

Reactivity and codeposition of Co_3O_4 powders with nickel in a Watts bath

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The effect of the physico-chemical characteristics of Co_3O_4 powders on their reactivity in solution and their incorporation in a nickel matrix has been investigated in a Watts nickel plating bath. The results showed that the surface area of the powder present in suspension not only catalyses the adsorption or desorption phenomena occurring at the particle/solution interface but also has a significant effect on the incorporation of the particles into the nickel matrix. It has been found that the use of Co_3O_4 with high specific surface area ($40 \text{ m}^2 \text{ g}^{-1}$) significantly limits the growth rate of the electrodeposited composite coatings. Furthermore, it has been shown that the codeposition of these more reactive particles leads to significant changes in the microstructure and texture of the nickel matrix. Finally, it has been found that, according to their specific surface areas, the amount of H^+ , Ni^{2+} and $\text{Ni}[\text{B}(\text{OH})_4]^+$ ions adsorbed on the Co_3O_4 oxide surfaces and the quantities of particles codeposited can vary considerably.

Keywords: Co_3O_4 oxide particles, oxide characteristics, oxide reactivity, pH changes, adsorption-desorption phenomena, composite coatings

1. Introduction

Composite coatings, produced by codeposition of powders such as carbide, oxide or organic compounds with a metal, offer interesting engineering possibilities for purposes of wear-resistant, anti-friction and anti-seizing applications in cold-starting, dry-lubrication and dispersion hardening. Because the physical properties of such composites are strongly dependent on the distribution, nature and percent of particles incorporated, it is necessary to understand the mechanism of formation of the electrodeposited composite coatings in order to efficiently control their characteristics.

According to the Guglielmi model [1] and the more recent models of Celis [2] and Fransaer [3], the codeposition of particles commonly involves five stages: (i) adsorption of ionic or neutral species on the particle surface when they are added to the plating bath; (ii) movement of the particle by forced convection towards the cathode; (iii) diffusion of the particle through the diffusion layer; (iv) adsorption of the particle, still with its adsorbed ionic cloud, at the cathode surface; (v) and incorporation of particles in the metallic matrix after the reduction of their adsorbed ions.

From the literature it appears that agitation and current density are important parameters, but also that the physico-chemical characteristics of solution and powder are very important and must be taken into account. Although there is much discussion

about the effects of particle size [4, 5] and conductivity [6, 7] on the codeposition process, little attention was paid in earlier work to the particle specific surface area and reactivity in solution. However, recently, Bhagwat [8] and Szczygiel [9] have shown that the pH change occurring after Al_2O_3 or SiC particle addition to a nickel plating bath, which is a linear function of the surface powder present in solution, considerably affects their rate of incorporation into the metallic matrix. In view of this, we chose to investigate this effect on the mechanism of formation of Ni/ Co_3O_4 electrodeposited coatings.

2. Experimental conditions

The Co_3O_4 powders were prepared by decomposition in air of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ oxalate precursor. As shown by the scanning electron micrographs in Figure 1, these powders are made up of small needles $17 \mu\text{m}$ long and $0.7 \mu\text{m}$ thick. As reported [10] for other oxides obtained by soft chemistry, increase in decomposition temperature allows, by internal sintering of particles, a decrease in the specific surface areas without change in particle size to be achieved. The specific surface areas measured by the BET method using nitrogen adsorption change from 40 to $8 \text{ m}^2 \text{ g}^{-1}$.

The various batches of oxide were added and kept in suspension by magnetic stirring at a concentration of 50 g dm^{-3} , in a 150 cm^3 plating cell containing 100 cm^3 of a conventional nickel plating solution with

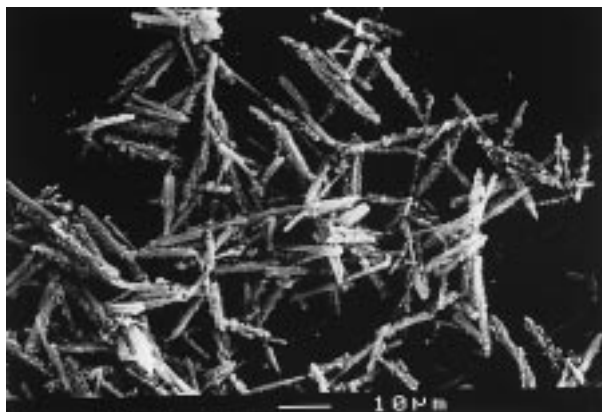


Fig. 1. SEM micrograph of a Co_3O_4 oxide.

