

PROPERTIES OF COMPOSITE COATINGS TRANSFORMED FROM NICKEL ELECTRODEPOSITS CONTAINING SILICON PARTICLES

KONIECZNY Marek, CIEŚLIK Michał

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

Abstract

Composite (Ni) + Ni₃Si coatings on C45 steel-substrate could be easily developed via three-step technology: electrodeposition of nickel interlayer, sediment co-deposition of Ni+Si and subsequent vacuum annealing at 980 °C for 5 h. The results of hardness measurements showed that as-plated Ni+Si coating was 1.7 times harder than the electrodeposited Ni coating, but the hardest was (Ni) + Ni₃Si coating (820 HV) due to the presence of the super hard Ni₃Si phase. At 1000 °C, (Ni) + Ni₃Si coatings followed parabolic oxidation kinetic. During oxidation a thin continuous SiO₂ layer formed below a layer of NiSiO₃. After 100 h at 1000 °C a mass gain for (Ni) + Ni₃Si coating was about 6 times lesser than for nickel coating. The wear mass loss of the (Ni) + Ni₃Si coatings was approximately 2.5 times smaller than for as-plated Ni and Ni+Si coatings. The oxidised for 50 h (Ni) + Ni₃Si coatings containing hard and wear-resistant SiO₂ particles also showed smaller wear mass loss than Ni and Ni + Si coatings.

Keywords: Nickel, silicon, composite coating, oxidation behavior, wear resistance

1. INTRODUCTION

The main purpose of a composite coating is to give various properties, such as high temperature oxidation resistance, corrosion protection, wear resistance or self-lubrication to the coated surface. In recent years, composite coatings consisting of a metal matrix with particles have been studied extensively and used for a number of industrial applications [1 - 8]. The phases based on Ni (Ni₃Al and Ni₃Si) has attracted appreciable attention because of its great potential for applications as a high-temperature structural material due to its low density, high strength and good oxidation resistance at elevated temperatures. Fortunately, nickel, Ni₃Al and Ni₃Si have not only a similar structure (FCC), but also a modest lattice mismatch (with a lattice constant of 0.3524, 0.3570 and 0.3504 nm for Ni, Ni₃Al and Ni₃Si, respectively) [3]. Electrodeposition is a very simple and cost-efficient practical method. There are two main types of electrodeposition techniques: one with the cathode vertically inserted in the bath and second with the cathode set horizontally. Both methods are used to produce composite coatings containing randomly dispersed hard ceramics (Al₂O₃, SiC, ZrO₂) [9], polymers (PTFE) [10], metallic [2, 5, 6, 11] or metalloid particles [1, 8, 12, 13] in a nickel matrix. When the co-deposited particles react at high temperature with the metal matrix, the layers with the properties different from those achieved without heat treatment can be produced. The purposes of the present work were to produce electro-co-deposited Ni+Si composite coatings with high silicon content to form after heat treatment double-phase (Ni) + Ni₃Si coatings as well as to investigate their oxidation resistance and wear behavior.

2. EXPERIMENTAL PROCEDURE

2.1. Specimen preparation

Specimens with the sizes of 20 x 20 x 5 mm were cut from a plate of C45 non-alloy quality steel (0.43 wt.% C, 0.75 wt.% Mn, 0.04 wt.% S, 0.02 wt.% P, and balanced Fe) and then ground using SiC papers up to 1000-grit finish. Next the specimens were coated with a 15 μm thick film of pure nickel from a Watt's type nickel bath containing 300 g / l NiSO₄·7H₂O, 50 g / l NiCl₂·6H₂O and 35 g / l H₃BO₃. The used operating conditions were:

current density $3 \text{ A}\cdot\text{dm}^{-2}$ and temperature $40 \text{ }^\circ\text{C}$. The anode was a pure electrolytic Ni (>99.9 %) plate. After that, the specimens with as-plated Ni coatings were polished with a $1 \text{ }\mu\text{m}$ diamond suspension and again electrodeposited using the SCD technique (**Figure 1**).

