region of the present alloy and improve the corrosion resistance. Moreover, Zr is known to stabilize the passive film formed in Cu alloys,[16] which would also attribute the enhanced corrosion resistance of the present alloy.

As shown in Figure 2, a small degree of intergranular corrosion was observed in Cu-6Ni-2Mn-2Sn-2Al-0.1Zr alloy. In order to understand the tendency for the intergranular corrosion in the Zr containing specimen, the grain boundary areas of the alloys, with and without Zr addition, were examined by using a high-magnification SEM. As shown in Figure 4, fine precipitates were observed only in the Zr-added specimen along the grain boundaries. Among the several possible mechanisms, either a galvanic type of corrosion between these fine precipitates and matrix or an oxidization of the fine precipitates may be responsible for the intergranular corrosion in Cu-6Ni-2Mn-2Sn-2Al-0.1Zr alloy, even though the quantitative analysis of the precipitate was not conducted in the present study.

During swaging, a mechanical refining and solution treatment further reduced the Sn segregation.[8] As a result, the resistance to corrosion of the alloy was improved with swaging, and the corrosion mode changed from general corrosion to pitting type of corrosion, as shown in Figure 2, regardless of Zr addition. The number and depth of pits were substantially decreased with Zr addition, which is again believed to be due to the reduced Sn segregation. The EDX analysis indicated that the Sn content in the pit area was relatively higher than that in the matrix. The XRD analysis also showed that the surface of the present alloy was covered with Al_2O_3 passive film, regardless of Zr addition (Figure 5). It is therefore speculated that the pits are formed through the breakage of Al_2O_3 films by the attack of Cl^- in aqueous NaCl solution and propagate through the relatively Sn-rich regions in the matrix.

The stress corrosion cracking study in Table I reflects the trends observed in the potentiostatic test of Cu-6Ni-2Mn-2Sn-2Al-xZr alloys. For those without the Zr addition, a severe interdendritic attack in its as-cast condition and a pitting corrosion in as-swaged condition substantially lowered the tensile elongation after exposure. The Zr-added specimens, on the other hand, did not show any reduction in tensile elongation after exposure, despite the small degree of intergranular corrosion and pitting corrosion. As demonstrated in Figure 6, which shows the SEM side views of 60 pct swaged Cu-6Ni-2Mn-2Sn-2Al-xZr alloys after exposure and tensile test, well-developed cracks originated from corrosion pits were frequently observed in the Zr free specimen. Even though the pits were often observed in the Zr-added specimen, they had not grown to form cracks that participate in the tensile fracture process.

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A New Hybrid Process for Surface Modification by Combining Brush Plating with Nitrocarburizing

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In the past, electroplated hard chromium coatings have been very widely used to improve the corrosion and wear resistance of machine parts. Because of the cost and hazard issues associated with the Cr plating process, coatings based on a number of Ni-based alloys (*e.g.*, Ni-W) have been proposed as replacements for Cr electroplate.[1,2,3] However, these proposed replacement technologies have not been generally successful in improving wear resistance because of their low hardness.

For example, brush-plated Ni-W has a hardness of 495 VHN, which compares with 819 VHN for tank-plated hexavalent Cr.[4] Conversely, it has been suggested that a coating based on a metal-matrix composite with ceramic particles as reinforcement phases should exhibit much better wear resistance.[1,5] The wear resistance of a Ni-Co-ZrO_2 composite coating was shown to be 1.81 times greater than that of an unreinforced Ni-Co coating because the ZrO_2 particles readily bear the operating load and the Ni-Co matrix acts to hold the particles in place.[6]

Unfortunately, only a few composite materials are known that can be formed by codepositing alloys and ceramic particles.[6] In high-temperature coating processes, the ceramic particles may be partially melted during the coating processes and may not be uniformly distributed in the final deposits.[7] To overcome these two problems (the low hardness/wear resistance and nonuniformly distributed ceramic particles), a new hybrid coating process, in which an alloy is first coated on substrates and ceramic particles

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Table I. Nominal Compositions of the Steels (in Weight Percent)

Elements	C	Cr	Mo	V	Si
Substrate steel	0.68 to 0.78	6.5 to 7.5	1.90 to 2.25	0.7 to 2.2	0.7 to 1.2
Counterpart steel	0.9 to 1.0	11.0 to 13.0	0.2 to 1.2	0.4 to 0.6	—

