Oxidation characteristics of electrodeposited nickel–zirconia composites at high temperature

G.N.K. Ramesh Bapu *, Sobha Jayakrishnan

Electroplating and Metal Finishing Technology Division, Central Electrochemical Research Institute, Karaikudi 630006, India

Abstract

Oxidation behavior of electrodeposited nickel and Ni–ZrO$_2$ (9.9 vol%) composite was studied using a thermogravimetric technique. The weighed sample was oxidized in air for 2–8 h in the electric furnace at 873, 1073 and 1173 K. After predetermined time of oxidation, the specimens were removed and weighed after sufficient cooling. From the weight gain, time of oxidation and temperature, the kinetics of Ni and Ni–ZrO$_2$ oxidation process, oxidation rate constant and the activation energy were determined. The structure and distribution of ZrO$_2$ particles in the electrocomposites were examined using scanning electron microcopy. To explore the possible structural changes during oxidation, X-ray diffraction was used.
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1. Introduction

Among the electrodeposited metals, nickel is widely used because of its excellent physical and mechanical properties and its chemical and corrosion resistance [1]. However, it does not posses the high temperature oxidation and wear resistance, as required for most industrial applications. During the past few decades attention has turned towards the development of nickel, cobalt or chromium based electro-composites, particularly those containing hard ceramic particles, as possible oxidation and wear resistant coatings for high temperature applications [2]. For example, nickel composites containing SiC and cobalt composites containing Cr$_3$C$_2$ particles have been developed as coatings for injection moulds [3] and as a wear resistant coating in aero-engines at high temperature [4], respectively. ThO$_2$ dispersed nickel composite is now used as possible high temperature structural material in the nuclear, aircraft and aerospace industries [5].

As electrodeposited nickel does not have sufficient oxidation resistance to withstand high temperature oxidizing atmosphere for long periods, the present work aims to investigate the effect of inert dispersed particles codeposited in a nickel matrix on high temperature oxidation behavior. As a preliminary step in evaluating their usefulness as high temperature oxidation resistant coatings, the oxidation characteristics of electrodeposited Ni and composite Ni–ZrO$_2$ coatings have been studied. Conditions for the codeposition of zirconia into nickel matrix to obtain nickel–zirconia (Ni–9.9 vol% ZrO$_2$) electrocomposites have been optimized [6]. A thermogravimetric technique [7] was employed to study their oxidation behavior. The weighed sample was kept in the reaction tube and oxidation tests from 2 to 8 h were carried out in the electric furnace at 873, 1073 and 1173 K. After predetermined time of oxidation, the specimens were removed and weighed after sufficient cooling. From the weight gain, the time of oxidation and temperature, the kinetics of Ni–ZrO$_2$ oxidation process, oxidation rate constant and the activation energy were determined [8]. The structure and distribution of ZrO$_2$ particles in the composite were examined using scanning electron microcopy.

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.
E-mail address: bapu2657@yahoo.com (G.N.K.R. Bapu).

To explore the possible structural changes during oxidation, X-ray diffraction pattern of the oxidized specimen was recorded.

2. Experimental

2.1. Oxidation characteristics

Table 1 gives the composition of Ni–ZrO$_2$ composite plating bath [6]. The electrolyte was prepared from reagent grade chemicals using de-ionized water. By means of a mechanically controlled stirrer (Remi motors, India), $50\,g\,l^{-1}$ of zirconia particles of average size $8.1\,\mu m$ were kept in suspension in the plating bath. Five millimeters thick unbagged nickel sheet was used as anode. Electrodeposited nickel and Ni–ZrO$_2$ electrocomposites were plated to a thickness of $150\,\mu m$ on stainless steel substrate. The deposits were separated as foils and chemically polished to a bright smooth finish in a solution containing 60 vol% glacial acetic acid, 35 vol% nitric acid and 5 vol% hydrochloric acid. Squares of $2\,cm \times 2\,cm$ samples were cut from the polished specimen, degreased in acetone and ethyl alcohol and weighed (W_1).

