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メタデータ	言語: eng 出版者: 公開日: 2010-04-06 キーワード (Ja): キーワード (En): 作成者: Furukawa, Naoji, Hayashi, Tadao メールアドレス: 所属:
URL	https://doi.org/10.24729/00008595

Electrodeposition of Ni-B_4C dispersion coatings

Naoji FURUKAWA* and Tadao HAYASHI*

(Received Nov. 15, 1982)

The electrodeposition of Ni-B_4C dispersion coatings from a Watts nickel bath (1.2 M Ni) has been studied to determine the factors affecting the codeposition of B_4C particles in the coatings.

The influence of the concentration of dispersoids, current density, pH, and agitation on the codeposition of B_4C particles with nickel was examined at 45 °C.

The codeposition rate of the B_4C particles with nickel was found to increase with increasing current density. The Ni-B_4C coatings tend to become rougher than Ni-Al_2O_3 deposits. Addition of organic leveling and brightening agents to the plating bath, however, gave rise to the smooth deposits with high hardness (Hv 690).

1. Introduction

Functional application of dispersion coatings prepared by electroplating and electroless plating methods have attracted special interests in metal finishing industry.

Dispersion coatings are metallic coatings containing a dispersed phase of the fine particles such as metal oxides, carbides, and organic polymers to give increased wear resistance, corrosion resistance, dispersion hardening and self-lubrications, etc.[1-4)]

In general, codeposition process could be characterized by three major stages, viz., 1) transporting and movement of the suspended particles to the cathode surface by mechanical agitation of plating solution, 2) adsorption of the particles on the cathode surface governed by the electrostatic forces and adhesion of particles to the metal surface, 3) engulfment of particles in the growing deposit at the cathode surface. However, the mechanism of the formation of the electrodeposited dispersion coatings, particularly the factors affecting the entrapment of solid particles into growing deposit are not fully established.

Foster et al.[5)] have shown that both the current density and the agitation of plating solution affect the particle-cathode adhesion during the formation of the electrodeposited dispersion coatings. Kariapper et al.[6)] proposed that the dispersion coatings can be produced if the particles in suspension have a positive surface charge by the adsorption of metal ions from the plating solution, and the adsorbed metal ions assist in the creation of an efficient mechanical bond between particles and the cathode surface.

It was also shown by many workers that codeposition of the particles into metal matrix was promoted by the addition of cations such as thallium, cecium and surface active agents.[7-9)]

In the present work, plating parameters affecting the formation of nickel base dispersion coatings have been studied in a Watts nickel bath with B_4C particles as a dispersoids. The influences of concentration of B_4C particles in suspension, cathode current density, addition agents, agitation and pH on the codeposition of the particles with nickel have been examined. The cathode polarization curves have also been measured

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* Department of Applied Chemistry, College of Engineering

in the Watts nickel bath.

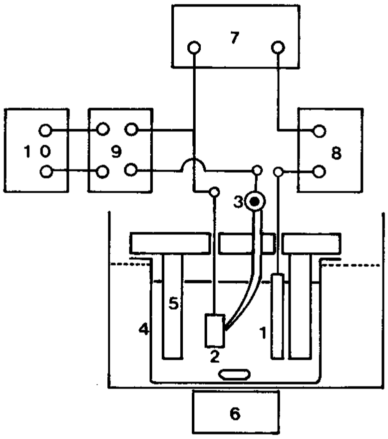
2. Experimental

2.1 Plating condition

The Ni-B_4C dispersion coatings were electrodeposited from a conventional Watts nickel bath of the composition, 1.0 M $NiSO_4$, 0.2 M $NiCl_2$, 0.5 M H_3BO_3. The plating solutions were prepared from special grade chemicals and distilled water.

Powders of B_4C (Mitsuwa Chemicals Co.) and Al_2O_3 (Fujimi Kenmazai Kogyo Co.) were used as a dispersoid. The mean particle size of B_4C was 9 μm and that of Al_2O_3 was 5 μm. The Al_2O_3 particles were used only when the effect of particle conductivity was examined. They were washed thoroughly with 0.5 M H_2SO_4 solution to remove any soluble impurities and then kept in suspension in a Watts nickel bath using a magnetic stirrer revolving at 450 rpm.

Electrolytic cell and circuit for the electroplating and polarization measurement are shown in Fig. 1. The electroplating was carried out using an electrolytic cell of 300 cm^3 capacity. Each cathode was a flat copper disk or stainless steel strip with an exposed area from 1 to 3 cm^2 and was held vertically in the center of the cell.