Table II. Composition of the Ni-W Brush Plating Solution

Composition	Content (g/L)
$Ni_2SO_4 \cdot 7H_2O$	393
$Ni_2WO_4 \cdot 2H_2O$	23
H_3BO_3	31
$H_3C_6H_5O_7 \cdot H_2O$	42
Na_2SO_4	6.5
$CoSO_4 \cdot 7H_2O$	2
NaF	5
CH_3COOH	20 mL/L
CHOOH	35 mL/L

are formed *in situ* in the deposit during a subsequent heat treatment, is proposed. A hybrid process may be defined as the application of two individual surface modification processes to engineer the surfaces of components in order to produce combined mechanical, metallurgical, and chemical properties that cannot be obtained by any individual process.[8] One of the examples is to use nitrided substrates for hard coating to achieve higher wear resistance and better adherence of the coating.[9]

To prove the concept of the new hybrid process, a relatively inexpensive coating process, brush plating, and a relatively simple alloy system, Ni-W, were used. Brush plating, which allows metal deposition onto selected areas, is a variation of electroplating.[10] Its process characteristics make it suitable for many applications where normal electroplating cannot supply the desired result or is too costly.[11] Brush-plated Ni-W alloys have excellent soundness and corrosion resistance but much lower hardness compared with Cr alloys.[1] Nitrocarburizing has been selected as the second part of the hybrid process, causing nitride and carbide particles to form in the brush-plated coating. Therefore, the objective of this work was to develop a combined brush plating and nitrocarburizing process to produce composite coatings with improved wear resistance compared to simple Ni-W alloy coatings. The chemical composition, microstructure, and wear resistance of the composite coatings produced by this hybrid process were studied.

The nominal compositions of the substrate material to be coated (a cold work die steel) and the counterpart steel for wear testing (a 12CrMoV cold work tool steel) are listed in Table I. The composition of the Ni-W brush plating solution is listed in Table II. The composition (in weight percent) of the brush-plated deposits was 98.5 to 99.2 Ni, 0.6 to 1.2 W, and 0.05 to 0.3 Co. The specimens used for microhardness testing, X-ray diffraction (XRD) and scanning electron microscopy (SEM)/energy dispersive x-ray spectroscopy (EDS) analysis, were of rectangular shape (25 × 50 mm and 10-mm thick). The wear specimen used for wear testing was cylindrical, of 45-mm outside diameter, 16 mm inside diameter and 10 mm thickness, with the coating on the outer rim. The substrate steel for the wear specimen was heat treated by quenching from 1120 °C into oil and tempering

twice at 540 °C for 60 min to produce the desired core mechanical properties. The counterpart specimen for use in the wear test, which was identical in geometrical design as the wear specimen, was heat-treated by quenching from 840 °C into oil and tempering twice at 240 °C for 60 min.

In this work, the sequence of surface processing involved surface machining, electro-cleaning, cold water flushing, electro-activating with a strong activating solution, cold water flushing, electro-activating with a weak electro-activating solution, cold water flushing, brush plating, cold water flushing and nitrocarburizing. The applied voltage during electro-cleaning, electro-activating, and brush plating was 14 to 16, 12 to 14 and 10 to 12 V respectively. In electro-cleaning and brush plating, the specimen was the cathode; the reverse polarity was used in electro-activating. The moving velocity of the brush electrode was 6 to 8 m/min. The temperature of nitrocarburizing was 540 °C, which is the same as the tempering temperature of the substrate steel. The nominal composition (in volume percent) of the nitrocarburizing atmosphere was 52 NH_3, 38 N_2, and 10 CO.

The XRD analysis using a Dmax/Rc type diffractometer with Cu K_α radiation was performed on the coating surface to identify the phases present. Surface morphology of the wear-tested coatings was observed using SEM. The EDS analysis was used to investigate the element distribution across the coating/substrates interface. Vickers hardness of the coating surface was determined with a load of 150 gf and a loading time of 20 seconds; each hardness value represented an average of ten tests. Wear tests were carried out using an M-200 type wear test machine, with a wheel on wheel configuration, a load of 2000 N, and an oil lubricant at a drip rate of 10 mL/min. The rotation speeds of the upper specimen wheel and lower counterpart wheel were 400 and 360 rpm, respectively, so that there was a 10 pct sliding occurring between the two contact surfaces.

