JOURNAL OF MATERIALS SCIENCE 31 (1996) 2931–2936

The corrosive wear of nickel coating on mild steel

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The abrasive wear of nickel coatings on steel substrates, under corrosive conditions was studied. For specimens with and without heat treatment, the wear rate was observed to depend upon the nature of the corrosive solution. The composition of the wear debris was noted to be a function of the corrosive wear conditions. The wear rate of the heat treated specimens was observed to be lower than that of the non-heat treated nickel-coated steel specimens.

1. Introduction

It is well established that various tribological properties such as the friction, wear, adhesion and lubrication of metallic materials are very sensitive to physicochemical processes occurring on the surface of those materials. Corrosion is also recognized as a very important factor in the damage and failure of metallic materials; in addition, it is well known that the synergetic effect between wear and corrosion causes several problems in various engineering components made from metallic materials.

To date, very limited research work has been reported on the corrosive wear of metallic materials. Stott and Macdonald, in a series of papers [1–4] reported the corrosive wear of cast iron in a lubricating oil containing various amounts of H_2SO_4 solution. The same investigators also studied the influence of the cast iron composition, microstructure, surface finish, H_2SO_4 concentration and temperature on the corrosive wear of the cast iron.

Miyoshi [5] examined the corrosive wear of iron in H_2SO_4 solutions and observed that the pH of the solution plays an important role in controlling the iron loss due to the corrosion–wear processes in the H_2SO_4 solution. Pyun *et al.* [6] studied the effect of passivating oxide films on the corrosive wear of Al–7% Si alloy in a H_2SO_4 solution at room temperature. These investigators noticed that, as the applied potential increases to 1.08 V_{sce} on the Al–7% Si alloy, the rate of corrosive wear increases and then decreases for applied potentials higher than 1.08 V_{sce}.

The present work examines the corrosive wear of nickel coatings on mild steel, which has not been previously published.

2. Experimental procedure

The specimens used as substrates in this study were squares, 10 × 10 cm, which were cut from a 0.5 mm thick, rolled sheet of mild steel. In the centre of the specimens, a hole of 0.6 cm diameter was drilled, followed by an annealling process for 2 h at 550 °C. The nickel coating was deposited electrolytically on the steel substrates from a Watts solution.

Prior to the deposition, the steel specimens were cleaned in a 0.2 M NaOH solution at 70 °C, rinsed with cold distilled water and then immersed in a pickling solution (Dreca), consisting of HCl and various retardants, rinsed again and kept in a desiccator. Just before the deposition, the specimens were mechanically polished with 800, 1000 and 1200 grit SiC paper and, afterwards, were washed in methanol and distilled water.

Mild steel specimens were used as cathodes in a typical electrochemical cell using cast nickel anodes. The Watts solution used during the deposition of nickel had the following composition:

$NiSO_4 \cdot 6H_2O$	$317\ g\,l^{-1}$
$NiCl_2 \cdot 6H_2O$	$45\ g\,l^{-1}$
H_3BO_3	$37\ g\,l^{-1}$

The solution had a pH = 3 and its temperature was kept at 57 °C. The current density was $25\ mA\,cm^{-2}$.

The thickness of the nickel coatings was measured with a Jenavert optical microscope. Microhardness measurements were made with a Vickers M17 microhardness testing instrument with a pneumatic identer, using a 5 g load for 20 s.

Wear tests were conducted on nickel-coated steel specimens and also on the same specimens that had been heat treated at 350 °C for 1 h. The wear behaviour of nickel-coated mild steel specimens was examined with the help of Taber abrasion machine (Frank Co, Germany). This machine consists of two rotating abrasive wheels which produce a circular wear track of 1.3 cm width and 6.4 cm inner diameter. The specimens rotated about a vertical axis at a constant speed of 60 r.p.m against the sliding rotation of the two abrasive wheels. These wheels were driven by the specimen under test about a horizontal axis displaced tangentially from the vertical axis. Wear was quantified by weight loss which was measured every 150 cycles.

Teledyne CS 17 wheels (Calibrade Co, USA), which consist of rubber impregnated with silicon carbide particles, were used for all tests. The abrasive wheels were cleaned every 150 cycles to avoid capping or clogging. Surface examination of the worn specimens was also made with a Jenavert optical microscope. The wear debris was also examined with the above microscope and with a Philips X-ray diffraction machine using Co*K*α radiation ($\lambda = 0.1791$ nm) monochromated with an iron filter.