1. Anode.
2. Cathode.
3. Reference electrode.
4. Electrolytic cell.
5. Acrylic resin plate.
6. Magnetic stirrer.
7. Galvanostat.
8. Coulometer.
9. Impedance converter.
10. Recorder.

Fig. 1 Electrolytic cell and circuit

Cathode current efficiency was estimated by the weight of nickel in deposits and the amount of electricity used for the electrolysis. Cathode polarization curves in the electrodeposition of nickel with or without dispersoids were obtained by the galvanostatic method. Saturated calomel electrode (S. C. E.) was used as a reference electrode.

2.2 Composition and morphology of dispersion coatings

The Ni-B_4C dispersion coatings were plated on stainless steel substrates and stripped mechanically from the substrates for the test. The weight percent of B_4C particles in the coatings were determined by dissolving the deposits in H_2SO_4-H_2O_2 solution followed by the seperation of B_4C particles with the aid of membrane filter and then weighing the particles.

The content of particles in the dispersion coatings were also determined by counting the number of particles in unit area in photomicrograph. In this case, a flat copper disk (1 cm^2) electroplated with bright nickel was used as a substrate for the dispersion coatings. One side of the cathode was coated with an insulating resin, Fullontex (Furuto Sangyo Co.).

Particle distribution in the deposits and surface morphology of the dispersion coatings were examined by an optical microscope. The hardness of the dispersion coatings was also measured by the micro-hardness tester.

3. Results and Discussion

3.1 Effects of the concentration of dispersoids in Watts bath on the formation of Ni-B_4C coatings

The effect of the concentration of B_4C particles in Watts nickel bath on the codeposition of particles is shown in Fig. 2. The B_4C content in the dispersion coatings increased linearly with an increase of the particle concentration in the bath up to about 10 g/l, however, with further increase in the particle in the bath, no appreciable changes were observed in the B_4C content in the dispersion coatings.

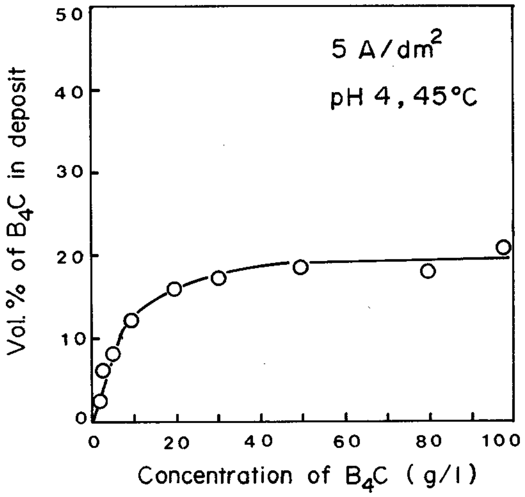


Fig. 2 Relation between B_4C content in the dispersion coatings and the concentration of B_4C in the bath

This behavior is in fairly good agreement with the results of other investigators in many plating systems.[10-12] In the rather lower concentration range (below 10 g/l) of the particles in the bath, unoccupied sites with B_4C particles on cathode surface seemed to be very large. Increasing the concentration of B_4C particles in the Watts nickel bath leads to an increase in number of the particles reaching and striking on the cathode, therefore the further adsorption of the particles on cathode could be inhibited by mutual interference or steric effect.

3.2 Effects of current density

The effect of the cathode current density on the codeposition of B_4C particles in nickel matrix in the electrolysis of the Watts bath containing 30 g/l of the B_4C particles was shown in Fig. 3.

The Ni-B_4C coatings were formed under constant current densities varied from 0.5 to 15 A/dm^2. The B_4C content in the dispersion coatings deposited under the normal agitation conditions (450 rpm) increased sharply with increasing the current density up to about 1 A/dm^2 leading to a maximum at 2 A/dm^2, and then decreased gradually with further increase of the current density. Under the vigorous agitation (800 rpm), the amount of B_4C particles codeposited below 5 A/dm^2 decreased, however, the codeposition of B_4C particles seemed to be insensitive to agitation condition in the current density range between 5 and 15 A/dm^2.

