Dispersion Coating Containing High Content of Diamond Particles in a Nickel Matrix Using Azobenzene Surfactant

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The influence of a redox active surfactant (4-Ethylazobenzene-4′-(oxyethyl)trimethylammonium bromide, AZTAB) and a redox inactivating surfactant (n-Dodecyltrimethylammonium bromide, DTAB) on the codeposition of diamond particles with nickel has been investigated. A nickel bath containing DTAB did not deposit a higher amount of diamond particles with nickel, whereas the nickel bath containing AZTAB deposited more than twice the amount of the particles (45.5 vol.%), that were deposited by the former bath (21.6 vol.%). An electrochemical investigation showed that AZTAB is reduced during the nickel deposition. Therefore, it has been assumed here that the reduction of free AZTAB at the cathode surface leads to desorption of AZTAB adsorbed on the particles in the vicinity of the cathode. As a result, deposition of these particles at the cathode surface takes place before these particles are being entrapped in the layer of growing nickel.

The wear resistance of the Ni/diamond composite coatings containing various volumetric content of particles was also investigated. This showed that a higher degree of wear resistance accompanied increased particle content.

**Key Words**: Dispersion Coating, Nickel, Diamond, Redox Active, Azobenzene-Surfactant

1. Introduction

Researches on metal matrix dispersion coatings containing hard particles such as alumina\(^{1-6}\), silicon carbide\(^{7-9}\), boron carbide\(^{10}\), titanium carbide\(^{11}\), diamond\(^{12-18}\), etc have been growing due to their higher degree of wear and corrosion resistances. The anti-wear performance of these coatings depends upon the amount of the particles incorporated into the coatings, and generally a high volume fraction of the particles in such coatings is desirable in order to apply these coatings as a good wear protection coating. In an attempt to incorporate high volume percentage of the various particles in a nickel matrix, recently we have developed the 'Two-step' composite coating technique\(^{19}\) and have demonstrated that the composite coatings prepared by this technique contains high volume percentage of particles. These coatings exhibited a better anti-wear performance than the composite coatings of the same type prepared by the classical method of single step electrodeposition technique. In another technique, we have shown that high volume percentage of SiC particles could be deposited with nickel using a redox active cationic surfactant containing an azobenzene group in Watt’s nickel bath and the composites of a wide composition ranges could be coated\(^{20-22}\).

Diamond, the hardest material ever known, has been used in making cutting, drilling and grinding tools. One of the commercial produce of such tools is done by the electrolytic codeposition of diamond particles with nickel matrix. In order to codeposit high volume percentage of diamond particles and other hard ceramic particles with metals, a sediment codeposition technique\(^{23-25}\) is generally applied in which the substrate is placed horizontally in the plating bath. This process is time consuming for thick deposits and it may codeposit agglomerated particles\(^{26}\). Moreover, this method is generally limited to the plate like structured. In such case, a vertical arrangement of the electrodes during the electrolysise is beneficial. However, one needs to add a surfactant in the bath, which can promote the codeposition of particles. In this regard, a cationic surfactant with an azobenzene group might be beneficial. Therefore, the present study was carried out to investigate the influence of AZTAB (Fig. 1(a)) on codeposition of the diamond particles with nickel. Similarly, DTAB (Fig. 1(b)), a cationic surfactant which has an equivalent hydrophobicity\(^{27}\) to that of the AZTAB was also used in the present study to compare its influence on codeposition of the diamond particles, with that of the AZTAB. Besides these, the present work was also directed to coat the substrates with various ranges of incorporated diamond particles.

![Molecular structure of surfactants](image_url)

Fig. 1 Molecular structure of surfactants.
using AZTAB surfactant and to explore the abrasive wear resistance of these composite coatings briefly.

2. Experiments

Synthesis and purification of AZTAB were described in our previous paper\(^7\). G.R. grade DTAB (Tokyo Chemical Industry, Japan) was used without further purification. Natural diamond powders (particle size 1 and 2.3 \(\mu\)m, De Beers, Ireland) were used without any treatment.