The wear behaviour of the as-received nickel-coated steel specimens was examined under dry conditions with the action of a 5 N load and also, under the effect of various solutions. A feeding system was constructed which was able to drop on the wear track approximately 10 mg of the following solutions, per cycle.

Distilled water
H_2SO_4 0.01 M
NH_4OH 20% v/v
HNO_3 1% v/v
HNO_3 1% v/v + inhibitor (Na_2CrO_4) 10% v/v

The wear behaviour of the nickel–coated steel specimens after their heat treatment was also examined under the same dry conditions, but with the dropping of the following solutions:

H_2SO_4 0.01 M
NH_4OH 20% v/v
HNO_3 1% v/v

The experimental values given in this study are the average of four measurements.

3. Results and discussion

Fig. 1 shows that the thickness of the nickel coating on mild steel increases linearly with increasing electrodeposition time, in the range of electrodeposition times examined, 0–60 min. The 15 μm thick nickel coating was studied in the microhardness and wear tests.

3.1. As-received specimens

The microhardness as a function of depth for the above non-heat treated specimen was measured. The microhardness of the coating was found to have an average value of 260 HV (260 kg mm^{-2}). Significant differences in the microhardness values of the nickel coating near to, and away from, the interface with the substrate were not observed, indicating a uniform growth of the nickel coating during electrodeposition.

A significant increase in the substrate microhardness was observed near the interface with the coating. This increase in microhardness might be attributed to the presence of compressive stresses at the substrate near the interface with the coating, which balance the tensile stresses generated in the coating during deposition [7]. It may also be attributed to the presence of solute hydrogen and dislocation hardening due to the hydrogen concentration gradient [8]. Atomic hydrogen can be introduced into the substrate either during the surface preparation processes before the electrodeposition, or during the electrodeposition process itself.

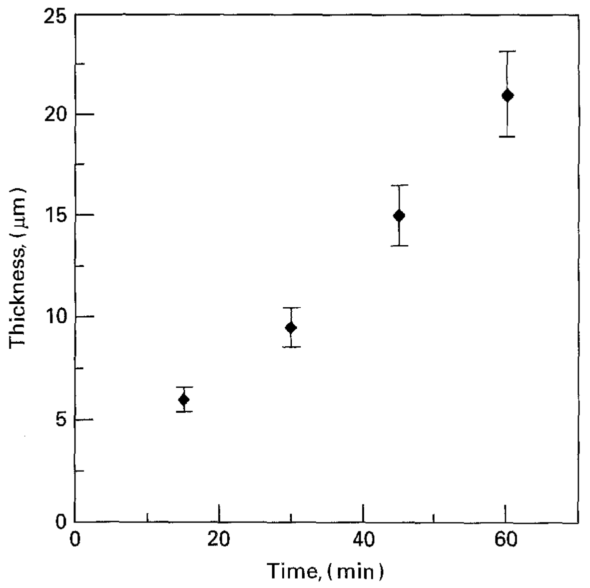

Figure 1 Thickness of electrodeposited nickel coating on steel specimens, as a function of electrodeposition time.

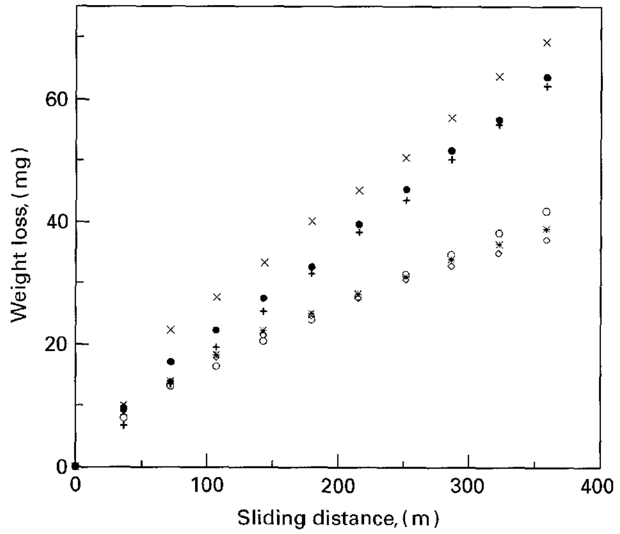

Figure 2 Weight loss as a function of sliding distance for as-received nickel-coated steel specimens, (+) dry, (●) H_2O distilled, (×) H_2SO_4 0.01 M, (◇) NH_4OH 20% v/v, (○) HNO_3 1% v/v, (*) HNO_3 1% + 10% inh. v/v.