the following composition: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 280 g dm^{-3} – $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g dm^{-3} – H_3BO_3 45 g dm^{-3} – Na_2SO_4 50 g dm^{-3} and $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ 100 mg dm^{-3} . The initial pH of the solution was adjusted to the required value using NaOH or HNO_3 solution. The pH modified after powder addition, reached a steady-state value after two hours mixing. When this equilibrium state was reached two kinds of experiment were made.

In the first series of investigations, after pH measurement, the stirring was stopped and the slurry allowed to settle for five hours. After filtering and washing several times with distilled water, the powder was dried and analysed by atomic adsorption.

In the second series of experiments, when the equilibrium state was reached, plating was carried out. As shown in Figure 2, the working electrode was a 0.8 cm diameter copper disc and the anode electrode a nickel sheet of commercial purity (99.9%). The current density was fixed at 2.5 A dm^{-2} for a deposit thickness around $30 \mu\text{m}$. The volume percent of Co_3O_4 in the deposit was determined, after selective dissolution of the sample in trichloroacetic acid and ammonia solution, by atomic adsorption spectroscopy. The surface appearance of the electrodeposited coatings was examined by scanning electron microscopy and the structure by X-ray diffraction.

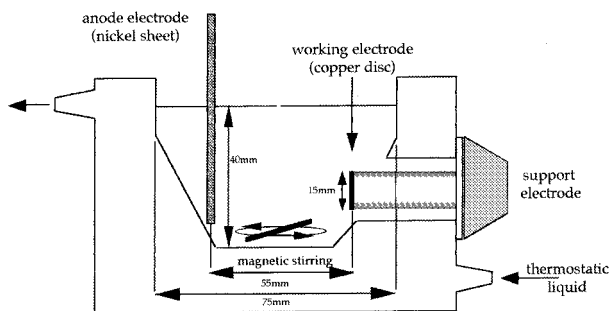


Fig. 2. Electroplating cell.

3. Experimental results and discussion

3.1. Particle reactivity with H^+

It has been shown [9–13] that the pH change which occurs, in aqueous solution, after oxide particle addition, depends on the acid-base properties of the powders and indicates the magnitude of the H^+ exchange on their surface.

Figure 3 shows the change in pH (noted ΔpH) caused by Co_3O_4 addition to nickel baths at different pH values. The existence of three typical ranges of pH is evident. In the first zone (I), after introducing the oxide powders, an increase in the bath pH occurred, in the second and third zones (zone II and III), a negative change in pH occurred, this change being less strong beyond pH 4.5 i.e. in the third zone. Between zones I and II, a particular value of pH (noted $\text{pH}_{\Delta=0}$) for which no change is observed after powder addition is evident. This pH is dependent on the specific surface area of the powders. Referring to the literature [11–13], a positive change in pH can be interpreted as an adsorption of protons on the powder surface which becomes partially hydroxylated according to the following reaction: $-\text{MOH} + \text{H}^+ \rightarrow -\text{MOH}_2^+ \rightarrow -\text{M}^+ + \text{H}_2\text{O}$. In contrast, a decrease in bath pH occurs when particles tend to release protons into the solution, owing to the following reaction: $-\text{MOH} + \text{H}_2\text{O} \rightarrow -\text{MO}^- + \text{H}_3\text{O}^+$. In the present case, the results obtained show the relationship between the degree of acceptance or release of a proton by the oxide group and the size of the powder surface area in suspension; a larger area of Co_3O_4 surface in suspension leads to a higher H^+ exchange with the solution.