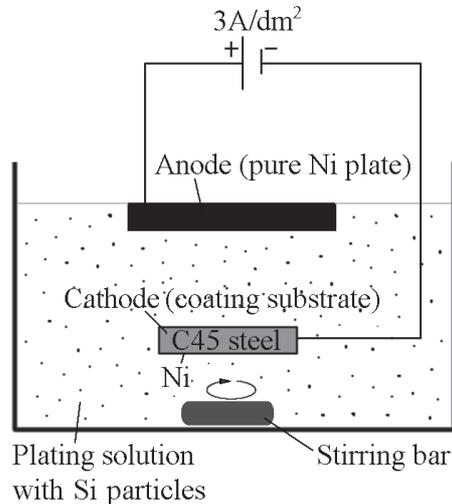


Figure 1 Schematic diagram of used sediment co-deposition technique (SCD)

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 50 g/l of pure Si powder with particles size of $1\text{-}10 \text{ }\mu\text{m}$ in diameter. 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 2 hours. When the silicon particles are not pretreated with electroless nickel deposition, the content of particles in the layer usually is in the range between 1 and 5 wt. % [1, 8]. The as-deposited coatings contained about 4.5 wt. % of Si particles. The content of particles was determined by weighing. The coated samples were then annealed in a furnace with a vacuum of 10^{-5} Pa . The specimens were heated to $980 \text{ }^\circ\text{C}$, soaked for 5 h for the reaction synthesis and then furnace-cooled naturally to room temperature.

2.2. Cyclic oxidation

Cyclic oxidation tests of as-received composite coatings were performed in static air at $1000 \text{ }^\circ\text{C}$, which is above the maximum service temperature for nickel-base materials [3]. The as-plated Ni coated specimen was used as a reference. Test samples were held in high-purity alumina boats with one specimen per boat. The test cycle consisted of holding at $1000 \text{ }^\circ\text{C}$ 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 (Ni) + Ni_3Si 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 1000 grit. The polishing step with a $1 \text{ }\mu\text{m}$ 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 Nikon ECLIPSE MA 200

optical microscope. The chemical analysis was performed using an Oxford Instruments ISIS-300 energy dispersive X-ray spectrometer (EDX). The microhardness along the cross-section of the layers was performed by a Matsuzawa MMT tester under load of 0.981 N with a testing time of 15 s. The 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 dimension 16 mm length, 10 mm height and 6.35 mm width. A 100Cr6 steel counter-specimen was used, hardened in the range 61-63HRC, in the form of a crowned ring of 9 mm width and 35 mm diameter. The investigations were performed at room temperature at a constant sliding velocity 130 rpm (0.24 m / s) for a load of 150 N applied via a cantilever beam. All wear test specimens were cleaned in alcohol and weighted to an accuracy of 0.001 g at regular intervals (10 min) during the test. A total wear time for all specimens was 60 minutes what gave the total sliding distance of 864 m.

3. RESULTS AND DISCUSSION

3.1. Coating microstructure

As-deposited Ni + Si composite coatings are characterized by grey, mat surface, with easy visible Si particles covered and uncovered with nickel deposit. It has been found that the heat treatment of Ni+Si composite coatings influenced the surface development. The surface after heat treatment was less developed in comparison to the untreated. Typical layered (Ni) + Ni₃Si/Ni composite coating is shown in **Figure 2**. The coating is uniform in its thickness, which was controlled to be about 15 μm for the Ni interlayer and about 60 μm for the composite (Ni) + Ni₃Si layer.

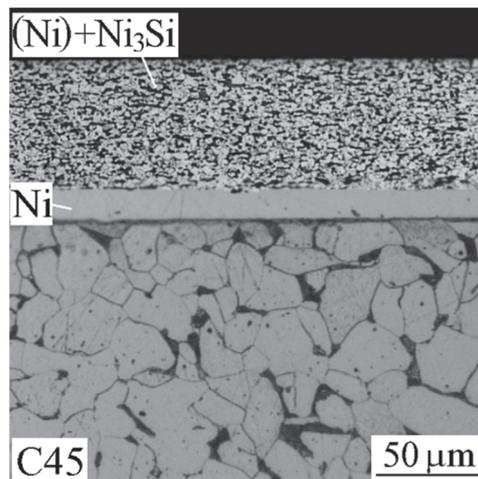


Figure 2 Optical micrograph of annealed (Ni) + Ni₃Si/Ni coating after 5 h at 980 °C

