Corrosion of Electroless Ni-P-Cu Alloy In an Atmospheric Gas Chamber

By E. Yang, S.K. Doss and P. Peterson

Electroless Ni-P-Cu on Al-Mg alloy substrates became increasingly rough when successive 15-µm-thick deposits were produced. Corrosion rates in an atmospheric gas chamber correlated with increasing surface roughness, but became almost constant when this roughness effect was factored out. Weight gain during the corrosion test was 0.23 to 0.28 $\mu g/cm^2/hr$, slightly lower than that of permalloy in the same environment. Although the $HCl:SO_2$ ratio was 1:100 in the gas flowing to the corrosion chamber, the ratio found in corrosion products was 1:4, indicating a greater reaction rate for HCl.

Corrosion resistance and magnetic properties account for many applications of electroless nickel-phosphorus alloy deposits. Nickel-phosphorus-copper alloy is Of special interest because of its magnetic characteristics. Corrosion resistance aspects of the ternary alloy are discussed in this report.

Experimental Procedure

Electroless Ni-P-Cu alloy was deposited on surface-ground and polished Al-Mg alloy (AA 5086) samples after alkaline cleaning, conditioning in an acid deoxidizer and double zincating in a proprietary acid bath. The proprietary electroless nickel alloy plating bath was operated at 93° C and contained at the beginning of each series of plating experiments 40 g/L of sodium hypophosphite, 7 g/L of nickel and 20 mg/L of copper. The amorphous deposits contained, on the average, 88 percent nickel, 11.3 percent phosphorus and 0.7 percent copper. Knoop hardness was 600 kg/mm', measured with a 25-g load.[1] The deposits were smooth and bright and free of defects.

The surfaces of the deposits were examined microscopically at a magnification of 500X. Surface roughness
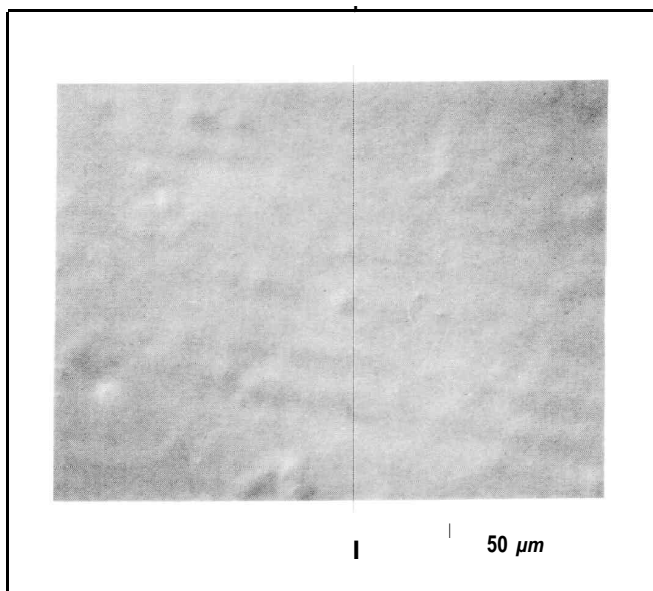

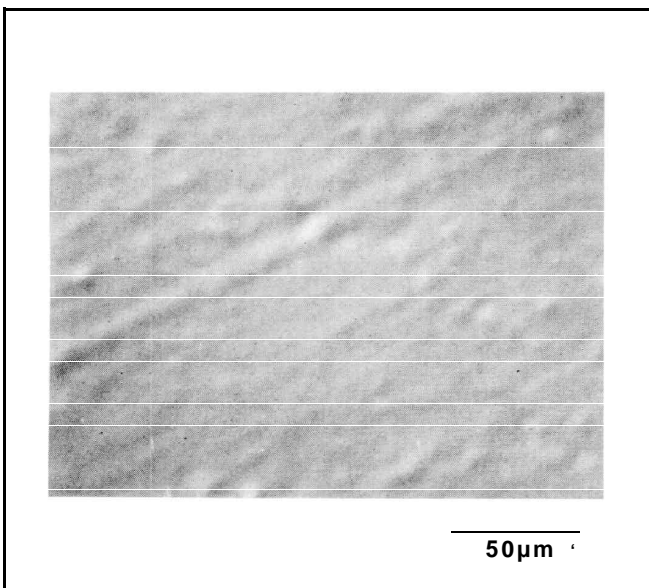Fig, 2—SEM photograph of Ni-P-Cu deposit from experiment 5.

