the second with the cathode set horizontally. The conventional electrodeposition (CED) technique, in which the anode and cathode are vertically set in the bath, is the most popular. Nevertheless, both methods are used to produce composite coatings containing randomly dispersed hard ceramics (Al_2O_3, SiC, ZrO_2) [8], polymers (PTFE) [9] or metallic particles [10-12] in a nickel matrix.

Recent interests have been to adopt electro-co-deposition to prepare nickel aluminide coatings. This is a two-step process including the co-deposition of nickel matrix/Al particle composites, and subsequent heat treatment to form alloy coatings. In sediment co-deposited (SCD) coatings, the Al particles are effectively isolated from each other by the Ni matrix and thus at elevated temperatures, phase formation takes places locally around the individual particles. Therefore many investigators [13-15] have reported the presence of pores throughout the microstructure in γ-Ni+γ' coatings, which were formed due to local density changes as the Al particles and Ni matrix transform into intermetallic phases.

The purposes of the present work were to produce electro-co-deposited Ni+Al composite coatings with a high aluminium content to form after heat treatment, double-phase fully dense γ-Ni+γ' coatings as well as to investigate the influence of the employed manufacturing method on the wear behaviour and oxidation resistance of the coatings.

EXPERIMENTAL PROCEDURE

Armco iron was used as the coating substrate, whose chemical composition is as follows: 0.034 wt.% C, 0.038 wt.% Mn, 0.021 wt.% S, 0.01 wt.% P, and balanced Fe. Specimens with the sizes of 20 x 20 x 2 mm were cut from a plate and then ground using SiC papers up to a1200-grit finish. The specimens were coated using the CED technique, in which the cathode and anode were vertically set in the bath. 15 μm thick electrodeposits of nickel were obtained from a Watt's nickel bath containing 300 g/l $NiSO_4 \cdot 7H_2O$, 50 g/l $NiCl_2 \cdot 6H_2O$ and 35g/l H_3BO_3. The applied operating conditions were: current density 3 A/dm^2 and temperature 35°C. The anode was a pure Ni (> 99.9%) plate. After that, specimens with the as-plated Ni coatings were again electrodeposited using the SCD technique in which the cathode and anode were horizontally inserted in the bath. The coatings were deposited on the 20 x 20 mm surface whereas the other side of the specimen was isolated using a chemically-resistant glue (Distal). The composition of the bath and operating conditions were the same as before. The bath additionally contained 40 g/l pure Al powder with an average particle size of 3 μm. During SCD, the plating solution was magnetically stirred (250 rpm). The SCD plating time was 3 hours. The as-deposited coatings contained about 25 volume percent Al particles. The coated samples were then annealed in a special furnace with a vacuum of 10^{-5} Pa [15]. Some samples were heat treated without and others under a uniaxial pressure of 1 MPa that was applied to reduce porosity. Firstly, the specimens were heated to 600°C and soaked for 2 hours for the synthesis. Subsequently, the temperature was increased to 900°C for rapid development of the structural processes. The samples were held at 900°C for 3 hours to produce a γ-Ni+γ' coating microstructure and then furnace-cooled to room temperature. After that, the oxidation resistance of the as-received Ni and γ-Ni+γ' coatings was investigated. Exposure tests were performed in static air at 1000°C. Individual samples were removed from the furnace after 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 hours. For characterisation, microstructural observations were conducted using a JEOL JMS-5400 scanning electron microscope (SEM) and a Carl Zeiss NEOPHOT 2 optical microscope. Electron probe microanalysis (EPMA) was performed using an Oxford Instruments ISIS-300 system to quantitatively identify the composition of the phases in the coatings. The phase structure of the coatings was determined using X-ray diffraction (XRD), which was performed on a D/max RAPID II-R Rigaku diffractiometer with CuK$_\alpha$ incident radiation. Vickers measurements were performed by a Hanemann microhardness tester mounted on a NEOPHOT 2 microscope under a load of 0.981 N for 15 s. Dry sliding wear tests were carried out on a commercial T-05 testing machine with a block-on-ring configuration. The coated specimens were mounted to steel using a cyanoacrylate glue. The tested specimens were prepared as perpendicular blocks with dimensions of 16 mm in length, 10 mm in height and 6.35 mm in width. A 100Cr6 steel counter-specimen was used, hardened in the range of 61-63HRC, in the form of a crowned ring of 9 mm in width and 35 mm in diameter. The investigations were performed at room temperature at a constant sliding velocity of 130 rpm (0.24 m/s) for a load of 150 N applied via a cantilever beam. All the wear test specimens were cleaned in alcohol and weighed to an accuracy of 0.001 g at regular intervals (10 min) during the test. A total wear time for all the specimens was 60 minutes, which gave a total sliding distance of 864 m.