Heat treatment results in diffusional reaction between the Si particles and nickel matrix to produce a range of Ni-Si compounds [8, 12]. Phases formed concentrically around the original Si particles or at the Ni-Si interfaces. During heating at lower temperatures (up to 800 °C) NiSi₂ and NiSi are formed by a rapid, exothermal reaction. When the temperature is higher than 966 °C the liquid phase appears and diffusional processes accelerate. The composite coatings after heat treatment at 980 °C for 5 h consist of a two-phase mixture and a nickel sublayer neighboring to the C45 steel substrate. Using X-ray microanalysis, it was found that the dark-gray single phase is Ni₃Si containing 74.66 at. % Ni and 25.34 at. % Si. The lightly shaded region surrounding the Ni₃Si particles is the (Ni) solid solution consisting of 94.27 at. % Ni and 5.73 at. % Si (**Figure 3**). It was shown also previously by Desyatková et al. [12] that the homogenizing annealing of Ni+Si coatings leads to the formation of super hard Ni₃Si phase.

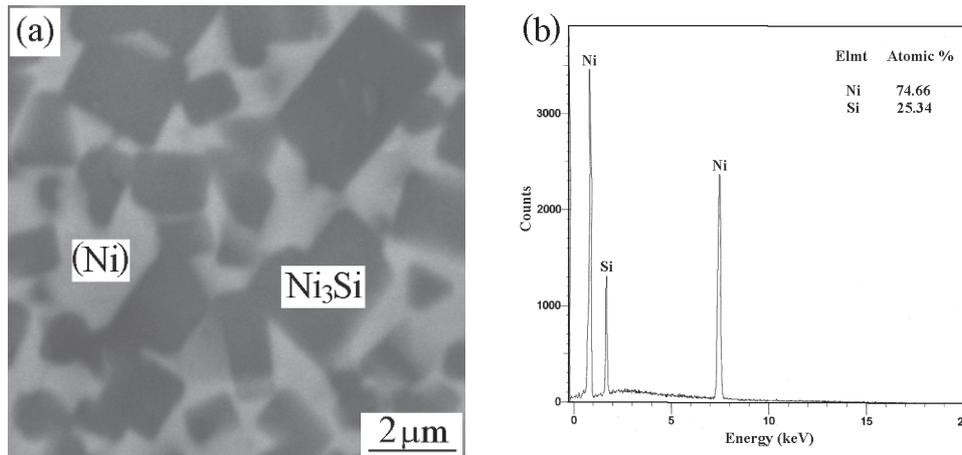


Figure 3 SEM micrograph of (Ni) + Ni₃Si coating (a) and the energy spectrum for emitted X rays for Ni₃Si (b)

3.2. Oxidation resistance

Figure 4 provides the mass changes of as-plated Ni and (Ni) + Ni₃Si coatings prepared during cyclic oxidation at 1000 °C for the periods of up to 100 h.

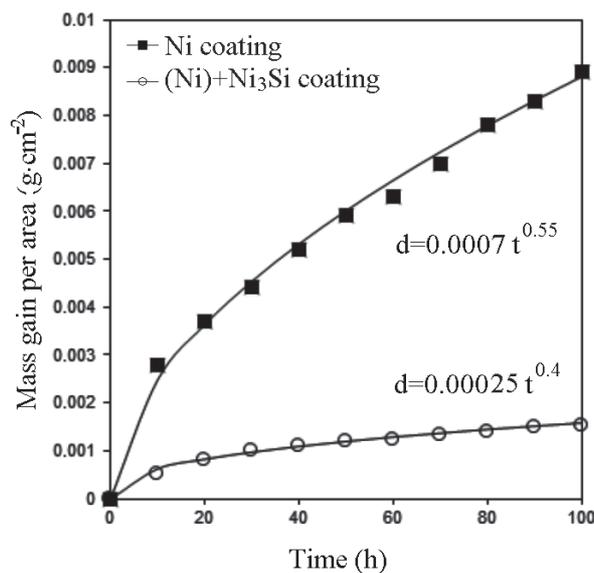


Figure 4 The cyclic-oxidation behavior at 1000 °C for Ni and (Ni) + Ni₃Si coatings

At 1000 °C, the nickel coating and (Ni) + Ni₃Si coating 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 $\text{g}\cdot\text{cm}^{-2}$) of the oxidized specimens and the holding time (t - expressed in hours) have been determined and they are $0.0007\cdot t^{0.55}$ and $0.00025\cdot t^{0.4}$ for Ni and (Ni) + Ni₃Si coatings, respectively (**Figure 4**). A high mass gain for nickel and about 6 times lesser for (Ni) + Ni₃Si coatings are found after 100 hours at 1000 °C. EDS analysis showed that the surface scale was composed of non-protective NiO for Ni and mainly silica NiSiO₃ for (Ni) + Ni₃Si coatings. Below the NiSiO₃ spinel zone, a continuous SiO₂ layer was formed in composite coatings. The (Ni) + Ni₃Si coatings are capable of forming continuous protective silicon dioxide scales below an outer NiSiO₃ layer because the Si concentration in the coatings is high enough and the diffusion rate is fast enough to supply Si to the surface in order to maintain SiO₂ scale growth.