In Figure 4, the modification of the specific surface area of the powder caused by its ageing for two hours in nickel bath is presented. Whatever the initial bath pH and the Co_3O_4 sample considered, the specific surface area measured by the BET method after filtering, washing in distilled water and drying, increases in the first, second and third pH zones i.e. in a pH range where adsorption or desorption of protons occurs on the particle surface. In contrast, at $\text{pH}_{\Delta=0}$ for which no H^+ exchange is observed, the surface area of the powders remains constant.

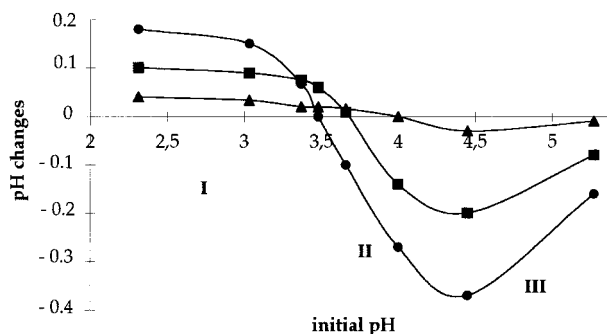


Fig. 3. Dependence between the changes in pH of a nickel plating bath and the surface area of the Co_3O_4 oxides added. \blacktriangle $8 \text{ m}^2 \text{ g}^{-1}$, \blacksquare $24 \text{ m}^2 \text{ g}^{-1}$ and \bullet $40 \text{ m}^2 \text{ g}^{-1}$.

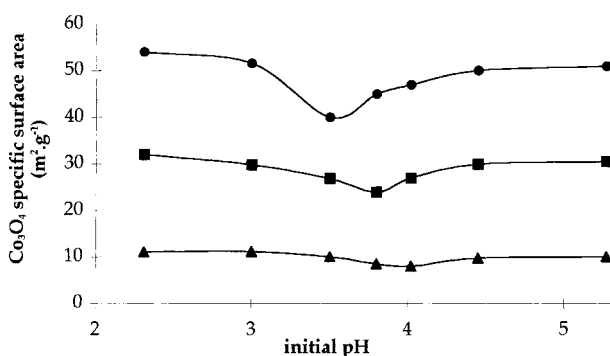


Fig. 4. Variation of specific surface area of Co_3O_4 powders after their addition to a nickel plating bath of different pH. ▲ $8 \text{ m}^2 \text{ g}^{-1}$, ■ $24 \text{ m}^2 \text{ g}^{-1}$ and ● $40 \text{ m}^2 \text{ g}^{-1}$.

The relationship between the surface area of the powder and the amplitude of hydrogen adsorption and desorption at the particle/solution interface having been confirmed, it was decided to study the influence of the specific surface area of the particles on the codeposition process. In order to operate under the same conditions for all batches of particles, the plating experiments were carried out at pH values for which the particles are the least reactive towards protons i.e. pH 3.5, 3.8 and 4 for the 40, 24 and $8 \text{ m}^2 \text{ g}^{-1}$ Co_3O_4 powders, respectively.

3.2. Surface area of particles and physical and chemical characteristics of the composite coatings

Figure 5 shows that the amount of particles in the deposits decreases as the specific surface area of the powders increases; i.e. the highest incorporated percentages (7.3 vol.%) were obtained for oxides with the lowest specific surface area ($8 \text{ m}^2 \text{ g}^{-1}$). However, although the use of powder with a high specific surface area is not favourable to their incorporation in the metallic matrix, their presence in the electrolytic solution seems to modify the reduction kinetics of nickel. As seen in Figure 6, the nickel current efficiency decreased from 100 to 83% when the specific surface area of the codeposited particles was varied from 8 to $40 \text{ m}^2 \text{ g}^{-1}$. Moreover, the use of the more reactive powders leads to extensive modifica-

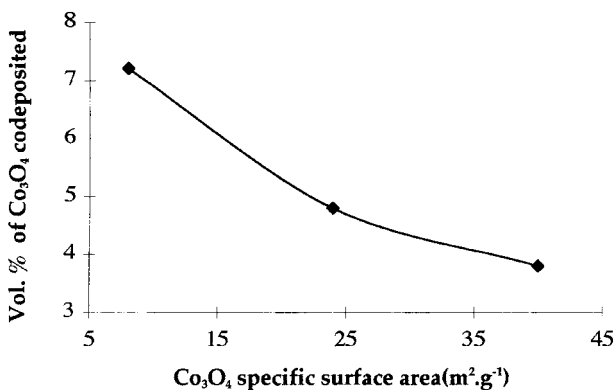


Fig. 5. Influence of specific surface area of Co_3O_4 oxides on their incorporation in a nickel matrix.