A thermogravimetric technique was employed to study the oxidation behavior of the electrodeposited nickel and Ni–ZrO$_2$ (9.9 vol%) specimen. The weighed sample was kept in the reaction tube and oxidation tests from 2 to 8 h were carried out in the electric furnace at 873, 1073 and 1173 K. After predetermined time of oxidation, the specimens were gradually removed from the hot zone of the furnace, cooled in a desiccator and weighed after sufficient cooling (W_2). The difference in weight ($W_2 - W_1$) gave the weight gain due to oxidation of the samples. The square of the weight gain was plotted against various time of oxidation (t) and the oxidation rate constant k_p ($g^2\,cm^{-4}\,s^{-1}$) was determined. From the temperature dependence of the oxidation rate constant, the activation energy E_a ($kJ\,mol^{-1}$) was calculated. A minimum of three specimens was used for each test and the average value was used for calculations.

2.2. Structure of the deposits

The structure and distribution of ZrO$_2$ particles in the electrocomposites were examined using scanning electron microcopy. To explore the possible structural changes during

Table 1
Plating bath and operating conditions

Nickel fluoborate ($g\,l^{-1}$)	280
Free fluoboric acid ($g\,l^{-1}$)	5
Boric acid ($g\,l^{-1}$)	40
Sodium lauryl sulphate ($g\,l^{-1}$)	0.1
Zirconia ($g\,l^{-1}$)	50
pH	3.0
Current density ($A\,dm^{-2}$)	6
Temperature (°C)	50

Table 2
Oxidation data of nickel and Ni–ZrO$_2$ composite deposits[a]

Oxidation temperature (K)	Specimen	Weight gain (mg cm^{-2})			
		2 h[b]	4 h[b]	6 h[b]	8 h[b]
873	Nickel	0.19	0.23	0.25	0.28
	Ni–(9.9 vol%) ZrO$_2$	[c]	[c]	[c]	0.10
1073	Nickel	0.70	1.20	1.58	1.84
	Ni–(9.9 vol%) ZrO$_2$	0.36	0.46	0.59	0.70
1173	Nickel	2.70	3.28	3.69	3.91
	Ni–(9.9 vol%) ZrO$_2$	0.74	0.86	0.95	1.07

[a] Deposit thickness 150 μm.
[b] Time of oxidation.
[c] Weight gain is insignificant.

oxidation, X-ray diffraction pattern of the oxidized specimen was recorded.

3. Results and discussion

3.1. Oxidation characteristics

In Table 2 is given the weight gain values for electrodeposited nickel and Ni–ZrO$_2$ electrocomposites oxidized in air for 2–8 h at 873–1173 K. In general, the weight gain due to thermal oxidation is related directly to the quantity of metal being oxidized in air under given conditions and hence can be taken as measure of resistance to oxidation [9]. It can be seen that at 873 K, Ni–ZrO$_2$ composite did not show significant weight change during 6 h of oxidation where as nickel began to oxidize from 2 h. The Ni–ZrO$_2$ composite was found to tarnish only after 8 h of oxidation at 873 K. With increasing time and temperature, the weight gain due to oxidation of Ni and Ni–ZrO$_2$ was found to increase significantly. However, under investigated temperature and duration, Ni–ZrO$_2$ oxidized to lesser extent compared to pure nickel deposit.
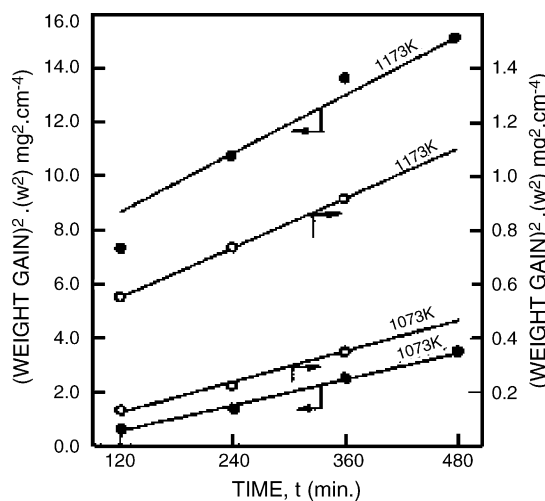