Fig. 2 shows the weight loss as a function of sliding distance, for specimens that have not been heat treated. In this figure, the weight losses under all conditions have been plotted together, so that comparisons can be easily made. As observed, the variation of weight loss with sliding distance is linear only for the dry condition. This observation is in accordance to the Archard equation for abrasive wear [9]:

$$Q = \frac{KW}{H} \tag{1}$$

where Q is the volume of the material removed per unit sliding distance, W is the total applied normal load, H is the hardness of the softer surface (the coating compared with the material of the abrasive wheels) and K is the dimensionless wear coefficient. In the case of the other solutions, the variations of weight loss

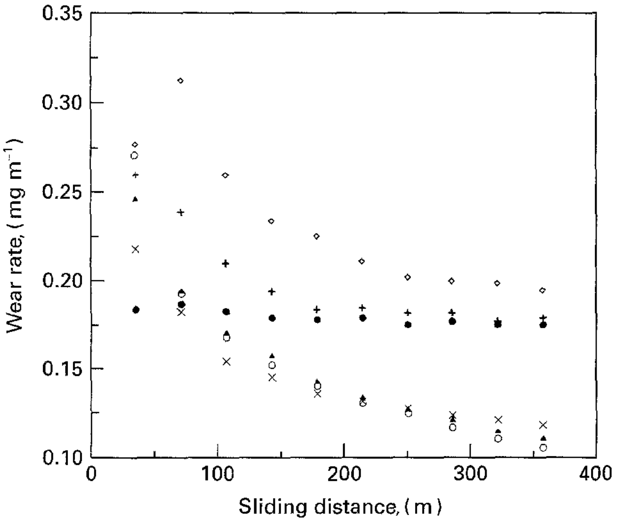

Figure 3 Wear rate as a function of sliding distance for as-received nickel-coated steel specimens, (●) dry, (+) H_2O distilled, (◇) H_2SO_4 0.01 M, (○) NH_4OH 20% v/v, (×) HNO_3 1% v/v, (▲) HNO_3 1% + 10% inh. v/v.

with sliding distance are not linear but consist of two linear segments.

Fig. 3 shows the wear rate as a function of sliding distance during the above wear experiments. The wear rate was calculated according to the formula:

$$\text{wear rate} = \frac{\Delta m}{L} \tag{2}$$

where Δm is the total weight loss at a value of the sliding distance and L the total sliding distance.

A common behaviour of the specimens is observed for the tests performed under the dropping of various solutions. The wear rate is highest at the beginning of the tests, decreasing to lower values as the sliding distance increases. For the distilled water and the H_2SO_4 solution, the wear rate is seen to stabilize before the end of the test. This tendency of the wear rate might be attributed to the fact that the surface of the coating contains more defects and irregularities than its interior, leading to higher corrosion and mechanical wear rates respectively in the first stages of the wear experiment.

Corrosion tests of the nickel coating have shown that the corrosion rate is highest in the HNO_3 and HNO_3 + inhibitor solutions, takes its lowest values for the distilled water and has intermediate values for the H_2SO_4 and NH_4OH solutions [10].

From the above figure, after the first 100 m of sliding distance, it is observed that the highest wear rate is seen for the case of H_2SO_4 solution. The wear rate during the experiment with the dropping of distilled water is similar to the wear rate under dry conditions, while the wear experiments with the dropping of the other three solutions, give similar wear rates of lower values than the dry conditions.

During the corrosive wear experiments under the action of the H_2SO_4 solution and the distilled H_2O, the corrosion product formed on the surface of the nickel coating (as corrosion tests have shown), is removed easily by the abrasive particles, due to the defects in the corrosion product (e.g. cracks and pores) and its poor adhesion to the coating, leading to a higher wear rate than in the case of dry conditions under the same load.