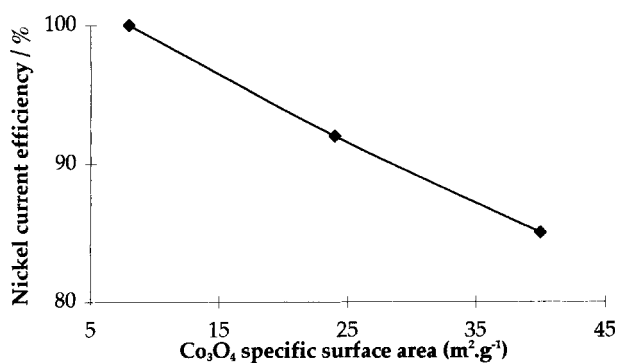


Fig. 6. Influence of specific surface area of Co_3O_4 oxides on the nickel current efficiency.

tions of the structure and microstructure of the nickel matrix.

The XRD patterns of the nickel coatings with the specific surface area of the codeposited powders, reported in Figure 7, reveal the existence of two peaks in the angular range $40^\circ < 2\theta < 80^\circ$. These peaks correspond to the (1 1 1) and (2 0 0) planes of the γ structure of nickel. However, a change in relative intensity of the diffraction peaks occurred when the specific surface area of the Co_3O_4 particles varied: the (2 0 0) preferred orientation of nickel grains is progressively replaced by the (1 1 1) plane when particles of high surface area are present in solution. Amblard et al. [14] showed that the crystalline orientation of electrolytic nickel depends on the competitive adsorption of H_2 , H_{ads} or $\text{Ni}(\text{OH})_2$ during the electrocrystallization. These adsorption phenomena may change when particles are adsorbed onto the nickel grains. Broadening of the diffraction peaks, indicating a refining microstructure, can also be observed when the particles used have a high specific surface area. These results are, in fact, in agreement with the SEM observations of the different samples. As shown in Figure 8, a decrease in nickel grain size occurred when particles with high specific area are present during the electrocrystallization of nickel.

The fact that the electrodeposition process is significantly influenced by the specific surface area is difficult to explain because, contrary to the results obtained by other authors [15–16], in our case, the maximum changes in the metal matrix structure and microstructure are obtained when the quantities of powders incorporated are minimum. In fact, if we consider the five-step codeposition model proposed by Celis et al. [2], when particles have the same shape, grain size and chemical composition, it is only a difference in the mechanisms of their adsorption at the cathode which can explain the difference in their codeposition behaviour. In this hypothesis, the nature and the force of the physical and chemical bonds created between the particles and the cathode surface, i.e. the nature and the thickness of the layer adsorbed onto the powders will then be the determining factors in their incorporation. In the present case, a difference in powder reactivity with respect to protons cannot explain the Co_3O_4 codeposition behaviour

