

ELECTRODEPOSITED NICKEL COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS

(Mrs) MALATHY PUSHPAVANAM and K BALAKRISHNAN
Central Electrochemical Research Institute, Karaikudi 623006

ABSTRACT

Although widely used because of its excellent physical and mechanical properties at room temperature on the one hand and its chemical and corrosion resistance on the other, nickel does not possess the wear resistance required for high temperature applications in many practical environments. Numerous nickel base alloys have been developed for their strength and resistance at high temperatures. Recently nickel base composites, containing hard inert particles are receiving attention as possible wear resistant coatings for high temperature applications. In this paper, a critical analysis of the available composites are made for their usefulness for different applications as high temperature resistant as well as wear and corrosion resistant materials.

INTRODUCTION

Though electrodeposits are traditionally thought of as protective and decorative coatings, they do find application in other areas such as wear control [1-3]. However, the wear properties of the commonly known electrodeposits are such that their range is limited to those in which the conditions of wear are mild or lubrication is involved. One of the most severe forms of wear is that which occurs between contacting materials at high temperatures as in aeroengine parts. One of the best methods known for controlling it is by the use of flame sprayed coatings. But not all parts can be treated by this technique.

There has been considerable interest in recent years in the development of metal matrices containing dispersed particles [4-7]. This type of material has been investigated for such applications as increased lubricity in moving parts [8-11], increased wear resistance and hardness [12-14]. The selection of suitable matrices and ceramic additives was based on the constituents employed in other wear protective methods. The insoluble additives employed were those with known high temperature properties and which could be obtained in fine powder form with average particle size of about 0.5-5 μm . This involved a number of oxides [15-21], borides [14], nitrides [22] and carbides [13]. The dispersion has been accomplished by various techniques such as (1) blending of the additive particles with fine metal powder into a homogeneous mixture and compacting under pressure of $4.5\text{--}5.5 \times 10^3 \text{ kg/cm}^2$ (2) precipitation of the salt of the metal matrix from the solution containing the colloidal suspension of the dispersoid, and drying and compacting the resultant precipitate under high pressure and (3) by electrodeposition of dispersoid along with metal from a suitable electrolyte. The deposit consists of a matrix of the metal containing a random dispersion of the insoluble additives.

So far, composites of nickel-tungsten carbide, nickel-titanium carbide, nickel-silicon carbide, nickel-diamond powder, are reported for their high wear resistance.

Though electrodeposited nickel is widely used because of its excellent physical and mechanical properties, chemical and corrosion resistance and relatively lesser cost, it lacks the required wear resistance for many industrial applications, especially for those involving high temperatures. In order to improve the above property major part of the research in electrodeposited composites is concentrated on nickel matrix. Although interest has been focussed on the mechanical and wear resistant properties, little is reported about the oxidation and corrosion behaviour, internal stress etc. In this paper, the above properties of the nickel composites are discussed, with the probable reason for the increased strength of these materials.

Technique of composite preparation

Nickel cermets can be deposited from sulphate, chloride or sulphamate electrolytes [23]. They can be deposited from a Watts or hard nickel plating electrolyte [18,21] depending upon the kind of wear resistance required. A hard nickel would be selected for a part requiring high dimensional stability, whereas a soft nickel coating is best suited for bearing applications where dimensional conformity and ability to absorb contaminant particles is required. To achieve uniform mixing of the suspended particles, which may include alumina, titanium dioxide, silicon carbide, tungsten carbide, boron nitride etc. in the electrolyte, solution circulation, plate pumping process [24], ultrasonic agitation [25], mechanical agitation [26], etc., have been adopted. Composites can be prepared by using vertical or horizontal cathodes, depending upon the required properties [27,28,29,30].

Wear and abrasion resistance

The general level of wear resistance of the nickel composite is high, the best of the group being nickel-tungsten carbide [29] and the next best being nickel-silicon carbide [31] (Table I). The additions improved the wear performance of the deposit but not significantly to reduce the adhesive nature of nickel. The wear results obtained above 300°C are better than those obtained at low temperatures since the oxide glaze formation on the load bearing areas of the contact during motion is responsible for the wear resistance and this property is greater at higher temperatures.