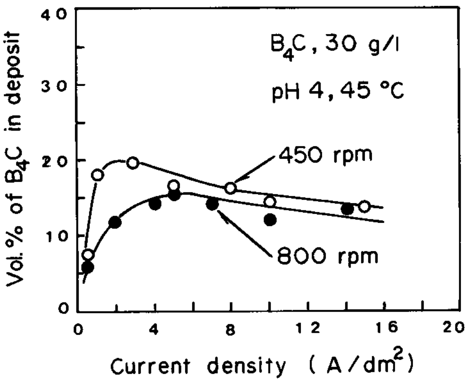


Fig. 3 Effect of current density on the B_4C content in dispersion coatings

Microscopic examination of the dispersion coatings suggested that Ni-B_4C coatings obtained with the relatively higher current densities (7 to 15 A/dm^2) tended to form agglomerates containing particles, while with the relatively lower current densities (1 to 2.5 A/dm^2) the coatings were found to become smoother and contained uniformly distributed B_4C particles.

It can be seen from Fig. 3 that the B_4C content in the coatings increased to give the maximum values in the first stage, followed by a gradual decrease with increasing current density. It should be noted that the less pronounced effect of the current density on the B_4C content in the Ni-B_4C coatings was observed in the current density range between 5 and 15 A/dm^2. The deposition rate of the B_4C particles increased with an increase of the current density (Fig. 6), therefore, the interaction of the particles to the electrode surface may be favored to bring the promotion of the codeposition of particles in the dispersion coatings. Decrease in the B_4C content in the coatings in the lower current densities (0.5 - 1 A/dm^2) can be explained by the initial weak attraction of the particles to the cathode.

3.3 Effects of pH

The relationship between the pH of the plating bath and B_4C content in the coatings is shown in Fig. 4, where the pH was changed from 1 to 5.

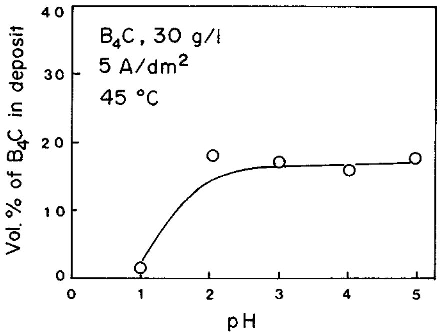


Fig. 4 Effect of pH of Watts bath on the B_4C content in deposit

The amount of B_4C particles in the coatings formed at 5 A/dm^2 was found to be almost constant in the pH range of 2 to 5, which is commonly used for the conventional nickel plating bath. However, the B_4C content in the coating decreased sharply with lowering the pH below 2. Violent agitation of the solution near the cathode surface might be caused by hydrogen evolution reaction at lower pH range ($<$ pH 2) resulting in the decrease of the B_4C content in the deposits due to the inhibition of the adsorption of particles to the cathode.

In the preceding paper$^{8)}$, it was reported that the content of the metal oxides (Al_2O_3 and ZrO_2) in the nickel matrix increased linearly with decreasing pH of the Watts nickel bath under the constant current efficiency. This might be attributed to the promoted interaction of the oxide particles to the cathode by the adsorbed H^+ ions on the oxide surface.

In the Ni-B_4C system, positive charge developed by the adsoption of Ni^{2+} ions on the B_4C particles seemed to have an important role in the initial stage of the adsorption of particles to the cathode.

3.4 Codeposition rate of B_4C particles into nickel matrix

Figure 5 shows the relationship between the number of B_4C particles codeposited with nickel and plating time at 5 A/dm^2. Codeposited B_4C particles inreased rapidly up to about 20 sec., and after that increased gradually with increasing the deposition time. After two or three minutes, the content of the B_4C particles on nickel cathode seemed to approach a maximum value (ca. 2×10^3 particles/mm^2). Under these conditions, the codeposition of the B_4C particles was found to be in steady state, resulting in the uniform distribution of the particles in the deposit.

Deposition rate of B_4C particles at 5 A/dm^2 estimated from the initial part ($<$ 20 sec.) of the curve in Fig. 5 was 5.6×10^1 particles/mm$^2 \cdot$ sec.. The change in the deposition rate of B_4C particles with various current densities (1 to 20 A/dm^2) was shown in Fig. 6. The codeposition of B_4C particles was found to increase with increasing current density. These results imply that the metal deposition promotes the adsorption and engulfment of the particles on the cathode surface. The amount of nickel deposited