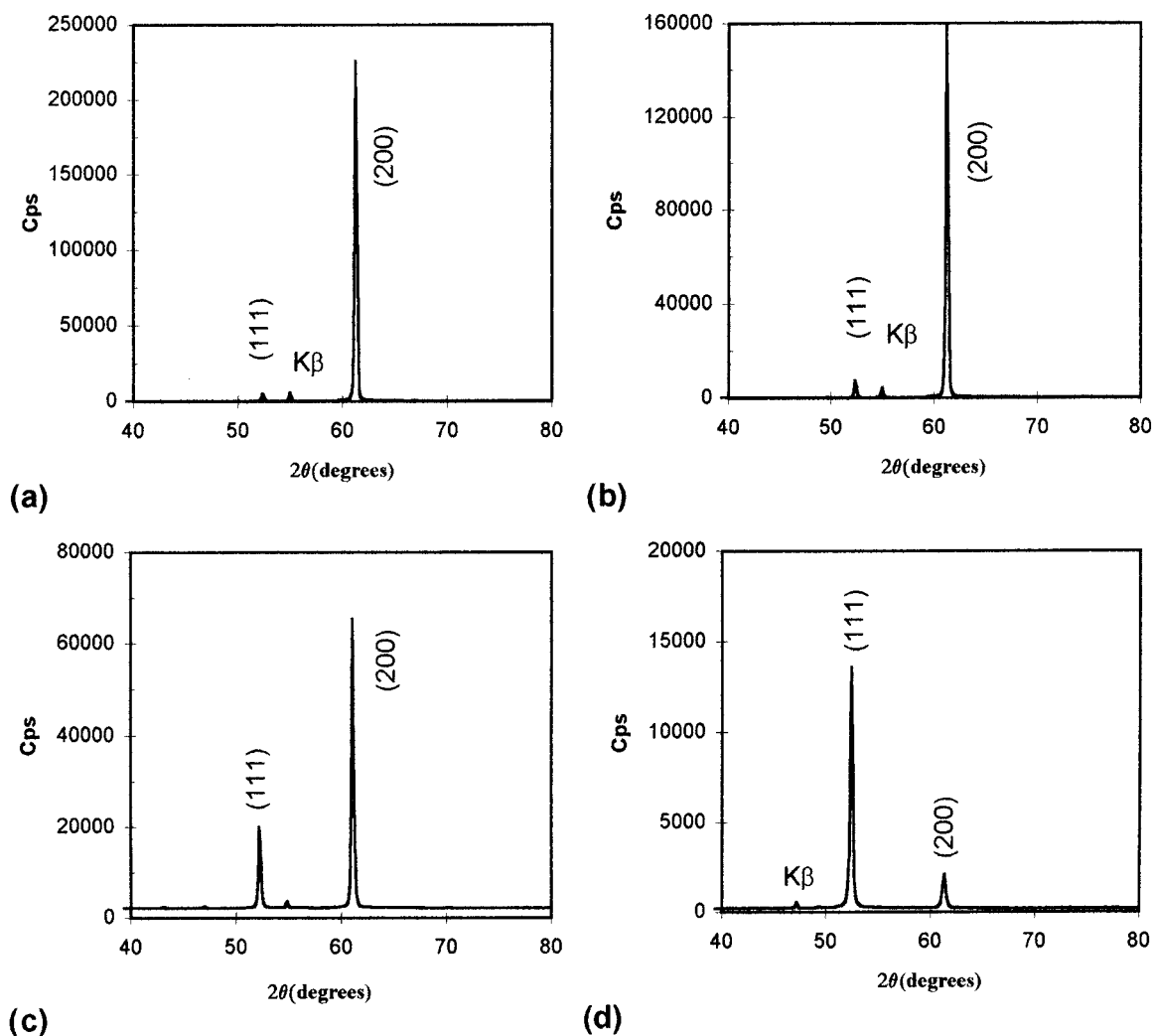


Fig. 7. X-ray diffraction patterns of nickel coatings a) before and b, c, d) after incorporation of Co_3O_4 oxides with different specific surface area (8, 24 and 40 $m^2 g^{-1}$ respectively).

because over the different pH investigated, no adsorption or desorption of proton occurred on the particle surface. However, the local pH in the cathodic region of the bath was probably higher than the bulk pH and desorption of protons can occur when the particles are transported through this region. In order to understand the results obtained and to show the relationships between the specific surface area of the powders, their reactivity in solution and their incorporation in the deposits, two kinds of investigations were carried out. In the first series of experiments, we studied the effect of the bath pH on the percentage codeposition (α) of Co_3O_4 particles of different specific surface areas; in the second, we analysed the nature and the magnitude of the ion exchange between the particles and the electrolytic bath.