A copper plate with a dimension of 10 \(\times\) 30 \(\times\) 3 mm\(^2\) was polished to a mirror finish using a polishing reagent, Pikal (Nihon Maryoku-Kogyo Co., Ltd., Japan) and it was ultrasonically cleaned in chloroform for 5 minutes followed by acetone for another 5 min. An area of 1 cm\(^2\) on either sides of this copper substrate was exposed using an insulating adhesive tape and this substrate was then placed vertically parallel to a nickel anode at a distance of 2 cm in Watt’s bath according to the following composition: 300 gdm\(^{-3}\) NiSO\(_4\)-6H\(_2\)O, 60 gdm\(^{-3}\) NiCl\(_2\)-6H\(_2\)O, and 40 gdm\(^{-3}\) H\(_3\)BO\(_3\). The pH of this bath was adjusted to 1 with a concentrated solution of H\(_2\)SO\(_4\) (35%). A known amount of AZTAB was dissolved in the above bath and then particles were added to the bath. This bath was ultrasonically agitated for 5 min and the mixture was stirred for 30 min using a magnetic stirrer. This bath was then subjected for the composite plating and the particles during plating were kept in suspension using a magnetic stirrer. In the case of DTAB, pH of the above bath was adjusted to 3.5 and all the other plating procedures were the same as described above for the case of AZTAB. After plating for 15 min, the deposits were rinsed thoroughly with running water and wiped simultaneously with wetted tissue paper. Then the deposits were cleaned ultrasonically in acetone for 20 min followed by water for 5 min. The surface and the cross-sectional morphology of the coatings were studied using a scanning electron microscope (SEM).

Diamond content in the coating was analyzed gravimetrically by dissolving five replicas of the deposits in nitric acid (30%), diluting the solution, and then separating the particles using a membrane filter with pore size of 0.2 \(\mu\)m (ADVANTEC, Toyo Roshi Kaisa, Ltd., Japan).

Copper plates with a dimension of 20 \(\times\) 40 \(\times\) 3 mm\(^2\) were coated with the nickel/diamond composite containing various amount of diamond. The anti-wear performance of these deposits was assayed using an abrasion tester (SUGA ABRASION TESTER, NUS-ISO3, Sugawara Test Instruments Co., Ltd., Japan). Wear analysis was carried out by oscillating a coating sample over the counter disk, mounted with a SiC (10 \(\mu\)m) abrasive paper, for 300 cycles under the load of 2.5 kg force in air at room temperature. After the wear test, the specimen was cleaned ultrasonically in acetone for 10 min and it was weighed out. The degree of wear resistance of the coatings was considered here in terms of the reciprocal of weight loss during the wear experiment.

3. Results and Discussion

Figure 2 shows the influence of surfactants on particle codeposition with nickel. A higher volume percentage of diamond particles was deposited into the nickel matrix using AZTAB. However, DTAB, which has an equivalent hydrophobicity to that of the AZTAB\(^7\) did not deposit as much diamond particles into the nickel matrix as deposited by AZTAB. In order to understand the influence of these two types of surfactant on particle codeposition, their interactions with the particles, the cathode surface, as well as the behavior within the diffusion layer have to be considered. Lee et al.\(^{10}\) have shown that the pH corresponding to the isoelectric point of diamond is approximately 3.2 and the pH lower than this value provides a net positive charge to the diamond particles. Therefore, diamond particles in a plating bath of the present study might be positively charged even in the absence of nickel ions and the AZTAB. This is similar to the case of SiC particles for which the pH corresponding to its isoelectric point was reported to be 2.3\(^{15}\). In our previous study\(^9\), we found the adsorption of AZTAB on SiC particles (3.2 \(\mu\) moles of AZTAB/m\(^2\) of SiC) at pH 1 under the equilibrium condition of adsorption isotherm at 25°C. Because of lack of the diamond powder, the authors could not study the adsorption isotherm of AZTAB on diamond particles. However, a similar type of the physical adsorption of AZTAB supposed to be taken place on the diamond as it took place in the case of the SiC particles at pH 1. Similarly, the adsorption of DTAB on the diamond

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Fig. 2 Influence of surfactant concentration on the codeposition of diamond particles with nickel. (\(\bigcirc\)) AZTAB, 1 \(\mu\)m diamond particles, (\(\blacksquare\)) AZTAB, 2.3 \(\mu\)m diamond particles, (\(\bigcirc\)) DTAB, 1 \(\mu\)m diamond particles. Watt’s nickel bath (pH 1 for AZTAB containing bath and pH 3.5 for DTAB containing bath) operated under the current density of 5 A dm\(^{-2}\) for 15 min at 50°C.
particles at pH 3.5 of the bath may also be the physical in nature as in the case of AZTAB, since the pH of the electrolyte is near to the isoelectric point of diamond and it is our belief that these cationic surfactants adsorb on these particles with their hydrophobic tail pointing positively charged head towards solution. Adsorption of all these cations on particles develops a positive charge to the particles and thereby, increases the affinity of these particles for the negatively charged cathode.