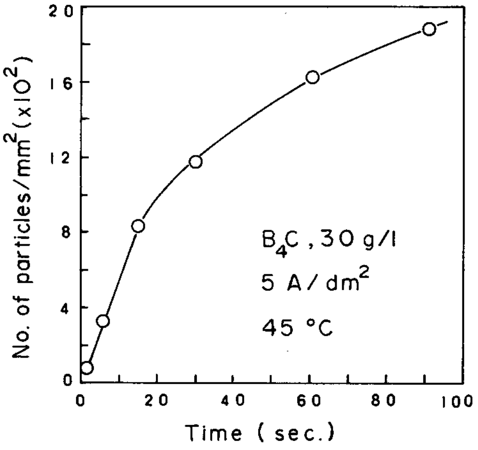


Fig. 5 Relation between the number of codeposited particles and the plating time

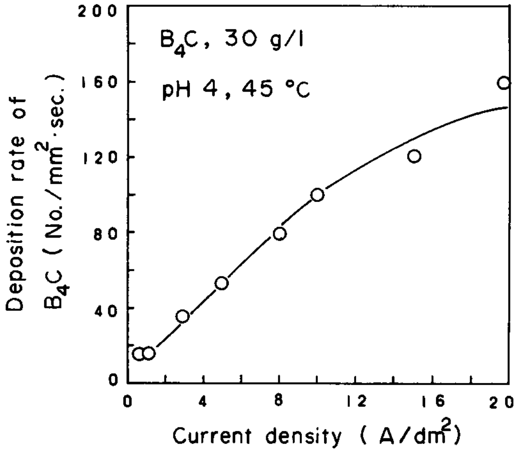


Fig. 6 Effect of current density on the deposition rate of B_4C particles

should be proportional to the quantity of electricity under the constant current efficiency.

From these results, decrease in the B_4C content resulted from the lower current density in Fig. 3 can be explained by the initial weak attraction of the particles to the cathode due to the decrease of the deposition rate of nickel, that is, decrease in the mechanical bonding of the particles to the cathode.

3.5 Cathodic polarization in Watts nickel bath

Fugure 7 shows the cathode polarization curves for the electrodeposition of pure nickel and also of the Ni-B_4C dispersion coating from the Watts bath.

An addition of B_4C particles in the Watts nickel bath decreased the cathode polarization in the current density range of 0.5 to 40 A/dm^2. On the other hand, the cathode current density at -1.10 V (vs. S. C. E.) in the electrodeposition of Ni-B_4C dispersion

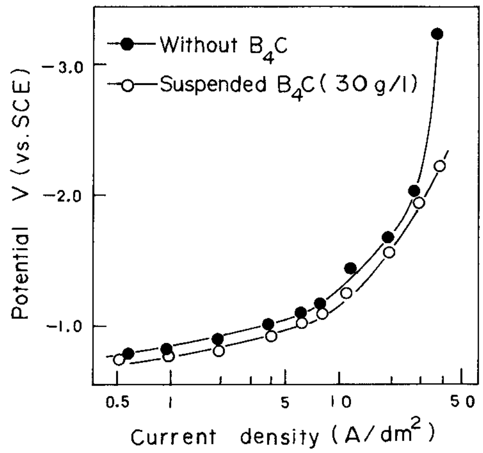


Fig. 7 Cathodic polarization curves in Watts nickel bath with or without dispersoids

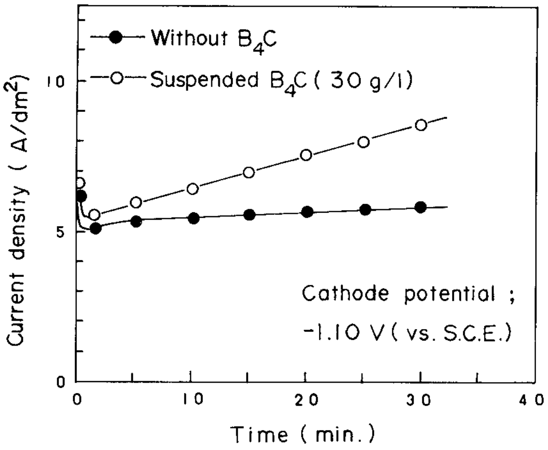
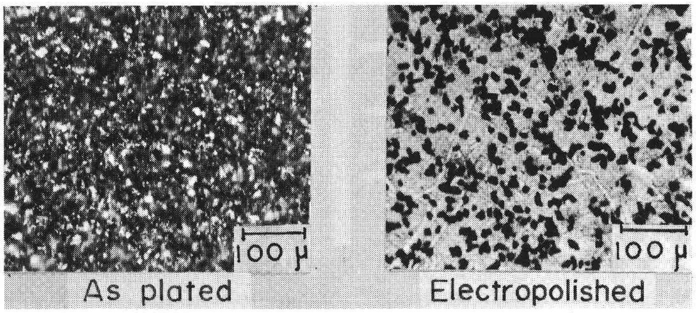