3.3. Reactivity in solution, incorporation amounts and surface area of particles

The results shown Figures 9 and 10 depict opposite variations of the plots of α versus pH according to the specific surface area of the powders and the initial pH of the solution, as well as different adsorption or desorption phenomena at the particle surface. As

already observed (Figures 3 and 5), these results confirm the existence of three characteristic ranges of pH for which a decrease in the amount of particles embedded is observed when the specific surface area of the powders increases.

In the first zone of pH (pH < 3.5) i.e. in a pH range for which proton adsorption occurs on the particle surface, strong dissolution of the powder is observed. The quantity of cobalt ions present in solution, which appears to be proportional to the Co_3O_4 specific surface area, decreases as the bath pH increases and becomes zero above pH 4.5 (Figure 10a). However, in the first pH range, whatever the Co_3O_4 powder considered and the initial pH of the bath, i.e. whatever the magnitude of the dissolution phenomena, the amount of particles codeposited is not modified (Figure 9). Thus, the adsorption of protons on the surface of the particles when they are added to the bath, promoting their dissolution, has no effect on their incorporation into the nickel matrix.

In the second pH zone (zone II) i.e. in the zone where we previously observed desorption of protons from the powder surface into the bulk solution, strong adsorption of nickel ions onto the surface of

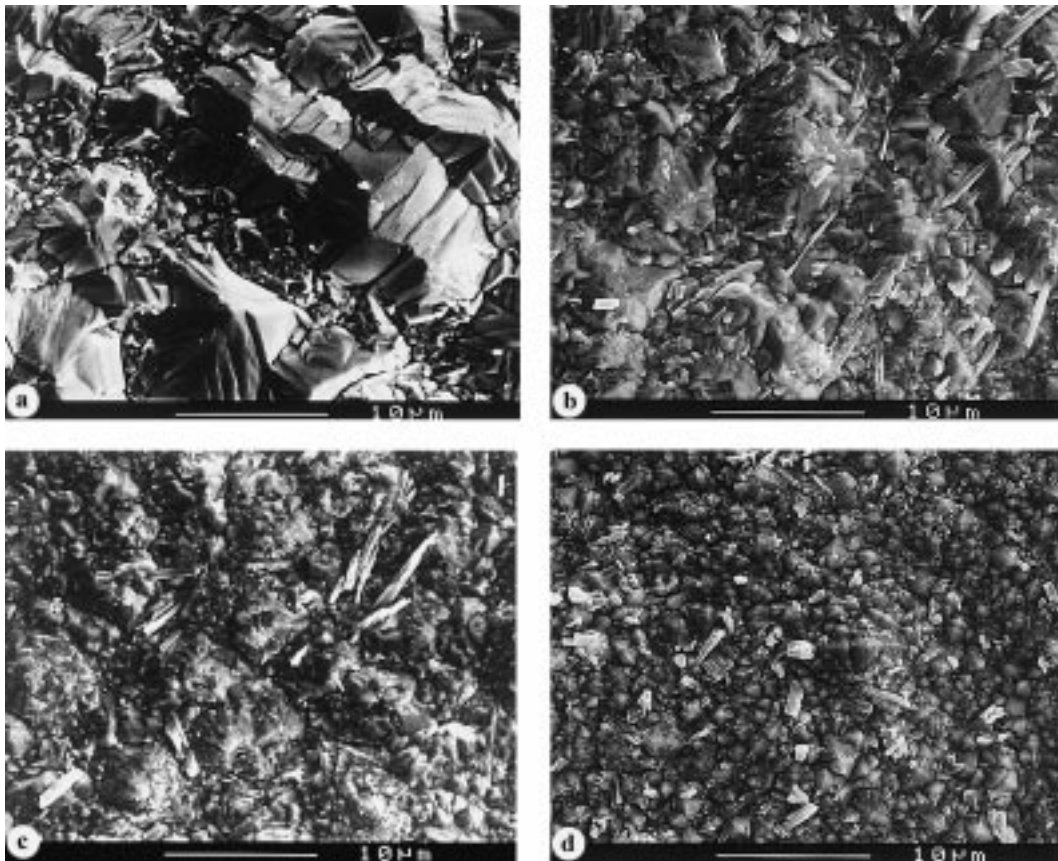


Fig. 8. SEM micrographs of nickel coatings a) before and b, c, d) after the codeposition of Co_3O_4 oxides with different specific surface area (8, 24 and $40 \text{ m}^2 \text{ g}^{-1}$ respectively).