Besides the particles, some surfactants may also adsorb at the cathode surface, which might affect the extent of the codeposition of particles. In order to study this effect on particle codeposition, a voltametric technique was used. A linear sweep voltammogram of AZTAB in 0.1 M HCl showed the reduction peak of AZTAB at about −0.15 V vs. SCE (Fig. 3(a), curve (ii)). This reduction is due to the cleavage of the nitrogen-nitrogen bond of an AZTAB molecule. The voltammograms of the bath containing 5 mM NiSO₄ (Fig. 3(a), curve (iii) and (iv)) showed an increased current from approximately −0.65 V. Beyond this potential, no other peaks or inflections in the voltammogram curve were observed. Therefore, this increasing current is probably due to the deposition of nickel and the evolution of hydrogen, which seem to take place at potentials close to each other. Since the positions at which this current started to rise in the curves (ii) and (iv) are almost the same, the presence of AZTAB in the nickel bath does not significantly affect the deposition of nickel. The voltammograms in Fig. 3(a) show that the reduction potential of AZTAB is more positive than that of the nickel. Therefore, reduction of the free AZTAB at cathode surface takes place during the deposition of nickel. After reduction, this surfactant loses its amphiphilic function. On the other hand, this reduction decreases the concentration of free AZTAB in the vicinity of the cathode, which perturbs the equilibrium condition of the adsorption. In order to satisfy this adsorption equilibrium, AZTAB adsorbed on diamond particles seems to desorb. As the result, these particles can not remain in suspension in the solution near the cathode, which leads to the deposition of these particles on the cathode. This phenomenon of particle deposition is more or less similar to the electro- and electroless deposition of organic particles using a ferrocenyl and an azobenzene group surfactant, respectively. These deposited particles are then embedded under the growing layer of nickel. Unlike AZTAB, DTAB is not a redox active surfactant. This statement is also supported by the linear sweep voltammogram of a 1 mM DTAB in an aqueous solution of 0.1 M KNO₃ (Fig. 3(b), curve (ii)), which shows that DTAB is electrochemically inactive. The voltammograms of an unstirred electrolyte containing nickel ions (Fig. 3(b), curve (iii) and (iv)) showed a peak at about −1.1 V vs. SCE. However, these peaks did not appear in the presence of 0.1 M HCl as a supporting electrolyte (Fig. 3 (a)).

On the other hand, the peak height did not alter proportionally with the concentrations of the nickel ion. From this, it is clear that these peaks are not due to the reduction of nickel ions present in the solution. As explained earlier, there was an evolution of hydrogen gas simultaneously with the reduction of nickel ions. Hence, during the reduction of nickel ions, the solution very close to the working electrode becomes more alkaline. Consequently, nickel present in this solution region, precipitates as hydroxide and deposits on the electrode, which undergoes reduction in the further cathodic sweeping. Therefore, the above peaks may be assigned to the reduction of nickel hydroxide. A similar phenomenon of precipitation of nickel hydroxide at the Pt electrode and its reduction on cathodic sweeping has been reported previously.

Fig. 3 Linear sweep voltammograms at 25°C under nitrogen atmosphere. Working electrode: 0.082 cm² glassy carbon. Counter electrode: Pt. Scan rate: 10 mV/s.

(a) Study of the influence of AZTAB on nickel reduction. (i) 0.1 M HCl. (ii) 1 mM AZTAB + 0.1 M HCl. (iii) 5 mM NiSO₄ + 0.1 M HCl. (iv) 1 mM AZTAB + 5 mM NiSO₄ + 0.1 M HCl.