Fig. 1—SEM photograph of Ni-P-Cu alloy deposit from experiment 1 on Al-Mg substrate.
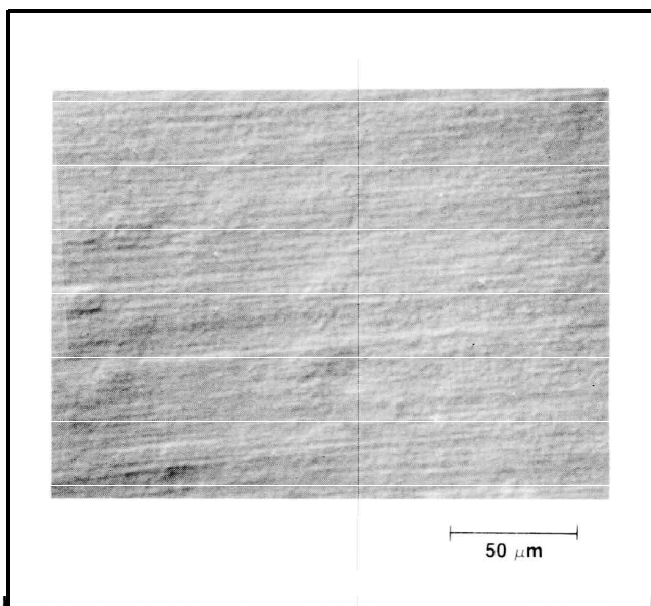

Fig. 3—SEM photograph of Ni-P-Cu deposit from experiment 10.

was measured with an interferometer*. Root-mean-square (rms), average roughness (Ra) and peak to valley (P-V) values are reported.

Accelerated corrosion tests were conducted at 25° C in an atmospheric gas chamber' with a relative humidity of 70 percent and a controlled gas flow with a face velocity of 0.5 m/see. The gas consisted of air carrying 500 ppb NO_2, 300 ppb SO_2, 40 ppb H_2S and 3 ppb HCl. Samples were exposed for up to 10 days. Soluble corrosion products were removed from the surfaces of representative electroless deposits by immersion in 100 mL of deionized water. Liquid chromatography was used to detect and quantify inorganic anions. Energy dispersive X-ray spectrometry (EDXS) was used to identify elements remaining on the surface of one sample after soluble corrosion products were extracted with water.

After cutting representative plated samples into small pieces, deposits were separated from the substrate by dissolving the aluminum alloy in hot, 3N sodium hydroxide solution. They were then weighed. Each 40- to 60-mg electroless nickel sample was dissolved in 2 mL of concentrated nitric acid and volumetrically diluted to 100 mL. The Ni, P and Cu contents were determined with a plasma spectrometer**. The results indicated that deposit composition was consistent during the cycle life of the bath.