The XRD spectra of coated surfaces in Figure 1 clearly indicate that new phases have formed in the Ni matrix during nitrocarburizing and they have been identified as WN and WC. Three of the most intense peaks of WC and WN are identified, *i.e.*, the peaks at $2\theta = 31.4$, 35.6, and 48.2 resulting from the (001), (100), and (101) planes of WC, and the peaks at $2\theta = 36.9$, 41.8, and 57.0 resulting from the (001), (100), and (101) planes of WN.[12] It follows that the hybrid two-stage process has created a composite coating (with Ni as matrix and WN and WC as reinforcement particles). Hardness testing indicated that this composite layer has a microhardness of 1229 ± 14 HV compared with that of 473 ± 11 HV for as-plated deposit and of 826 ± 12 HV for the substrate steel.

Comparisons of the wear rates for the steel substrate material with and without surface modifications are shown in Figure 2. Clearly, either brush plating or nitrocarburizing can improve the wear resistance of the substrate material. However, a combined process comprising brush plating and nitrocarburizing can further improve the wear resistance
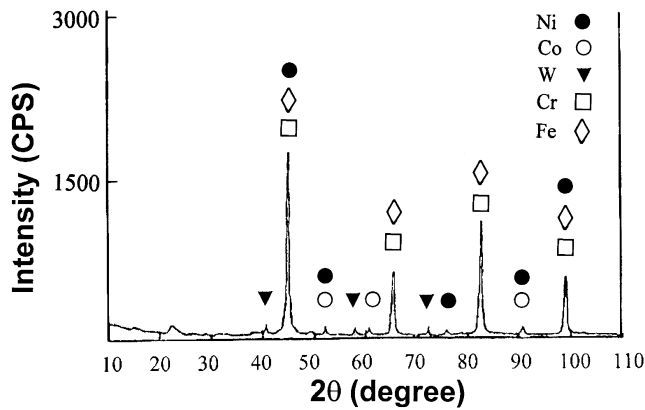
(a) As-plated
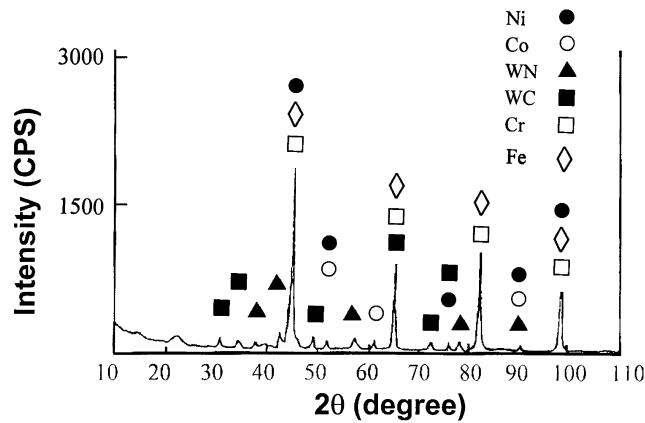
(b) After nitrocarburizing

Fig. 1—(a) and (b) X-ray diffraction spectra of brush-plated coating surface before and after nitrocarburizing.
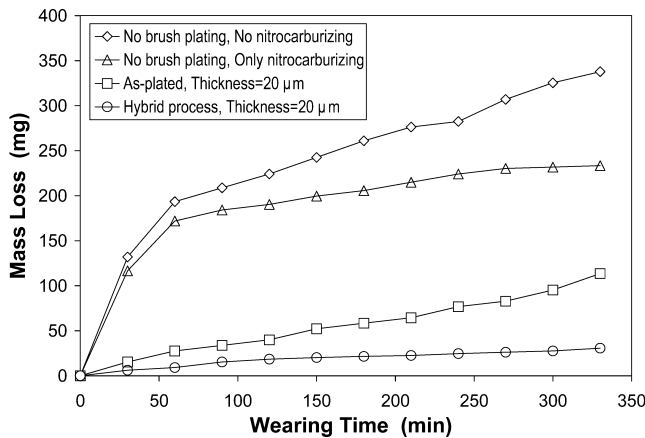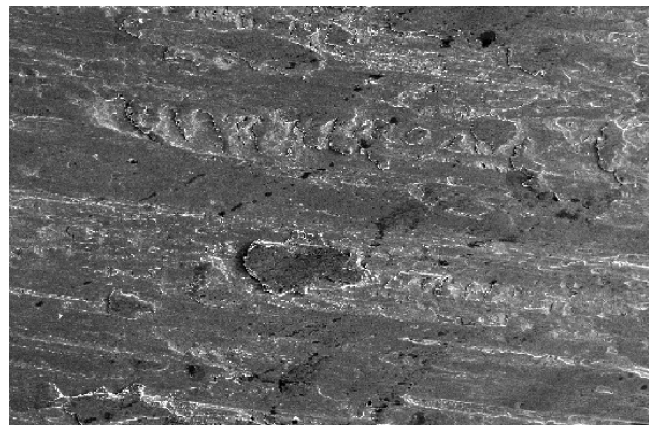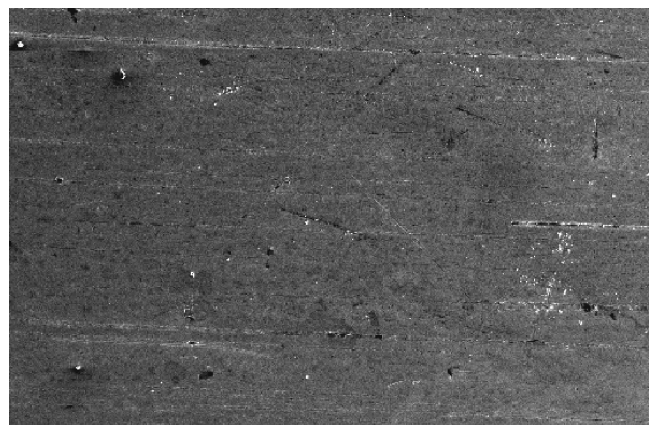