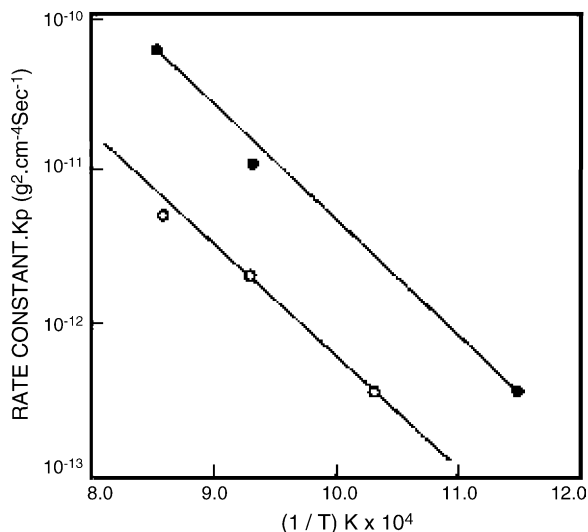Fig. 1. Parabolic plots for oxidation of electrodeposited nickel (●) and Ni–ZrO$_2$ (○) composite deposit.

Fig. 2. Temperature dependence of oxidation rate constants of nickel (●) and Ni–ZrO$_2$ (○) composite deposit.

Incorporation of ZrO$_2$ into nickel matrix, in general, lowered the rate of oxide growth at elevated temperature and improved their resistance to oxidation [10,11].

Plot of the square of weight gain versus time for the oxidation of nickel and Ni–ZrO$_2$ is shown in Fig. 1. Since the

Table 3
Oxidation rate constant of Ni and Ni–ZrO$_2$ composite deposits

Oxidation temperature (K)	Rate constant, k_p (g^2 cm^{-4} s^{-1})	
	Nickel	Ni–ZrO$_2$ (9.9 vol%)
873	3.51×10^{-12}	–
1073	1.10×10^{-10}	2.88×10^{-11}
1173	6.41×10^{-10}	5.50×10^{-11}
Activation energy, E_a (kJ mol^{-1})	143	139

oxidation product is generally retained on the metal surface, the oxidation rate is usually expressed as weight gain per unit area. Adherence to a straight line, as seen in Fig. 1 suggested that the systems were found to follow a parabolic rate law of the form, $W^2 = k_p t$, where W is the weight gain per unit area, k_p the parabolic rate constant and t is time of oxidation. Thus, at 1073 and 1173 K, the system follows a parabolic rate trend and the oxidation is controlled by a diffusion process [12]. This is in accord with earlier observations [13,14].