Fig. 8 Changes in current density with time in Watts nickel bath with or without B_4C

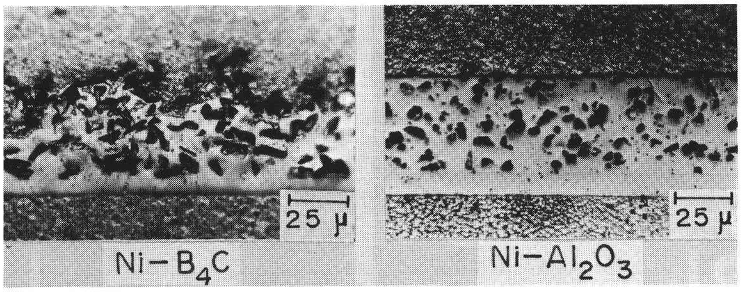
coatings increased appreciably with time (Fig. 8). The change in the cathode current density at the same potential in the deposition of pure nickel was found to smaller than that obtained in Ni-B_4C bath. Microscopic examination of the electrodeposited coatings revealed that the B_4C dispersion coatings tend to become rougher than pure nickel deposits during the electrolysis.

3.6 Morphology of the deposits

Figure 9 shows the photomicrographs of the Ni-B_4C and Ni-Al_2O_3 dispersion coatings electrodeposited from the Watts nickel bath at 5 A/dm^2 for 30 min.. Ni-B_4C coatings were found to have the uniform distribution of B_4C particles, however, they have rather rough surface. The codeposition of Al_2O_3 particles with nickel gave rise to the smooth surface compared to Ni-B_4C coatings (Fig. 9). The difference in the surface morphology of Ni-B_4C and Ni-Al_2O_3 coatings can be attributed to the changes in the



(a) Surface appearance of Ni-B_4C dispersion coatings



(b) Cross section

Fig. 9 Photomicrographs of Ni-B_4C and Ni-Al_2O_3 dispersion coatings electrodeposited from Watts nickel bath at 5 A/dm^2 (pH 4, 45 °C)

electrical conductivity of the dispersoids (B_4C; 2×10^2 Ωcm, Al_2O_3; 10^{16} Ωcm). In fact, conducting B_4C particles were rapidly involved by the growing nickel, while non-conducting Al_2O_3 particles were gradually engulfed in the course of electrolysis.

The B_4C particles adsorbed on cathode surface would serve as a protrusion of cathode, and then they were rapidly involved by the growing deposit. Thus, the Ni-B_4C dispersion coatings containing conducting particles would tend to become rougher than Ni-Al_2O_3 deposit under the same conditions.

It was found that the addition of butyne-1,4-diol (6×10^{-4} M) and 1,3,6-tri-sodium naphthalenesulfonate (6 g/l) in the Ni-B_4C plating bath inhibited the formation of rough deposit. These organic compounds are used as levellig and brightening agents in conventional Watts nickel bath. The Ni-B_4C deposit thus obtained gave rise to high hardness (Hv 690), which was higher than that of the same Ni-B_4C deposits (Hv 485) obtained from the bath without any addition agents.

4. Conclusions

The amount of B_4C particles (mean particle size, 9 μm) codeposited in the coatings was found to increase with increasing particle concentration in the bath and to reach maximum value of 18 - 20 vol.%.

The B_4C content in the dispersion coatings increased sharply with increasing current density up to about 1 A/dm^2, and then decreased gradually with a further increase of the current density.

Adsorption of B_4C particles on the cathode surface from Watts nickel bath seems to occur only when the electrolysis was carried out in the nickel bath, because the initial attractions of the particles to the cathode are weak.

Stronger agitation of the plating bath results in the decrease of B_4C content in the deposits obtained from a Watts bath at rather lower current densities.

The codeposition rate of B_4C particles into nickel matrix increased with increasing current density. From these results, it is suggested that the most important factors affecting the formation of Ni-B_4C coatings are the current density, which correspond to the deposition rate of nickel matrix.

Conducting B_4C particles are rapidly involved by electrodeposited nickel, while non-conducting Al_2O_3 particles are gradually engulfed. Consequently, the Ni-B_4C dispersion coatings tend to become rougher than Ni-Al_2O_3 deposits. Addition of organic leveling and brightening agents to the Ni-B_4C bath inhibited the formation of rough deposits. The Ni-B_4C deposits thus obtained gave rise to high hardness (Hv 690) having a fine grained microstructures.

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