Nickel-tantalum carbide [2] composite is used on components subjected to wear at ambient temperatures under nonimpacting conditions. The wear resistance of composites with 3-6 μm chromium carbide particles exhibited less weight loss before heat treatment than 1-2 μm and 5-7 μm particles. Heat treatment at 400°C for 30 minutes reduces the wear of 3-6 μm size composites slightly [32]. However, wear resistance of nickel-chromium carbide composites after heat treatment at 600°C, 800°C and 1000°C exhibited the same wear as in the original untreated condition. Nickel-thorium oxide and nickel-uranium oxide composites heat treated at 649°C crumbled on handling due to the possible grain boundary sulphur embrittlement [25].

Diamond powder incorporated in nickel matrix used as an abrasive saw for jewellery and grinding wheels shows the wear loss of only about 0.7% in the grinding test [32-34]. The wear loss of some of the composites are given in Table I.

Table I: Abrasion resistance of nickel composites [3]

Load 3.15 kg, duration 5 mts

| Material | Weight loss in mg/cm^2 |
|------------|----------------------------------------|
| Ni | 334.0 |
| Ni-SiC 17% | 20.0 |
| Ni-SiC 24% | 16.0 |
| Ni-WC 10% | 9.0 |

Hardness and effect of heat treatment

The hardness and other mechanical properties of these coatings depend on the type of bonding between the ceramic phase and the metal [35].

The hardness of the composites (Table II) fall rapidly on heat treatment. The hardness of the composite remained nearly two times greater than that of pure nickel deposits even after heat treatment upto 1000°C in hydrogen atmospheres for 1 hour [18, 21]. The boron carbide-nickel composite, even after heat treatment at 375°C showed no change in the surface structure. But some changes have been detected after 25 hours of heat treatment at 600°C. The heat treatment of nickel-alumina composites showed no change in the microstructure upto 750°C, but at 1100°C the oxide particles redistribute themselves to form large crystals of alumina. Studies indicate [36] that in nickel-alumina composite, in the as-plated condition, the particles were not confined to the grain boundaries, nor were they particularly associated with the twins. They were frequently surrounded by dislocations. The composite is in a state of

Table II: Hardness and adhesion of nickel composites [2]

| Inert particle used | % ceramic by volume | Particle size μm | Surface finish CLA μm | Hardness VHN | Adhesion $\text{kg}/\text{sq. cm}$ |
|-------------------------|---------------------|-----------------------------|----------------------------------|--------------|------------------------------------|
| Al_2O_3 | 50 | 1-2 | 25-35 | 562 | 259.6 |
| ZrO_2 | 40 | 0.5-1 | 25-35 | 453 | 182.1 |
| Cr_2O_3 | 30 | 1 | 10-15 | 533 | 439.0 |
| TiO_2 | 12-20 | 1-2 | — | 450 | — |
| SiO_2 | 10-22 | 1-2 | — | 270 | — |
| ThO_2 | 15-20 | 0.5-1 | — | 350 | — |
| TiC | 40 | 3-4 | 12-15 | 504 | 212.0 |
| SiC | 40 | 3-5 | 80-100 | 515 | 485.5 |
| TaC | 40 | 3-5 | 20-25 | 518 | 382.0 |
| ZrC | 40 | 3-5 | 30-40 | 533 | 396.4 |
| WC | 40 | 2-3 | 15-30 | 515 | 646.8 |
| BC | 25-40 | 1-2 | — | 600 | — |
| Cr_3C_2 | 40 | 2-3 | 10-20 | 420 | 216.7 |
| Diamond | — | 0.5-3 | — | 550 | — |
| Glass | — | — | — | 250 | — |
| BN | 25 | 1-5 | 30-40 | 450 | 196.0 |
| ZrB_2 | 50 | 3-4 | 10-15 | 515 | 196.0 |

severe inhomogeneous strain. After heat treatment for 1 hour in vacuum at 750°C the particles were situated within the grains, often as clusters and have no preference for grain boundaries. So, whatever restrictive role the dispersoid may play in preventing recrystallisation, a certain amount of recovery occurs on annealing. Hence, different changes were found in specimens annealed for 1 hour at 1100°C in vacuum, the dislocations within grains have mostly annealed out. The oxide particles have been distributed to form large crystals of alumina. Above 1200°C, there is a tendency for alumina particle to become coarser. The growth of alumina particle is greater the higher the alumina content in the deposit. Use of alpha-alumina gives better results than the gamma modification. This may be attributed to the higher solubility of alumina in aqueous electrolyte at low pH, forming $\text{Al}(\text{OH})_3$ or $\text{Al}_2(\text{SO}_4)_3$ [38], the dissolution being more pronounced in gamma-alumina, leading to more incorporation of aluminium salts, which dehydrate on heat treatment resulting in the loss of hardness.