Fig. 2—Wear rate of test samples with and without surface modification.

(a) As-plated

(b) After nitrocarburizing

Fig. 3—(a) and (b) SEM micrograph of wear tracks on brush-plated coating surfaces.

compared with substrates modified by either individual surface modification technique. This can also be seen from the morphologies of the wear-tested surfaces (Figure 3), where much smaller wear marks were produced on the coated and nitrocarburized surface than on the as-plated coating surface.

The improved wear resistance of the coated and nitrocarburized surface is fully consistent with the formation of a composite coating containing particles of WC and WN. Such a material can resist wear effectively because of the high hardness of the ceramic particles. The Ni matrix provides a tough and ductile base to hold these particles in place. In addition, the heat treatment during nitrocarburizing may produce metallurgical bonding at the coating/substrate interface, which was only quasi-mechanically bonded in the brush plating process (Figure 4). This enhancement of the bond could also be inferred from the interdiffusion of Ni and Fe across the plating/substrate interface during nitrocarburizing (Figure 4). A 10-μm-thick conversion layer with uniformly distributed ceramic particles at about 0.5 μm in size was produced when the coating thickness was about 20 μm and the holding time for nitrocarburing was 80 minutes at 540 °C.

Preliminary experiments were also performed to investigate the optimum coating thickness and nitrocarburizing time. As shown in Figure 5(a), the optimum coating thickness was found to be 20 μm. Clearly, a minimum coating thickness is required to change the structure and wear properties of the substrate surface. However, if the brush-plated deposit is too thick, high stresses developed in the coating due to differential thermal expansion may cause delamination of the coating, which was observed in subsequent nitrocarburizing. Figure 5(b) shows that the optimum holding
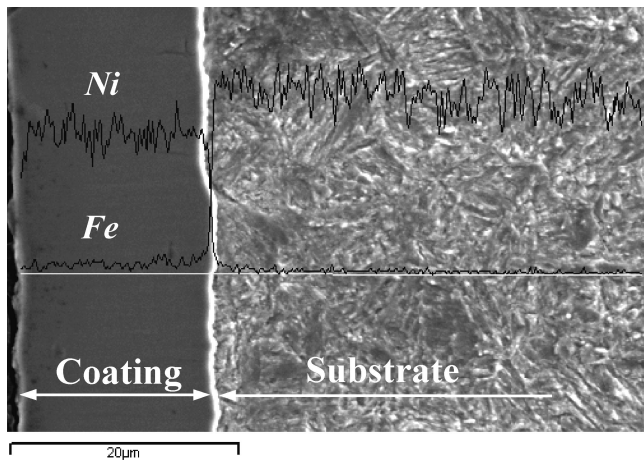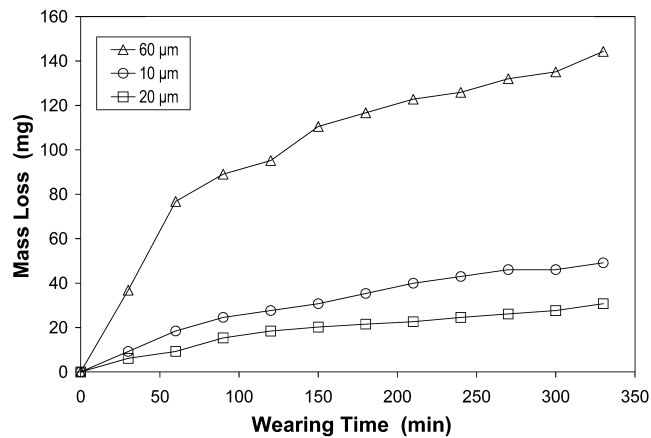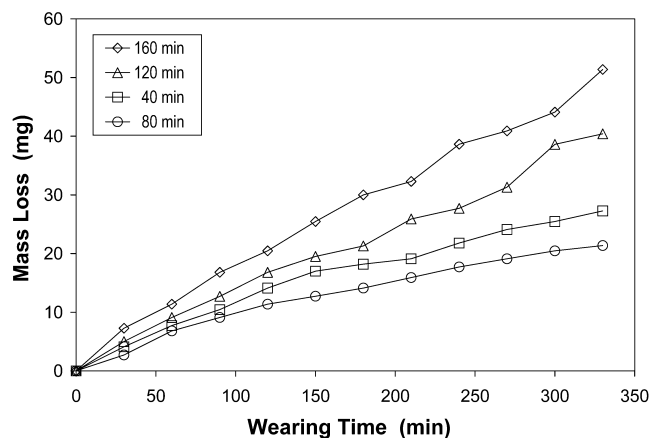
(a) As-plated
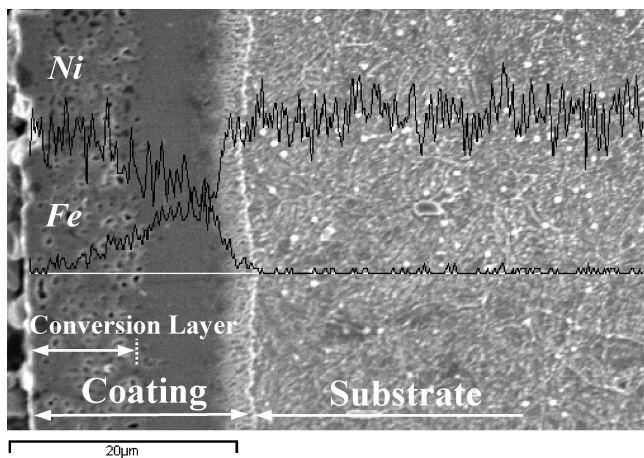