RESULTS AND DISCUSSION

Typical Ni+Al and γ-Ni+γ' composite coatings are shown in Figure 1. The coatings are uniform in their thickness, which was controlled to be about 15 μm for the Ni layer and about 100 μm for the composite Ni+Al or γ-Ni+γ' layers.

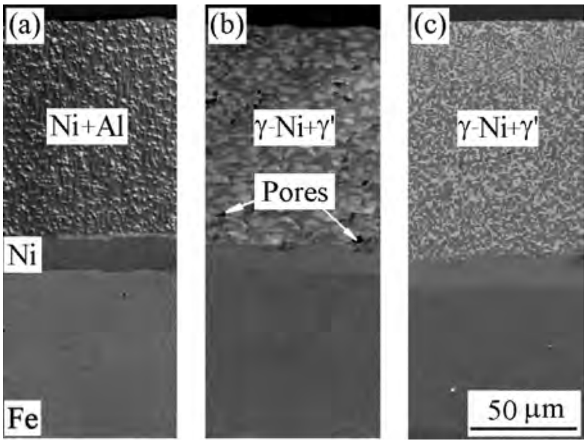

Fig. 1. Microstructure of as-plated Ni+Al coating (a), porous γ-Ni+γ' coating heat treated at 900°C without pressure (b), and γ-Ni+γ' coating heat treated under pressure (c)

Rys. 1. Mikrostruktura osadzonej galwanicznie powłoki Ni+Al (a), porowatej powłoki γ-Ni+γ' po wyżarzaniu w temp. 900°C bez docisku (b) oraz powłoki γ-Ni+γ' uzyskanej po zastosowaniu docisku (c)

The Ni+Al SCD coating contains about 25 vol.% Al and columnar nickel grains. The Al particles are homogeneously distributed and no defects such as pores or cracks are observed. Details of the synthesis of γ-Ni+γ'composite coatings during heat treatment at 900°C were discussed in detail in [15]. Unfortunately, due to density changes as the Al particles and Ni matrix transform to intermetallics in bulk reaction synthesis, porosity is found in the resultant microstructure (Fig. 1b). A significant amount of small pores within γ-Ni+γ' composite coatings have been also reported by Liu [10] and Susan [14]. It was shown before [15] that an effective solution to the pore formation problem is to apply pressure during the propagation stage of the reaction. After electrodeposition and heat treatment under pressure, the fully dense composite coatings consist of a two-phase mixture with blocky morphology and a sublayer neighbouring the iron substrate (Fig. 1c). Using X-ray microanalysis, it was found that the dark-grey single phase is the γ' containing 75.44 at.% Ni and 24.56 at.% Al. The lightly shaded region surrounding the γ' particles is the γ-Ni solid solution consisting of 92.47 at.% Ni and 7.53 at.% Al. The XRD results confirmed that the composite coatings contained an Ni and Al or γ-Ni and γ' phase before and after heat treatment, respectively (Fig. 2).