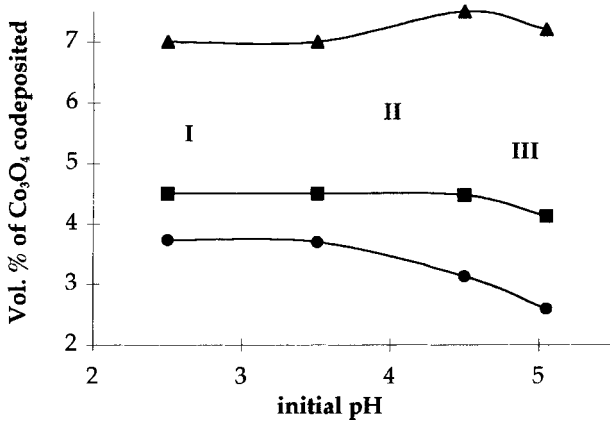


Fig. 9. Co_3O_4 particles incorporated in a nickel matrix versus the initial pH of the bath and the specific surface area of the powders added.

the particles (Figure 10b). This adsorption, which increases with the specific surface area of the powders, has been observed by other authors [8–9, 17, 18]. From these authors, the presence of metallic cations adsorbed on an oxide surface assists their migration and attraction to the cathode surface promoting their codeposition. In our case, in spite of the large amounts of nickel ions on the Co_3O_4 samples, which vary according to their specific surface areas, the curves of α versus pH are seen to present different patterns of variation (Figure 9). For the less reactive particles, when the initial pH of the suspension is

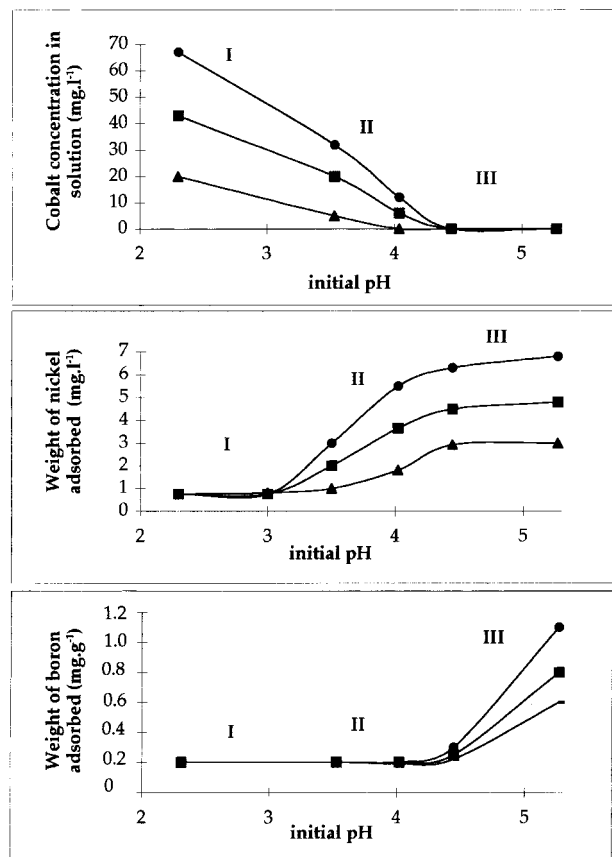


Fig. 10. a) dissolution or b and c) adsorption phenomena occurring on a Co_3O_4 oxide versus the specific surface area and the initial pH of the plating bath.

increased, the enhancement of the quantity of nickel ion adsorbed appears to favour their incorporation into the deposit, while for the same initial pH, the incorporation of the more reactive particles is limited. However, if we remember that, in the second range of pH, the addition of the more reactive particles to the electrolytic solution is followed by a strong decrease in pH, the particular codeposition behaviour of these compounds can be explained through the negative effect of such a change in pH. Thus, in this hypothesis, in the second pH range, the incorporation of the Co_3O_4 in the nickel deposit is dependent on the magnitude of the desorption phenomena occurring at their surface (amount of H^+ desorbed) rather than on the quantities of nickel ions adsorbed. This assumption explains why, according to the specific surface area of the powder, an increase or decrease in the amount of embedded particles is observed.