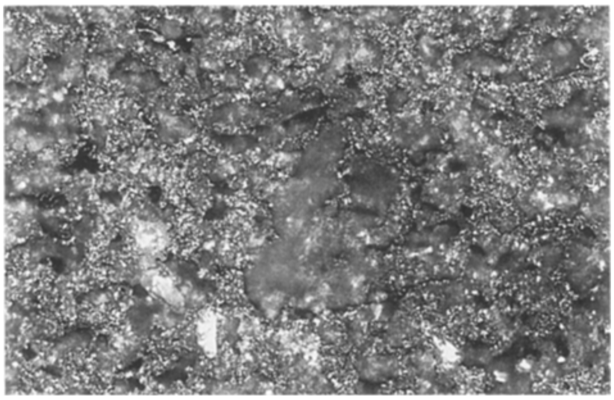

Figure 4 The surface of a wheel immediately after the end of a wear test with the dropping of HNO_3 solution. (×30)

In the case of HNO_3 and HNO_3 + inhibitor solutions, the values of wear rate are considerably lower than in the previous conditions. As has been stated in a previous paragraph, corrosion tests of the nickel-coated steel specimens have shown that nickel is less resistant to these solutions [10]. During the corrosion tests, the voltage values of the specimens against a SCE reference electrode were measured versus time. The continuous decrease of voltage with time for the two above solutions, showed an increasing corrosion rate, leading to the conclusion that the corrosion product formed is not precipitating on the nickel surface protecting it. During the wear tests the corrosion rate is further accelerated by the abrasive action of the SiC particles, which supply nickel particles with fresh surfaces which have a high tendency to react with the solutions and form additional corrosion products. A large amount of wear debris is formed at the beginning of the test in this way. The debris formed by the above suggested mechanism, either adheres to the silicon carbide particles of the wheels, decreasing their angularity and, thus, decreasing their abrading power [11] or accumulates in the spaces between the SiC particles carrying part of the applied load, reducing the amount of final wear.

Fig. 4 shows the surface of a wheel immediately after the end of a wear test with the dropping of HNO_3 solution. It is observed that the surface of the wheel is indeed partially covered by the wear debris as has been suggested in the above paragraph.

Examination of the wear debris in the optical microscope has proven that a fraction of the debris material between the wheels and the specimens is the result of the corrosive action of the solutions on the rubber wheels. The highest fraction of debris arising from corrosion action on the rubber wheels was observed for the case of the NH_4OH solution. The debris from the wheels contributes to the decrease in wear rate during the tests by carrying part of the applied load and by preventing direct contact between the SiC particles and the surface of the coating. The role of this kind of debris may be very important in the case of the

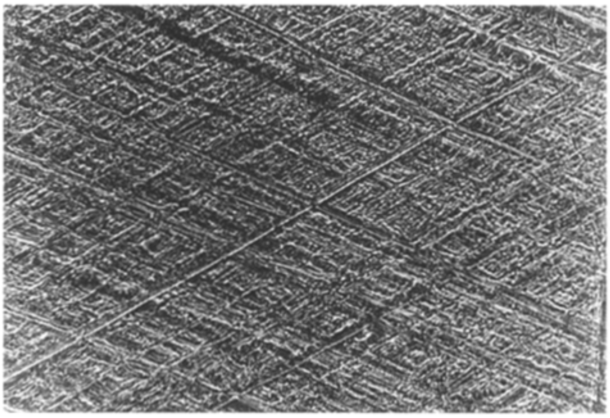

Figure 5 The surface of an as-received nickel coating in the centre of the wear track after 358 m sliding distance with the dropping of distilled H_2O. (× 67)

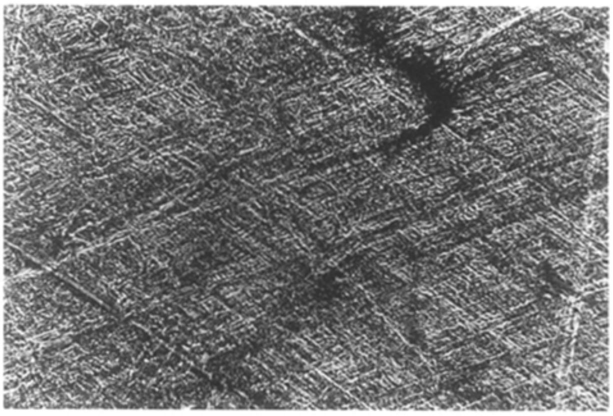

Figure 6 The surface of an as-received nickel coating in the centre of the wear track after 179 m sliding distance with the dropping of HNO_3 1% v/v solution. (× 42)