It is very important for composite coatings on an iron substrate to maintain a low concentration of Al, since Fe-Al-based brittle intermetallics could impair the mechanical properties of the iron/coating boundary. It is evident from the study that a 15 μm thick nickel interlayer can sufficiently block the diffusion of Al to the Fe side. The penetration of Al atoms across the nickel interlayer is very limited and therefore the possibility of the formation of brittle Fe-Al-based intermetallics is minimal. At 1000°C, the γ-Ni+γ' coating and comparatively examined nickel coating follow parabolic oxidation kinetics, which implies that oxidation is bulk-diffusion controlled.

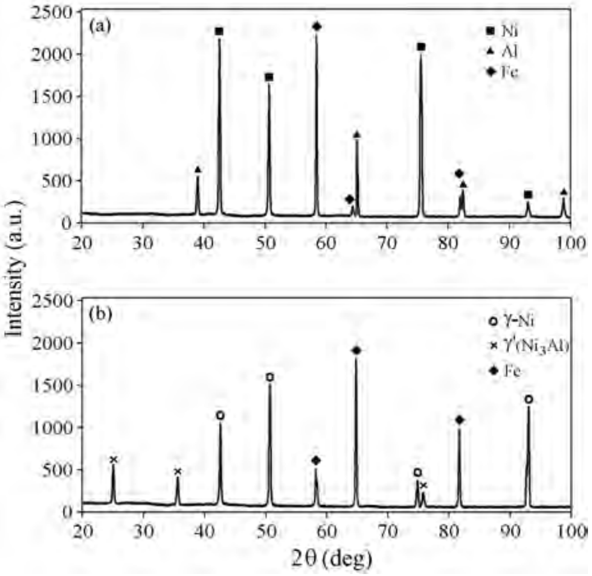

Fig. 2. XRD patterns of cross-section of as-plated Ni+Al composite coating (a) and γ-Ni+γ' coating (b)

Rys. 2. Dyfraktogram galwanicznej warstwy kompozytowej Ni+Al (a) oraz warstwy γ-Ni+γ' (b)

The EDS analysis (in combination with XRD) showed that the surface scale was composed of NiO for Ni and mainly $NiAl_2O_4$ for γ-Ni+γ' coatings. Below the $NiAl_2O_4$ layer, a continuous Al_2O_3 layer was formed. On the basis of measurement, relationships between the mass change per area (*d* - expressed in g/cm^2) of the oxidised specimens and the holding time (*t* - expressed in hours) were determined:

For as-plated Ni coating $d = 0.007\, t^{0.55}$ (1)

For γ-Ni+γ' composite coating $d = 0.00018\, t^{0.4}$ (2)

A high mass gain of 0.0089 g/cm^2 for the nickel and about 7 times less (only 0.0011 g/cm^2) for the γ-Ni+γ' coating are found after 100 hours at 1000°C (Fig. 3).

The results correspond well to previous studies of nickel and γ-Ni+γ' oxidation at moderate to high temperatures [13-15]. When specimens are exposed to 1000°C for long periods, depletion of the γ' phase occurs just below the external oxide layers near the coating surface. The width of the depletion zone increases with time, decreasing the γ-Ni+γ' layer within the coating (Fig. 4).

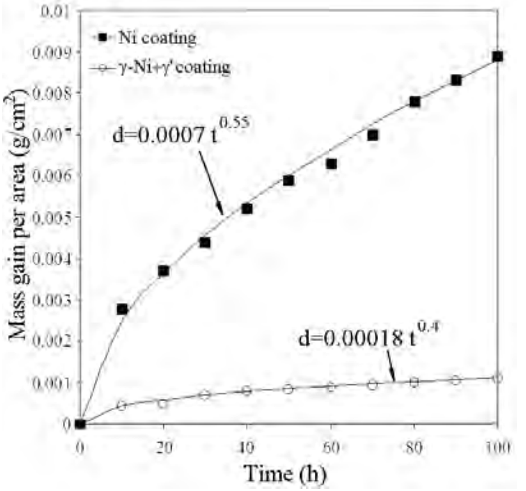

Fig. 3. Mass gain of oxidation zone of samples oxidised at 1000°C up to 100 h for as-deposited Ni and γ-Ni+γ' coatings