Nickel-titanium dioxide composites when heat treated in hydrogen atmosphere showed no change upto 800°C. But at 1100°C there is some change in the structure which can be attributed to the partial reduction of TiO_2 to Ti_2O_3 [21] (Table III).

Table III: Effect of heat treatment on hardness of nickel composites [18]

| Composite | Hardness in KPN | | | | | |
|------------------------------------|-----------------|-------|-------|-------|-------|--------|
| | Nil | 200°C | 400°C | 600°C | 800°C | 1000°C |
| Nickel | 240 | 225 | 185 | 140 | 105 | 75 |
| Ni- TiO_2 | 350 | 330 | 300 | 280 | 250 | 220 |
| Ni- $\gamma\text{-Al}_2\text{O}_3$ | 380 | 365 | 315 | 235 | 205 | 195 |
| Ni- $\alpha\text{-Al}_2\text{O}_3$ | 450 | 410 | 340 | 275 | 225 | 210 |
| Ni-SiC | 398 | — | 386 | 300 | — | — |

Tensile strength and yield strength

Ultimate tensile strength of nickel-alumina and nickel-titanium dioxide composites measured at room temperature and after heat treatment [38] shows that although these values are as high as 150 kg/mm² and 125 kg/mm² respectively at room temperature, after heat treatment they get reduced to 68 kg/mm² and 78 kg/mm² respectively. Retention in strength can be achieved by increasing the volume percent of the particles and decreasing the agglomeration [17]. With 5-6% alumina, long term heat treatment for 100 hours was 12.6 kg/mm² at 815°C and 3.9 kg/mm² at 1100°C and so, the tensile strength of composites at any particular temperature is dependent on the duration of treatment [39].

The retention of yield strength after heat treatment is more significant than the tensile strength. Yield strength also increases with increasing particle volume percent in the deposit, and it is much greater with the particles of smaller diameter than that of larger diameter which may be attributed to the smaller interparticle spacing due to the higher number of particles for a given volume. Inclusion of trace amounts of aluminium ion (0.04 W/V) as hydroxide [37] during codeposition has been accounted for the increased yield strength of nickel-alumina composite. Nickel-thoria [23, 40] composite has long term fatigue strength advantages only at temperatures greater than 1050°C–1100°C. Presence of molybdenum in the above composite

Table IV: Tensile strength and yield strength values of nickel [21, 40, 52]

| Material | Untreated | | Heat treated | | Treated temp. °C |
|---------------------------------------------------|--------------------|------|--------------------|------|------------------|
| | UTS | Y.S. | UTS | Y.S. | |
| | kg/mm ² | | kg/mm ² | | |
| Ni | 87.4 | 42.0 | 82.5 | 40.1 | 200 |
| | | | 69.3 | 34.0 | 400 |
| | | | 54.1 | 26.1 | 600 |
| | | | 42.0 | 20.2 | 800 |
| | | | 31.5 | 9.6 | 1000 |
| Ni-TiO ₂ (7%) | 137.0 | 97.0 | 120.0 | 58.0 | 200 |
| | | | 110.0 | 53.0 | 400 |
| | | | 95.0 | 46.2 | 600 |
| | | | 87.0 | 40.6 | 800 |
| | | | 80.0 | 37.4 | 1000 |
| Ni-TiO ₂ (5%) | 71.0 | 51.0 | 34.0 | 15.9 | 1000 |
| Ni- α -Al ₂ O ₃ | 150.5 | 72.4 | 138.0 | 67.6 | 200 |
| | | | 118.5 | 58.0 | 400 |
| | | | 98.4 | 48.3 | 600 |
| | | | 81.5 | 39.3 | 800 |
| | | | 77.5 | 37.4 | 1000 |
| Ni- γ -Al ₂ O ₃ (7%) | 130.5 | 63.0 | 126.1 | 60.8 | 200 |
| | | | 110.9 | 53.5 | 400 |
| | | | 77.1 | 37.2 | 600 |
| | | | 71.8 | 34.6 | 800 |
| | | | 68.3 | 32.9 | 1000 |
| Ni-SiC (4.2%) | 75.0 | 40.0 | 74.0 | 35.7 | 300 |
| | | | 9.1 | 4.4 | 980 |
| | | | 7.7 | 3.7 | 1050 |
| | | | 6.3 | 3.1 | 1100 |