(b) Study of the influence of DTAB on nickel reduction. (i) 0.1 M KCl. (ii) 1 mM DTAB + 0.1 M KCl. (iii) 5 mM NiSO₄ + 0.1 M KCl. (iv) 1 mM DTAB + 5 mM NiSO₄ + 0.1 M KCl.
The voltammogram of a bath containing nickel ions in presence of DTAB (curve-iv) shifted towards more negative potential than that of the voltammogram in absence of DTAB (curve-iii). These results indicate that DTAB is not reducible and it is adsorbed at the cathode surface, which increased the over-potential for nickel deposition. This increase in over-potential for nickel ion reduction is due to the hydrophobic layer of DTAB at the cathode surface, which inhibits the approach of water and hydrated nickel ions to the electrode. On the other hand, due to the redox inactivity of DTAB, the adsorption equilibrium of the DTAB is hardly perturbed and, this does not lead to desorption of DTAB molecules from the particles as in the case of AZTAB. As the result, these particles remain in suspension in the electrolyte and the incorporation of these particles into the growing nickel matrix at cathode is very difficult compared to the incorporation of the deposited particles at cathode due to desorption of AZTAB. Hence, a strong repulsive force between the surfactant layer on the cathode and an approaching particle decreases the codeposition of particles in the presence of DTAB. This explains the reason why AZTAB compared to DTAB enables one to increase the diamond content in the deposits. The inhibition effect of DTAB on particle codeposition becomes stronger when the concentration of DTAB becomes in excess in the bath. As the result, a decreasing trend of particle codeposition was observed when the concentration of DTAB in the bath was beyond 0.02 gdm\(^{-3}\) (Fig. 2). Like in the case of DTAB, there is a decreasing trend of particle codeposition beyond the optimum concentration of AZTAB in the bath (Fig. 2). This decreasing trend of incorporation of diamond particles is probably due to the decrease in the rate of desorption of AZTAB from the particle surface. At a lower concentration of AZTAB, this desorption may lead to deposition of the particles on the cathode. However, at a higher concentration of AZTAB, the free surfactant reduced at the cathode surface is soon substituted from the bulk and the particles are re-dispersed. This phenomenon near the cathode hinders the particle deposition on the cathode. Hence, the repulsive force between the AZTAB layer on the cathode and the particles hinders the approaching particles to the cathode surface, and thereby, reduces the incorporation of particles. Therefore, the reduction of free AZTAB at the cathode and desorption of the AZTAB from the particle surface in the vicinity of cathode seem to play a key role in the extent of incorporation of particles.

Particle size is also one of the factors that influence the extent of particle codeposition. In the present case, two different sizes of diamond particles were studied. In both cases, the extent of particle codeposition increased with increasing the concentration of AZTAB till about 6.5 gdm\(^{-3}\). Beyond this concentration of AZTAB, the extent of particle codeposition decreased (Fig. 2). The increasing trend of particle codeposition with respect to AZTAB concentration may be due to the strong adsorption of AZTAB, which might increase the number of dispersed particles and the surface charge of the particles as well. As the result, the affinity of these particles for the cathode increases which might increase the particle codeposition. The decreasing trend at higher concentration of AZTAB beyond 6.5 gdm\(^{-3}\) is due to the reasons as explained earlier. The amount of surfactant adsorbed on a smaller particle might be less than the amount adsorbed on a larger particle. Owing to this, AZTAB easily desorbs from smaller particles compared to that from larger particles and these smaller particles easily deposit on the cathode. On the other hand, the adhesion force between the smaller particles and the cathode is stronger than that between the larger particles and the cathode. Hence, the smaller particles can cling to the cathode surface with sufficient tenacity and for a sufficient period of time to be entrapped in the growing layer of nickel. However, the larger particles, owing to their weak interaction with the cathode, can be easily swept away by the bath agitation before they are being entrapped into the growing layer of nickel matrix. As the result, the maximum content of diamond in the composite is higher in the case of smaller particles.

Surface of the Ni/diamond composites prepared from the bath using AZTAB was smoother than that of the composites produced from the bath containing DTAB. An analysis of the coatings shows that the maximum amount of diamond particles deposited using AZTAB is 45.5 vol.% (Fig. 4a). However, the bath containing DTAB deposited only 21.6 vol.% of diamond particles. The surface morphology of the composite prepared using AZTAB (Fig. 4(a)) shows a uniform distribution of diamond particles in the composite coating. The uniformity of this coating is also evident from its cross section of this composite (Fig. 4(b)), which shows the uniform distribution of particles through out the deposits and it has a uniform thickness of about 10 \(\mu\)m for 15 min of electrodeposition. However, the distribution of particles in the composite prepared using DTAB is less uniform compared to that in the above composite prepared by using AZTAB. Moreover, this composite had many cracked when observed through an SEM (Fig. 5). This is probably due to the presence of incorporated DTAB in the deposits. As described earlier, DTAB is not a reducible surfactant. Therefore, the free DTAB as well as DTAB adsorbed on the particles incorporates into the deposits, which produces the highly brittle and stressed coating\(^{20}\) and hence, the deposits often become cracked.