3.3. Microhardness measurements

Microhardness measurements were conducted for the coated specimens. The results showed that the as-plated Ni+Si coating (385 HV) was 1.7 times harder than the electrodeposited Ni coating (230 HV). The results of hardness measurements after heat treatment showed that the hardness of the reaction-formed (Ni) + Ni₃Si layer was 820 HV. Desyatkova et al. [12] reported that layers converted from Ni + Si coatings are hard because of the formation of super hard Ni₃Si phase. The increase in hardness is typical for composite coatings containing particles [1, 4, 6, 7, 13]. The results for the specimens after oxidation tests performed for 50 h showed that the microhardness near the surface decreased from 820 HV to about 550 HV, which was attributed to the depletion of the Ni₃Si phase. A hardness peak of about 660 HV appeared at about 15 μm within the outer layer where SiO₂ particles were previously revealed.

3.4. Wear behaviour

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 C45 steel-substrate < Ni < Ni + Si < (Ni) + Ni₃Si. The wear mass loss of the (Ni) + Ni₃Si coating was found to be 2.2 - 2.8 times smaller than for as-plated Ni and Ni+Si coatings. Moreover, the wear mass loss of the oxidised for 50 h (Ni) + Ni₃Si coating was also much lesser than for Ni and Ni + Si coatings. **Figure 5** shows the relation between the wear mass loss of the C45 steel substrate, nickel, Ni + Si, (Ni) + Ni₃Si, oxidised for 50 h (Ni) + Ni₃Si coating and the testing time.

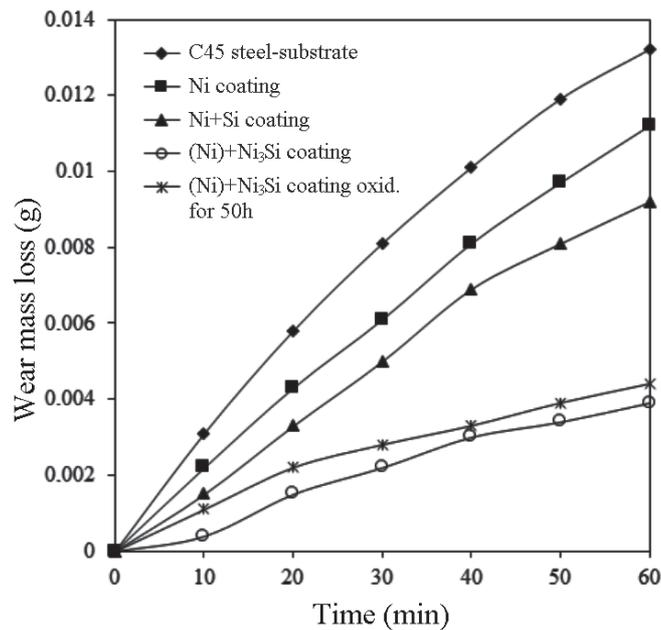


Figure 5 The wear mass loss with testing time for C45 steel, as-plated Ni and composite coatings

The worn surfaces of C45 steel substrate and nickel coating were smooth, accompanied by slight scratches showing the evidence of plastic deformation. The considerable layer detachment appeared on the worn surface of the Ni + Si coated sample, which was attributed to adhesion wear. For the (Ni) + Ni₃Si coating the worn surface exhibited negligible signs of plastic deformation and a small amount of debris particles stuck along the sliding direction. Locally, a mini-cracked surface layer was present. The worn surface of the oxidised for 50 h (Ni) + Ni₃Si coating was generally rougher, with remnants of the SiO₂ particles visible at the surface. In addition, occasional surface cracking was observed along the sliding direction.