(b) After nitrocarburizing

Fig. 4—(a) and (b) Fe and Ni distribution across the coating and substrate interface. Note a 10-μm-thick conversion layer with uniformly distributed ceramic particles at about 0.5 μm in size was formed after nitrocarburizing. The coating thickness was about 20 μm and the holding time for nitrocarburizing was 80 min at 540 °C.

(a)

(b)

Fig. 5—(a) and (b) Effects of (a) coating thickness and (b) nitrocarburizing time on the wear rates.

time of nitrocarburizing at 540 °C is 80 minutes. It is believed that, if the holding time of nitrocarburizing is too short, the formation of WC and WN and the metallurgical bonding at the substrate/coating interface would not be complete because diffusion takes time. But, further work is needed to determine what contributed to the reduced wear resistance when the nitrocarburing time was too long. It is suggested that this may be due to the formation of brittle compounds in the coating layer; however, XRD analysis so far has been unable to confirm that. While this work has clearly shown that the composite coating formed by the new hybrid process can produce dramatic increases in wear resistance, further work needs to be carried out to optimize the process conditions.

In summary, a new hybrid surface modification process has been developed combining brush plating with nitrocarburizing to create *in situ* a composite coating with Ni as the matrix and WC and WN as reinforcement particles. This composite coating has shown an improved wear resistance compared with that produced by either individual surface modification technique. The improved wear resistance is consistent with the improved hardness in the composite coating and the possibly improved metallurgical bonding at the coating/substrate interface. The optimum plating thickness was found to be 20 μm and the optimum holding time for nitrocarburizing was 80 minutes at 540 °C. While this work has clearly shown that the composite coating formed by the new hybrid process is responsible for the dramatic increases in wear resistance, further work needs to be carried out to understand the effects of process conditions.

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