A plot of k_p against $1/T$ is shown in Fig. 2 and from the slope of the straight lines, activation energy, E_a is calculated. In Table 3 is shown the oxidation rate constant for Ni and Ni–ZrO$_2$ at various oxidation temperatures and activation energy of the oxidation process. The observed equal activation energy value (140 ± 2 kJ mol^{-1}) for nickel and
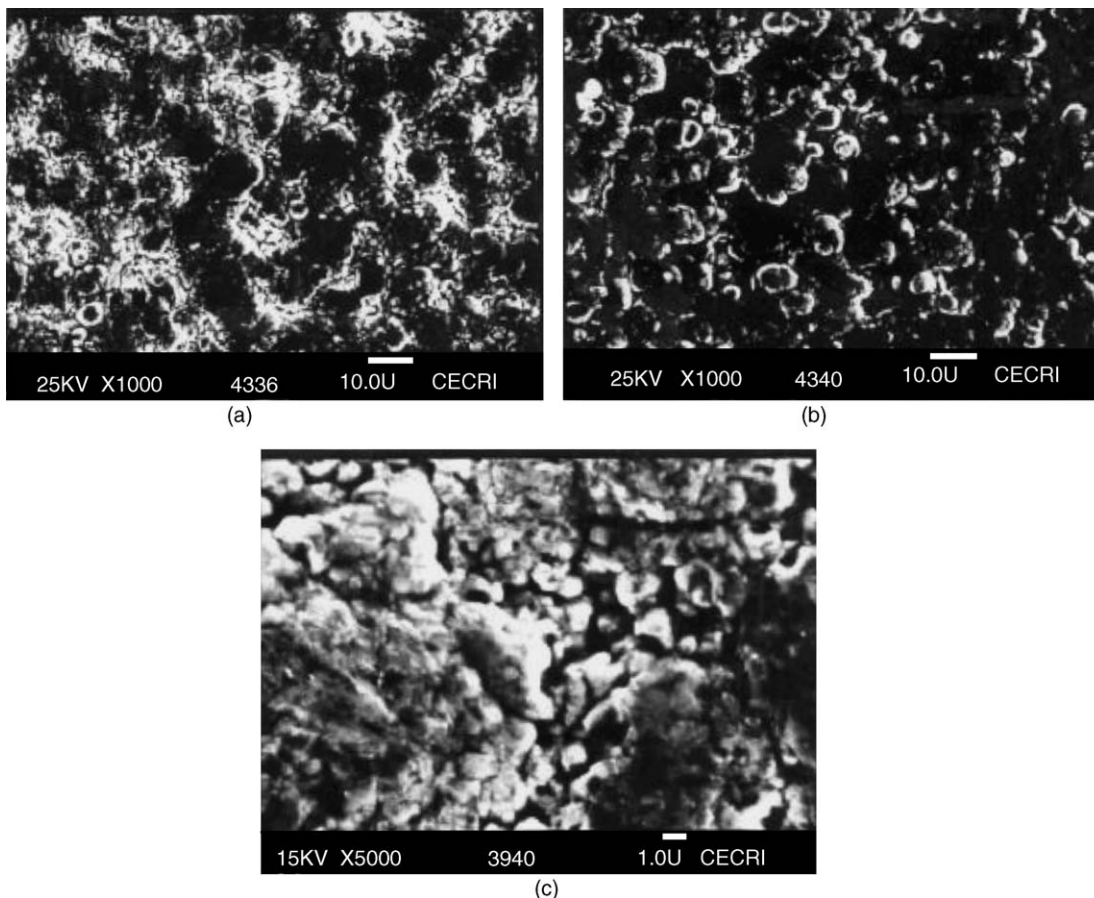

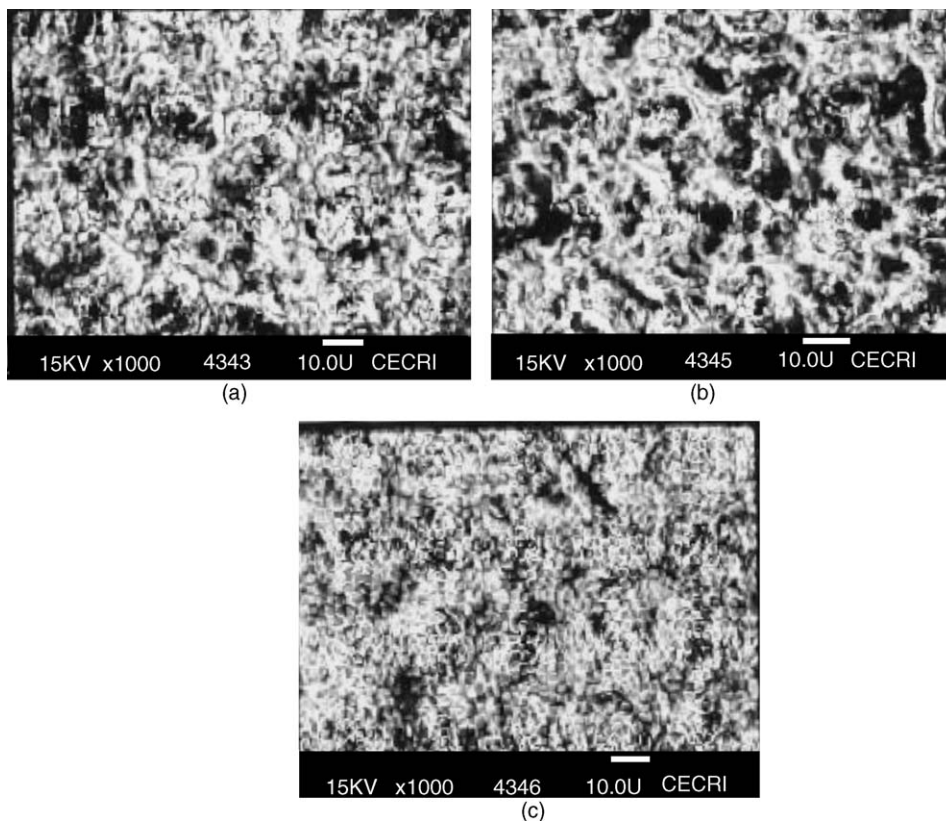Fig. 3. SEM photographs of Ni deposit oxidized at: (a) 873 K, (b) 1073 K and (c) 1173 K.