The bath pH had also an influence on the morphology of the coatings. In the case of DTAB, pH of the bath was optimized at 3.5. At lower pH, the bath produced the coatings with many gas pits, while the coatings at higher pH were brittle and rough due to the incorporation of hydroxide. As described earlier, the efficiency of AZTAB for codeposition of higher diamond particles into the coating is based on the
phenomenon of desorption of AZTAB from the particle surface in the vicinity of a cathode. This desorption phenomenon is related to the reduction of free AZTAB at the cathode surface. The reduction of AZTAB takes place in acidic medium which leads to the formation of aniline derivatives and semidine products by the cleavage of the nitrogen-nitrogen bond. Therefore, the redox potential of AZTAB depends on the pH of the electrolyte and was found to shift towards more negative potential with increasing the pH of an electrolyte. Due to this reason, an acidic bath having low pH was selected in the present study. However, the deposits prepared at pH 2 and higher were highly stressed, brittle and cracked. Therefore, no further experiment at pH other than 1 was carried out and all the plating experiments were optimized at pH 1. On the other hand, the coatings prepared in all cases, at higher current density than 15 A dm² were brittle and had many micro-cracks when observed with a SEM.

Ni/diamond coatings containing various volumetric content of diamond were produced using AZTAB and their degree of abrasive wear resistance was evaluated under dry sliding condition. These wear experiments exhibited an increasing trend of wear resistance with increasing the volumetric content of particles in the coatings (Fig. 6). A similar increasing trend of wear resistance with the volumetric content of particles was also reported by Bozini et al., up to 24 vol.% of diamond particles in a Ni-P alloy matrix, which was the highest amount of diamond (24 vol.%) incorporated with the matrix in their study. However, the amount of incorporated diamond with nickel in the present study was up to about 45 vol.% and the wear experiment revealed that the material loss from these coatings containing up to about 26 vol.% of diamond particles was more gradual. Thereafter, a sudden excessive material loss was observed for the coatings containing less than about 26 vol.% of the particles (Fig. 6), indicating the severe wearing of these coatings. From this result, it seems that a Ni/diamond composite should have more than about 30 vol.% of the incorporated diamond particles in order to act as a good anti-wear material. Diamond is a hard and an abrasive material. Therefore, dispersion of diamond
particles into a nickel matrix has been reported to increase the hardness of the coating with increasing the content of dispersed particles. Probably this is the reason for higher degree of wear resistance of the coatings containing higher volumetric content of particles. The particles have their influence only on a certain distance of their surrounding in a matrix. When the volumetric content of diamond particles in a nickel matrix is small, the space between these particles in the matrix becomes large. Therefore, the hardness of the matrix away from the dispersed particles is no more different from that of a nickel metal, whereas the matrix near the particles is harder. In such a case, the counter body easily damaged the nickel matrix in between the particles. In this process, some of the incorporated particles are also removed, leaving behind voids which increase the wear rate of the coating during the further wear mode. Probably, this is the reason for higher degree of wear resistance of the coatings with higher volumetric content of the particles.

4. Conclusions

The present investigation revealed that a redox active cationic surfactant, having more positive redox activity than that of a metal, can disperse a considerably higher amount of particles into the metal matrix, while a redox inactive surfactant having an equivalent hydrophobicity as that of the redox active surfactant can not disperse as much of the particles into the metal matrix as dispersed by the redox active surfactant. The higher efficiency of this redox surfactant has been assumed here due to desorption phenomena of the surfactant from the particle surface before being incorporated into the growing metal. AZTAB, a redox active cationic surfactant has such properties, which was shown here to disperse about 45.5 vol.% of diamond particles into a nickel matrix.

Besides its higher efficiency for promoting particle codeposition with nickel, it was shown that AZTAB could also be used as a probe to control the particle content in the coatings. The abrasive wear resistance of these coatings containing various volumetric content of diamond was shown to increase with increasing the content of diamond.

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