Rys. 3. Przyrost masy tlenków na powłoce niklowej oraz warstwie kompozytowej γ-Ni+γ' utlenianych w temperaturze 1000°C w czasie do 100 h

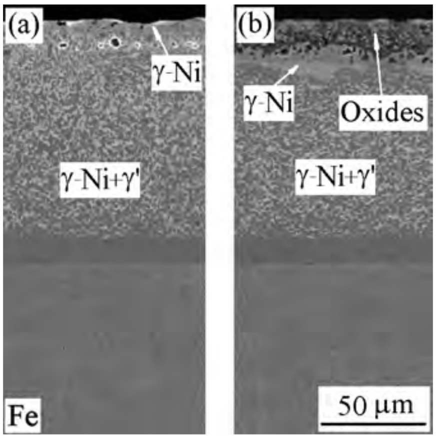

Fig. 4. Cross-sectional morphology of γ-Ni+γ' coating after 20 h (a) and 100 h (b) oxidation at 1000°C

Rys. 4. Struktura kompozytowej warstwy γ-Ni+γ' po 20 h (a) i 100 h (b) utleniania w temperaturze 1000°C

The coating was initially γ-Ni+γ' (Fig. 1c), but after 20 h at 1000°C, an about 15 μm wide γ' depletion zone developed near the coating surface (Fig. 4a). The width of the depletion zone continued to increase with time (Fig.4b), and after 100 h it reached about 30 μm. According to Susan and Marder [14], the depletion onset time for a 150 μm wide γ-Ni+γ' coating may last 500 h at 1000°C, 2000 h at 900°C and even 8000 h at 800°C.

Microhardness measurements were conducted for the coated specimens. The results showed that the as-plated Ni+Al coating (240 HV) was harder than the electrodeposited Ni coating (220 HV). The increase in hardness with the addition of soft Al particles could be surprising, but can be explained by the structural refinement of the Ni matrix when Al particles are added. The hardening effect is similar to the Hall-Petch type strengthening for a reduction in Ni grain size [15]. The results of hardness measurements after heat treatment showed that the hardness of the reaction-formed, fully-dense γ-Ni+γ' layer was 280 HV. The results for the specimens after oxidation tests performed for 20 h showed that the microhardness near the surface decreased from 280 HV to about 250 HV, which was attributed to the depletion of the γ' phase. A hardness peak of about 320 HV appeared at about 15 μm within the outer layer where Al_2O_3 particles were revealed (Fig. 4a).

The wear mass loss of the investigated materials gradually increased with increasing wearing time and simultaneously with sliding distance. The order of the wear mass loss in the experiment can be ranked as Fe-substrate < Ni+Al < Ni < γ-Ni+γ'. The wear mass loss of the γ-Ni+γ' coatings was found to be about 3 times smaller than the as-plated Ni and Ni+Al coatings. Moreover, the wear mass loss of the γ-Ni+γ' coating oxidised for 20 h tested at sliding distances greater than 360 m (above 25 min of testing time), was determined to be the smallest. The explanation of the phenomenon is very simple; because the coatings contain Al_2O_3 particles that are simultaneously very hard and wear-resistant. Figure 5 shows the relation between the wear mass loss of the iron substrate, nickel, Ni+Al, γ-Ni+γ', γ-Ni+γ' coating oxidised for 20 h and the testing time.