Fig. 4. SEM photographs of Ni–ZrO$_2$ composite deposit oxidized at: (a) 873 K, (b) 1073 K and (c) 1173 K.

Ni–ZrO$_2$ systems suggested that the inclusion of the ZrO$_2$ into nickel matrix has not altered the kinetics of nickel oxidation mechanism substantially. However, it has some effect on the ionic diffusion reaction, especially on adsorption of oxygen molecules on the nickel surface. Zirconia, which are incorporated in the NiO structure, are likely to decrease adsorption of oxygen molecules on NiO and restrict the multiplication of oxide nucleation. The observed lower oxidation rate constant for Ni–ZrO$_2$ is a good agreement with the above fact and confirms that Ni–ZrO$_2$ is more resistant to oxidation than nickel.

3.2. Structure of the deposits

SEM photograph of the Ni and Ni–ZrO$_2$ electrocomposites oxidized at various temperatures is shown in Figs. 3 and 4, respectively. In case of nickel (Fig. 3), the black oxide formation can be seen to increase with oxidation temperature whereas in Ni–ZrO$_2$ lesser black spots are found with brightening on the surface (Fig. 4). The surface morphology was completely different at 1173 K suggesting a complete coverage of the surface with formation of a new type of product (NiO ZrO$_2$) composed of oxides of nickel and ZrO$_2$. The observed peak intensity at 54.8° and 73.4° in XRD pattern (Fig. 5) of the oxidized Ni–ZrO$_2$ confirmed the possible structural changes and product formation during oxidation [15].
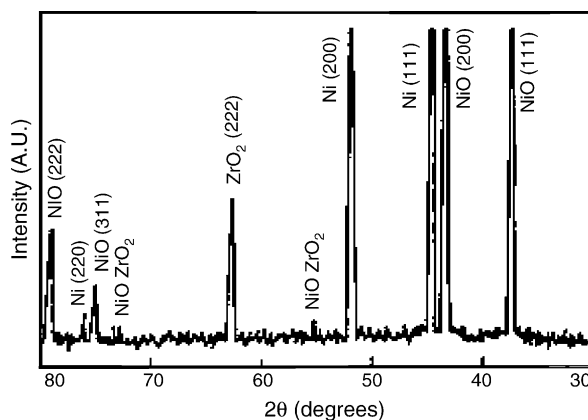

Fig. 5. XRD pattern of Ni–ZrO$_2$ composite oxidized at 1173 K.

4. Conclusion

Oxidation behavior of electrodeposited nickel and Ni–ZrO$_2$ (9.9 vol%) electrocomposites was studied for 2–8 h duration between 873 and 1173 K using a thermogravimetric technique. The results indicate that at 1073 and 1173 K, the system followed a parabolic rate trend and a diffusion process controlled the oxidation. The observed lower oxidation rate constant for Ni–ZrO$_2$ confirmed that they are more resistant to high temperature oxidation than electrodeposited nickel.

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