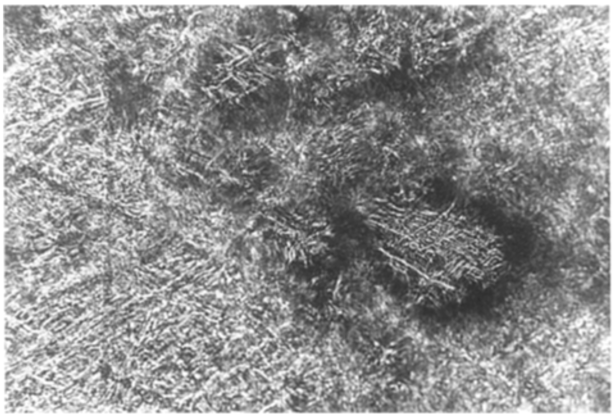

Figure 7 The surface of an as-received nickel coating at the periphery of the wear track after 179 m sliding distance with the dropping of HNO_3 1% v/v solution. (× 67)

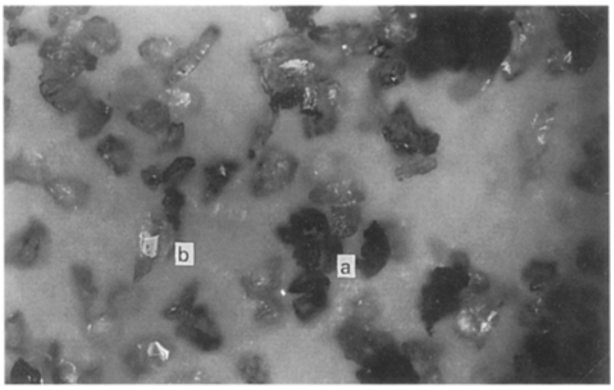

Figure 8 Optical micrograph of the wear debris collected after the wear experiment of an as received specimen under dry conditions and 5 N applied load, (a) particle from the abrasive wheels, (b) nickel particle. (× 30)

NH_4OH solution, where the lowest values of wear rate are observed, although the corrosive action of the above solution is less severe than the solutions of HNO_3.

Fig. 5 shows the surface in the centre of the wear track after a 358 m sliding distance with the dropping of distilled H_2O. The surface of the worn specimen exhibits a series of crossed grooves, each of which was produced by deformation of the material by an individual silicon carbide particle from the abrasive wheels. Severe corrosion of the surface is not observed. The last figure suggests that the material is removed by a chip being cut; this only occurs if the attack angle, i.e. the angle between the working surface of the particle and the direction of sliding, is greater than a critical angle [12, 13]; if not, the abrasive particle ploughs the surface of the specimen. The observed grooves can be attributed to the ploughing action of the abrasive particles.

Figs 6 and 7 show the surface in the centre and at the periphery of the wear track respectively, after a 179 m sliding distance with the dropping of HNO_3 solution. The grooves in the centre of the track are less intense than in the case of H_2O while the corrosion is more severe, particularly at the pheriphery of the track.

Examination of the X-ray diffraction spectra of the wear debris produced in each test showed that diffraction peaks of silicon carbide and nickel oxides were detected in every debris, while nickel as metal was only found in the debris produced after the corrosive wear experiments of nickel coatings in the H_2SO_4, HNO_3 and HNO_3 + inhibitor solutions.

Fig. 8 shows the wear debris collected after a wear experiment of an as-received specimen under dry conditions and a 5 N applied load. A detailed examination of the wear debris showed the presence of silicon carbide and nickel particles. Agglomerates of nickel and silicon carbide particles were not found under dry conditions, but this is not the case for the wear experiments with the dropping of the solutions.