The results obtained in the third pH zone indicate, whatever the oxide powders studied, similar variations of α versus pH. In this range, the particle content in the deposit decreases as the pH of the bath increases. In fact, when the particles are added to a nickel bath at $\text{pH} > 4.5$, they release protons into solution (a negative change in the pH of the bath is observed) but also, as shown in figures 10b and c, they adsorb large amounts of nickel and boron ions. The presence of such species on the particle surface, which has not been reported by other authors, can be explained by the formation and adsorption of a nickel-boron complex of general formula $\text{Ni}[\text{B}(\text{OH})_4]^+$ on the particle surface. This species may be produced in the nickel bath at $\text{pH} > 4.5$ because of the ionization of boric acid in solution according to the following reaction: $\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons [\text{B}(\text{OH})_4]^- + \text{H}^+$ [19–20]. In the present case, the decrease in the amount of oxide embedded in the third zone of pH suggests that the adsorption of the nickel-boron complexes on the particle surface does not have a favourable effect on the codeposition of the composite coatings. Furthermore, if we remember that only small quantities of H^+ are released into solution in the third pH range (the change in pH observed in this zone is low), it can be concluded that the incorporation of the Co_3O_4 into the nickel deposit is essentially dependent on the amount of nickel-boron ions adsorbed on their surface.

4. Conclusion

When this work was initiated, one factor for investigation was the influence of the specific surface area of powders on their reactivity in suspension and on their incorporation into electrodeposited coatings. Although recent work had suggested that the surface area of powders present in solution plays an important role on the extent of the ion cloud which surround them, no attempt had been made to correlate these parameters with the volume fraction (α) of codeposited particles. The results obtained here have shown, first, that the amount of Co_3O_4 particles

embedded in a nickel matrix decreases from 7.2 to 3.5 vol% when the specific surface area of the particles varied from 8 to $40 \text{ m}^2 \text{ g}^{-1}$. Moreover, it was shown that the codeposition of the $40 \text{ m}^2 \text{ g}^{-1}$ particles promoted extensive changes in the microstructure and texture of the nickel matrix. A different preferred orientation of the nickel grains, as well as a decrease in their size, was observed during the deposition of the more reactive particles. To explain these results the plating experiments were carried out at different pH values for which the particles were the least reactive toward protons but where a partial dissolution of high specific surface area Co_3O_4 occurs. The reduction of cobalt ions present in solution with nickel could provide an explanation for the decrease in nickel current efficiency and refining microstructure by the alloying effect. On the other hand, the change in grain orientation could result in a change in adsorption of the different competitive species reported by Amblard et al. [14] onto the cathodic surface as H_2 , H_{ads} , $\text{Ni}(\text{OH})_2$, organic compounds but also $\text{Co}(\text{OH})_2$ in the present case.

To understand these results, we then established the relationships between the specific surface area of the oxide, its reactivity in the Watts nickel bath and its incorporation into the nickel deposits. In this context, it has been found that the nature and the extent of the desorption or adsorption phenomena occurring on the Co_3O_4 surface, which varies with their specific surface area and the bath pH influences the incorporation of the powders. It was shown that the adsorption of protons, which occurs at the surface of Co_3O_4 particles when they are added to a nickel bath at $\text{pH} < 3.5$, has no apparent effect on their incorporation probably due to the partially dissolution of cobalt oxide and reduction of Co^{2+} . In contrast, the fact that particles release protons into solution when they are added to a bath at $\text{pH} > 3.5$ prevents their incorporation in the nickel matrix. A similar change in particle oxide codeposited versus bath pH has been reported by some authors [8, 15, 17]. As shown by Bhagwat et al. [8], higher incorporation of alumina particles in nickel is obtained when the nickel ions predominate in the adsorption region. It has been found in the present case that the presence of nickel-boron complexes on the particle surface impedes their codeposition, in contrast to the nickel ions.

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