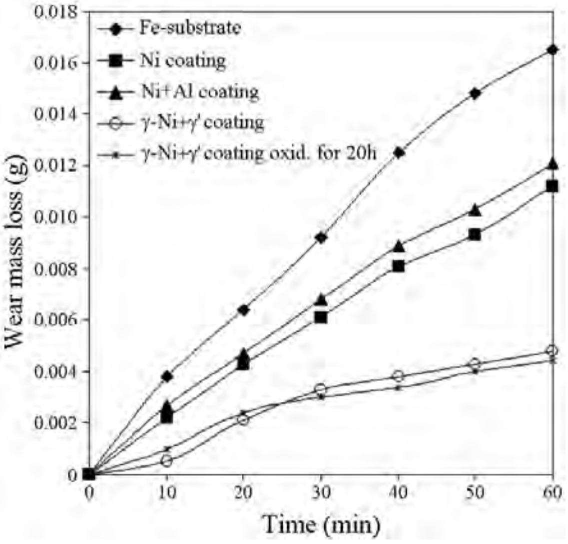

Fig. 5. Wear mass loss with testing time for Fe-substrate and as-plated Ni, Ni+Al, γ-Ni+γ' and oxidised γ-Ni+γ' coatings

Rys. 5. Ubytek masy próbek w funkcji czasu trwania testu ścierania dla żelaza oraz powłoki niklowej, Ni+Al, γ-Ni+γ' oraz utlenianej powłoki γ-Ni+γ'

Figure 6 shows examples of the worn surfaces for the four tested coatings: Ni, Ni+Al, γ-Ni+γ' and γ-Ni+γ' oxidised for 20 h, after wear testing for 60 minutes until a sliding distance of 864 m.

The worn surface of the nickel coating (Fig. 6a) was smooth, accompanied by slight scratches showing the evidence of plastic deformation. Considerable layer detachment appeared on the worn surface of the Ni+Al coated sample, which was attributed to adhesion wear (Fig. 6b). For the γ-Ni+γ' coating, as shown in Figure 6c, the worn surface exhibited negligible signs of plastic deformation and a small amount of debris particles stuck along the sliding direction.

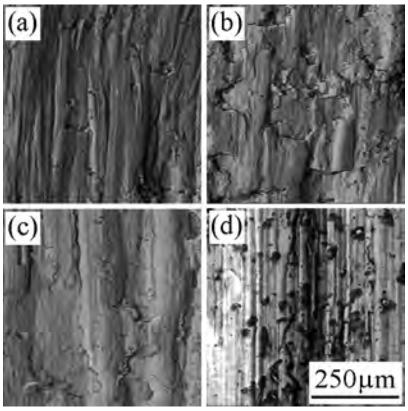

Fig. 6. Morphologies of worn surfaces of specimens wear-tested for 60 minutes: (a), (b), (c) and (d) corresponding to Ni, Ni+Al, γ-Ni+γ' and 20 h oxidised γ-Ni+γ' coatings, respectively

Rys. 6. Powierzchnie próbek po testach ścierania trwających 60 minut: powłoka Ni (a), powłoka Ni+Al (b), powłoka γ-Ni+γ' (c) oraz utleniana przez 20 h - powłoka γ-Ni+γ' (d)

Locally, a mini-cracked surface layer was present. The worn surface of the γ-Ni+γ' coating oxidised for 20 h was generally rougher, with remnants of the Al_2O_3 particles visible at the surface (Fig. 6d). In addition, occasional surface cracking was observed along the sliding direction.

CONCLUSIONS

Composite γ-Ni+γ' coatings on an iron substrate without cracking or porosity can be easily developed via three-step technology: electrodeposition of a nickel interlayer, sediment co-deposition of Ni+Al, and subsequent vacuum annealing under uniaxial pressure. At 1000°C, γ-Ni+γ' coatings follow the parabolic oxidation kinetics. During oxidation, a thin continuous Al_2O_3 layer forms below a layer of $NiAl_2O_4$. After 100 h at 1000°C, the mass gain for the γ-Ni+γ' coating is about 7 times less than for the nickel coating. The wear mass loss of the γ-Ni+γ' coatings is about 3 times smaller than for the as-plated Ni and Ni+Al coatings. The γ-Ni+γ' coatings oxidised for 20 h, containing very hard and wear-resistant Al_2O_3 particles, show the smallest wear mass loss after larger sliding distances.

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