3.2. Heat-treated specimens

The microhardness values of heat-treated specimens as a function of depth from the coating surface were measured. The microhardness of the coating has decreased considerably after the heat treatment, to an average value of 140 HV (140 $kg\,mm^{-2}$). The microhardness of the substrate is now uniform with depth, taking intermediate values (in relation to the range of values for the as-received specimen).

The changes in microhardness are the result of the heat treatment of the specimen. Under the chosen conditions (temperature and time) of the heat treatment process, "baking" of the specimen took place [14, 15]. A fraction of the hydrogen trapped in

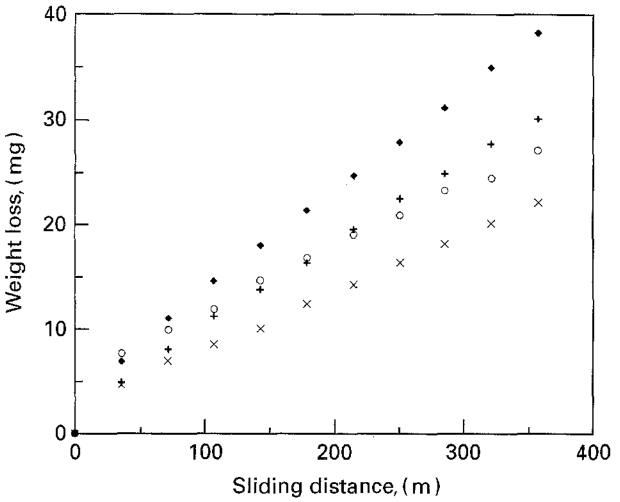

Figure 9 Weight loss as a function of sliding distance for heat-treated nickel-coated steel specimens, (◆) dry, (+) H_2SO_4 0.01 M, (O) NH_4OH 20% v/v, (×) HNO_3 1% v/v.

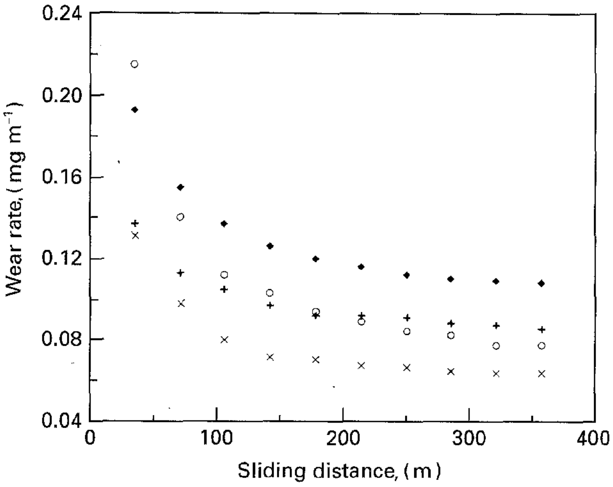

Figure 10 Wear rate as a function of sliding distance for heat-treated nickel-coated steel specimens, (◆) dry, (+) H_2SO_4 0.01 M, (O) NH_4OH 20% v/v, (×) HNO_3 1% v/v.

interstitial sites in the coating diffused to the atmosphere, leading to the decrease in coating hardness.

Fig. 9 shows the weight loss as a function of sliding distance for the heat-treated specimens. As in Figure 3, the weight losses under all conditions have been plotted together. It is observed that the weight loss of the heat-treated specimens is less than the weight loss of the as-received specimens under the same conditions. The decrease in coating hardness is not accompanied by an increase in weight loss.

The above result may be due to the fact that the abrasive wear resistance of a metallic material does not depend only on its hardness. An important factor affecting the wear rate is the ratio E/H where E is the Young's modulus and H is the hardness of the material. A low value of this ratio leads to a low critical attack angle δ_c [16]. SiC particles on the abrasive wheels have a certain distribution of attack angles. The fraction of the SiC particles that have an attack angle greater than the critical attack angle θ_c, will favour deformation by cutting rather than ploughing, leading to the removal of material. In the case of the heat-treated specimens, the decrease in hardness leads to an increase in E/H (E varies insignificantly after the heat-treatment processes). The increase in the above ratio will be followed by an increase of the critical attack angle θ_c [16]. This means that for a constant distribution of attack angles between the SiC particles, the fraction of those that have an attack angle $\theta > \theta_c$ and hence remove material by cutting decreases, leading to a decrease in the weight loss.