improves the strength at 650°C–870°C. This finds application in combustion chamber flame tubes but only for services above 1000°C. (Table IV).

Oxidation resistance

Weight gain is directly proportional to the quantity of metal oxidised. All cermets except γ -alumina have resistance equal to or better than pure nickel. The oxide cermets have superior resistance to oxidation than carbides or zircon. Oxides like alumina, SiO₂, ThO₂ are often employed to improve oxidation resistance of metals. The effect of these particles is to lower the rate of interface reaction, thus decreasing the rate of oxidation. Nickel-TiO₂ composite is more resistant to oxidation due to the substitution of ions with valence greater than + 2, which lowers the electrical conductivity of NiO film, thus lowering the adsorption of oxygen on NiO₂ film. In Ni-ThO₂ composite, the resistance to scale formation is higher than nickel and there is noticeable absence of intergranular oxidation. The oxidation follows a parabolic law at 600°C–700°C and a mixed parabolic law at 950°C–1100°C. At intermediate temperatures of 800°C–850°C, oxidation is logarithmic. In nickel containing yttrium oxide [41], at 850°C scale formation is reduced by the formation of yttrium oxysulfide.

After heat treatment, nickel-alumina composite remained intact and received a slightly dark, glossy and transparent oxide film. In the case of Ni- γ -Al₂O₃, the deposit turned green, powdery and became brittle and the oxidation rate is very high. This has been attributed to the porous nature of γ -Al₂O₃ which easily absorbs water. The absorbed water molecules evaporate at high temperatures giving rise to cracks in the cermet, thereby increasing the surface area enormously, leading to increased oxidation. The green compound is the reaction product of NiO and Al₂O₃ as aluminate. Hence, materials capable of absorbing moisture or other fluids, are not suitable for applications involving elevated temperatures [36].

In nickel-SiC composite, the weight gain is rapid during initial stages of heat treatment at 1100°C [32] (Table V).

Table V: Oxidation resistance of nickel composites [3, 46]

| Material tested | Wt. gained in mg/cm ² at 1000°C | | |
|----------------------------------------------|--------------------------------------------|-------|-------|
| | 1 hr | 2 hrs | 3 hrs |
| Ni | 0.90 | 1.28 | 1.54 |
| Ni-SiO ₂ | 0.22 | 0.37 | 0.51 |
| Ni- α -Al ₂ O ₃ | 0.43 | 0.68 | 0.93 |
| Ni- γ -Al ₂ O ₃ | 3.57 | 4.11 | 4.46 |
| Ni-Zircon | 0.57 | 0.91 | 1.11 |
| Ni-SiC (coarse) | 0.63 | 1.05 | 1.43 |
| Ni-SiC (fine 4%) | 0.40 | 0.50 | 0.60 |
| Ni-SiC (12%) | 0.21 | 0.30 | 0.35 |

SiC on the surface is oxidized while those deeper in the deposit provide silicon, which reacts with inward diffusing oxygen, mainly in the deposit grain boundaries to form internal oxide. In addition, silicon near the deposit-substrate boundary diffuses across the boundary and into the substrate, producing silicon gradients. The

silicon in the substrate is eventually precipitated as SiO_2 . For Ni-4% fine SiC and Ni-8% fine SiC composites, the oxidation rates are similar to that of electrodeposited nickel, during the first few hours of oxidation. Composite with coarser SiC particles oxidises faster than the one with fine particles. The closer proximity of the fine particles facilitate formation of SiO_2 and also because of the closer grain size, more extensive SiO_2 network are developed in the latter material during oxidation which is able to exert a blocking effect as the scale encroaches upon them than in the coarse particles.