4. CONCLUSION

It was stated that there is a possibility of the electrolytic production of Ni-based coatings embedded particles of silicon. The percentage of Si in the composite layers obtained from a bath with dispersed Si powder was about 4.5 wt. %. It was ascertained that the heat treatment of Ni + Si coatings led to production of a new kind of composite coatings containing a range of Ni-Si compounds. The composite coatings after heat treatment at 980 °C for 5 h consisted only of a two-phase mixture: Ni₃Si particles surrounded by the solid solution of silicon in nickel (Ni). Therefore, composite (Ni) + Ni₃Si coatings on C45 steel-substrate could be easily developed via three-step technology: electrodeposition of nickel interlayer, sediment co-deposition of Ni + Si and subsequent vacuum annealing. At 1000 °C, (Ni) + Ni₃Si coatings follow parabolic oxidation kinetic. During oxidation a thin continuous SiO₂ layer formed below a layer of NiSiO₃. After 100 h at 1000 °C a mass gain for (Ni) + Ni₃Si coating was about 6 times lesser than for nickel coating. The results of hardness measurements showed that as-plated Ni + Si coating was 1.7 times harder than the electrodeposited Ni coating, but the hardest was (Ni) + Ni₃Si coating (820 HV) due to the presence of the super hard Ni₃Si phase. The wear mass loss of the (Ni) + Ni₃Si coatings was about 2.2 - 2.8 times smaller than for as-plated Ni and Ni + Si coatings. The oxidised for 50 h (Ni) + Ni₃Si coatings containing hard and wear-resistant SiO₂ particles also showed smaller wear mass loss than Ni and Ni+Si coatings.

REFERENCES

- [1] FELLNER, P., CONG, P. Ni-B and Ni-Si composite electrolytic coatings. *Surface and Coatings Technology*, 1996, vol. 82, pp. 317-319.
- [2] SUSAN, D.F., MARDER, A.R. Ni-Al composite coatings: diffusion analysis and coating lifetime estimation. *Acta Materialia*, 2001, vol. 49, pp. 1153-1163.
- [3] SIKKA, V.K., DEEVI, S.C., VISWANATHAN, S., SWINDEMAN, R.W., SANTELLA, M.L. Advances in processing of Ni₃Al-based intermetallics and applications. *Intermetallics*, 2000, vol. 8, pp. 1329-1337.
- [4] MOLA R. The properties of Mg protected by Al and Al/Zn-enriched layers containing intermetallic phases. *Journal of Materials Research*, 2015, vol. 30, pp. 3682-3691.
- [5] NAPŁOSZEK-BILNIK, I., BUDNIOK, A., ŁĄGIEWKA, E. Electrolytic production and heat-treatment of Ni-based composite layers containing intermetallic phases. *Journal of Alloys and Compounds*, 2004, vol. 382, pp. 54-60.
- [6] KONIECZNY, M. Composite coatings γ -Ni+ γ '/Ni on iron transformed from electrodeposited Ni and sediment co-deposited Ni+Al films. *Composites Theory and Practice*, 2011, vol. 11, page 168-173.
- [7] DZIADOŃ, A., MOLA, R., BŁAŻ, L. The microstructure of the surface layer of magnesium laser alloyed with aluminum and silicon. *Materials Characterization*, 2016, vol. 118, pp. 505-513.
- [8] KUBISZTAL, J., BUDNIOK, A. Electrolytical production of Ni+Mo+Si composite coatings with enhanced content of Si. *Applied Surface Science*, 2006, vol. 252, pp. 8605-8610.
- [9] WANG, S.C., WEI, W.C. Kinetics of electroplating process of nano-sized ceramic particle/Ni composite. *Materials Chemistry and Physics*, 2003, vol. 78, pp. 574-580.
- [10] TRZASKA, M., KUCHARSKA, B. Influence of current density and bath composition on properties of Ni/PTFE composite coatings. *Composites Theory and Practice*, 2008, vol. 8, pp. 77-81
- [11] LIU, H., CHEN, W. Electrodeposited Ni-Al composite coatings with high Al content by sediment co-deposition. *Surface and Coating Technology*, 2005, nr. 191, page 341-350.
- [12] DESYATKOVA, G., YAGODKINA, L., SAVOCHKINA, I., KHALDEEV, G. Composite nickel-based electroplates. *Protection of Metals*, 2002, vol. 38, pp.466-470.
- [13] ISTRATE, G. Electrodeposition and characterization of Ni-Si nanocomposite coatings. *The Annals of University of Galati*, 2013, vol. 4, 96-99.