All the specimens show a common behaviour under the applied conditions. The variation of weight loss with sliding distance seems not to be linear but to consist of two linear segments. The change in the slope takes place after only 36 m of sliding distance. The observed deviations from a linear relation between weight loss and sliding distance may be attributed to the effect of corrosion on the wear mechanism.

Fig. 10 shows the wear rate as a function of sliding distance for the heat treated specimens. The highest wear rate is observed for the dry conditions, while the experiments with the dropping of solutions give similar values of wear rates, with the highest value for the H_2SO_4 solution and the lowest for the HNO_3 solution.

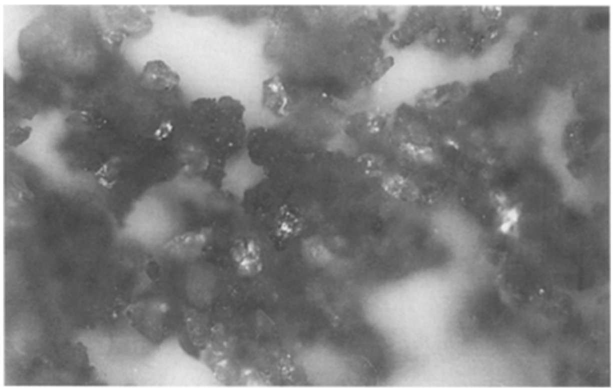

Figure 11 Optical micrograph of the wear debris collected after the wear experiment of a heat treated specimen, with the dropping of NH_4OH solution and 5 N applied load. (× 30)

Corrosion tests of the heat-treated nickel coatings have shown that the corrosion rates are lower in this case than the corrosion rates of the as-received coatings for the three solutions examined. The highest corrosion rate is observed for the HNO_3 solution and the lowest for the NH_4OH solution [10].

Again all the specimens show a common wear behaviour. The wear rate is higher at the beginning of the wear test decreasing to lower values and finally stabilizing for the last 200 m of the test. The possible origins of this behaviour have already been discussed in the case of as-received specimens.

The low values of wear rate can be attributed to its dependence on both the fraction of the abrasive particles which deform the material by cutting rather than ploughing and their geometry. As has already been discussed, a smaller fraction of abrasive particles deform the material by cutting for heat-treated specimens, leading to a decrease in the wear rate. A further decrease in the wear rate in the case of wear tests under the presence of different solutions, takes place due to the presence of wear debris as a corrosion product.

The X-ray diffraction spectra of the wear debris produced in each test show that diffraction peaks of silicon carbide, nickel and NiO were detected in every debris.

Fig. 11 shows the wear debris collected after the wear experiment of a heat-treated specimen, with dropping of NH_4OH solution. A large number of agglomerates were found in the debris collected after wear experiments with dropping of the examined solutions for both heat-treated and as-received specimens, indicating that the physical action between the debris, the wheels and the solution, possibly aids the formation of the agglomerates.

4. Conclusions

The abrasive wear of nickel coating on mild steel substrates under corrosive conditions was studied and the main conclusions are given below.

(1) The wear rate of both non-heat-treated and heat-treated specimens, was found to depend upon the nature of the corrosive solution. The effect of corrosion on the wear rate was synergetic for some solutions, while for the other it was antagonistic, with respect to the wear rate for the dry conditions. It was found that solutions that were highly corrosive for the nickel-coated specimens led to a decrease in the final wear rate, due to the protecting action of the debris formed by the combined action of wear and corrosion. Solutions that were less corrosive for the nickel-coated specimens were found to increase the wear rate.

(2) The wear rates of the heat-treated as well as non-heat-treated specimens, were noticed to be higher at the beginning of the wear experiments, decreasing to lower values as the sliding distance increases.

(3) The hardness of the nickel coating was found to decrease after the heat treatment process.

(4) The wear rates of the heat-treated specimens were observed to be lower than those of the non-heat-treated specimens, under indentical experimental conditions.

(5) The wear debris was analysed and found to consist of nickel, silicon carbide particles and particles of corrosion products. Agglomerates of nickel and silicon carbide particles were observed to form in the case of the wear experiments with the dropping of various solutions, while they were not observed to form under dry conditions.

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Received 21 March 1995
and accepted 15 December 1995