Corrosion resistance

The inclusion of particles lead to blocking of the active sites and the dissolution proceeds slowly due to the inhibitive effect [31]. The particles with different size included at the definite sites in the nickel deposit improves the corrosion resistance of the system in different ways. Coarse particles create pores in the bulk and the fine particles block the active sites of dissolution.

The composite coatings exhibit lesser porosity than pure nickel deposit. However, our experiments with salt spray tests in 5% sodium chloride solution indicated that nickel composites are as corrosion resistant as pure nickel deposits [21].

Polarisation experiments with 1 M sulphuric acid did not give consistent results due to an irreproducible formation and dissolution of a film of oxide. Polarisation curves for Ni, Ni-TiO₂ and Ni-SiC are identical [3]. Ni-TiO₂ shows a lower passivation current thereby indicating better performance under passive conditions. Anodic current values in sodium chloride and hydrochloric acid shows that the corrosion rate in the former is nearly same for all composites. But Ni-TiO₂ and Ni-SiC composites show much larger corrosion rates in hydrochloric acid and there is visible hydrogen evolution which is attributed to the semiconducting nature of TiO₂ film having a lower over-potential for hydrogen evolution. This is applicable to Ni-SiC composite also (Table VI).

Table VI: Corrosion current for nickel composites [3]

| Material tested | In NaCl mA/cm ² | In HCl mA/cm ² |
|---------------------|-------------------------------|------------------------------|
| Ni | 0.010 | 0.020 |
| Ni-TiO ₂ | 0.011 | 0.740 |
| Ni-SiC | 0.011 | 0.480 |

Density

The density of the composite is a linear function of oxide volume percent. On heat treatment, the initial decrease in density is very pronounced up to an oxide concentration of 15%. The difference in densities of plated composite before and after heat treatment can be attributed to the presence of adsorbed impurities on the surface of oxide particles present in the bath which are codeposited with oxide particles [42].

Internal stress [43]

For fatigue and adhesion considerations it is important to know the internal stress of an electrodeposited composite. Generally high internal stress values have been reported. Work on Ni-Al₂O₃

composite indicates that increase in stress is directly related to the surface area of the particles in contact with the deposit (Table VII). This area in turn is related to the amount of lattice misfit. The magnitude of stress observed is insufficient to cause any serious

Table VII: Stress in Ni-Al₂O₃ and Ni-ThO₂ [43, 25]

| Current density mA/cm ² | Stress kg/mm ² Concentration of Al ₂ O ₃ in g/l | |
|---------------------------------------|-------------------------------------------------------------------------------------|------|
| | 0 | 10 |
| 10 | 34.6 | 41.2 |
| 20 | 31.0 | 34.2 |
| 30 | 28.1 | 32.6 |
| 40 | 20.8 | 30.3 |
| 40 (ThO ₂) 4 (wt%) | | 21.0 |

CONCLUSIONS

For a number of applications, composites have been achieved and found to be superior to other coating systems such as flame spraying, hard chromium plating and nitriding [44]. Electrodeposited composites are now being used extensively in aeronautical, chemical, mechanical, marine, mining, agricultural, electrical and general engineering applications [43-49]. These coatings are superior to other coatings in that: (1) a greater range of coating materials are possible (2) they do not require heat treatment which enables the metallurgical properties to remain unaltered (3) smooth finish up to any desirable thickness (4) small capital investment (5) greater versatility in coating geometric shapes and (6) possibility of coating on any desired matrix. Some of the applications are given in Table VIII.

Table VIII: Applications of some of the nickel composites [7]

| | |
|-----------------------------------|--------------------------------------------------------------------------------------------------------|
| Ni-WC | — Wear resistant coating |
| Ni-TiC | — In turbine blades and other high temperature applications |
| Ni-Cr ₃ C ₂ | — As wear resistant coating in gas turbine and aircraft engineering |
| Ni-SiC | — In piston rings, cylinders and for internal combustion engines |
| Ni-BN | — To overcome problems of fretting wear |
| Ni-Y ₂ O ₃ | — In turbine blades and as startar vanes in gas turbines |
| Ni-ZrB ₂ | — As wear resistant coating at elevated temperature and at high loads |
| Ni-ThO ₂ | — In combustion chamber, flame tubes and other jet engine components for services greater than 1000°C. |

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