The 400-L plating bath was used for a total of 30 75-min successive experiments, equivalent to three nickel turnovers. Surface area plated during each experiment was 2.3 m^2. After each experiment, 10 percent of the initial nickel content and 40 percent of the hypophosphite were added to replenish the bath. Seven samples removed during
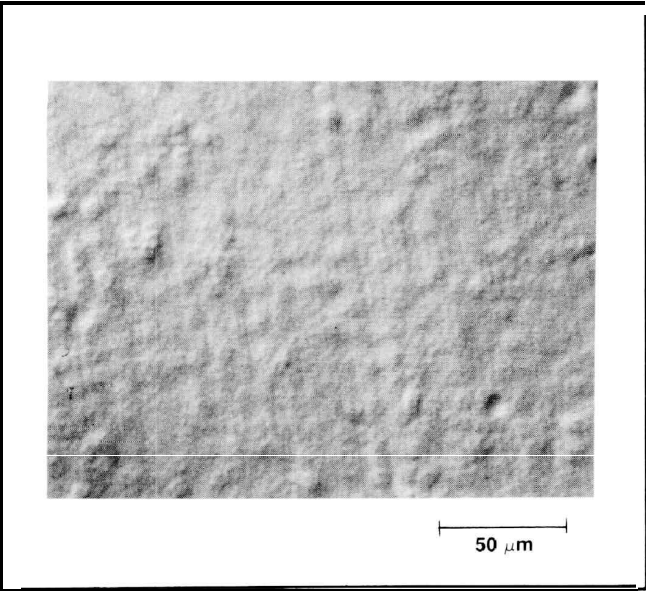
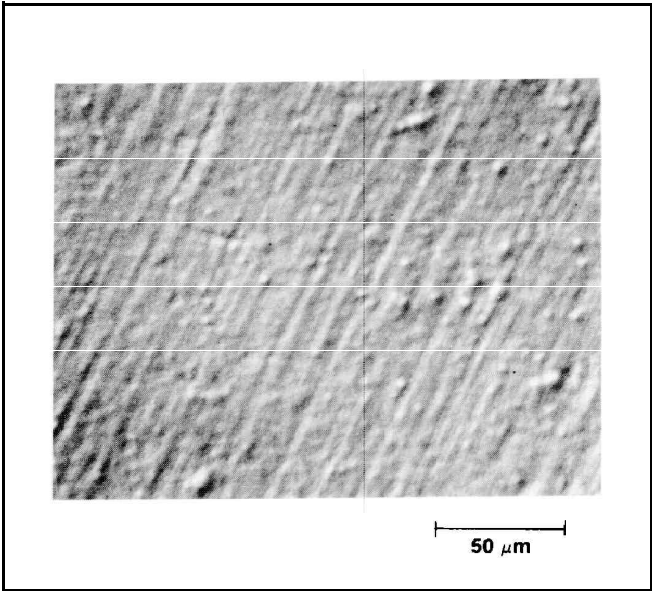Fig. 4—SEM photograph of NI-P-Cu deposit from experiment 15.

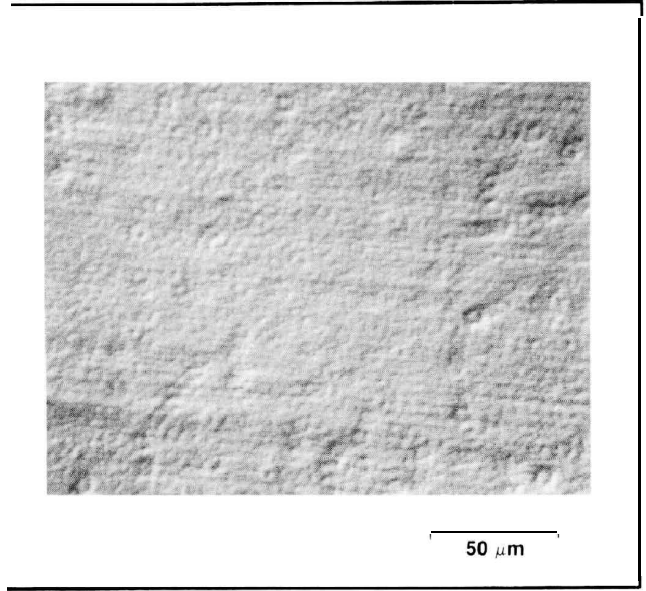Fig. 6—SEM photograph of Ni-P-Cu deposit from experiment 25.

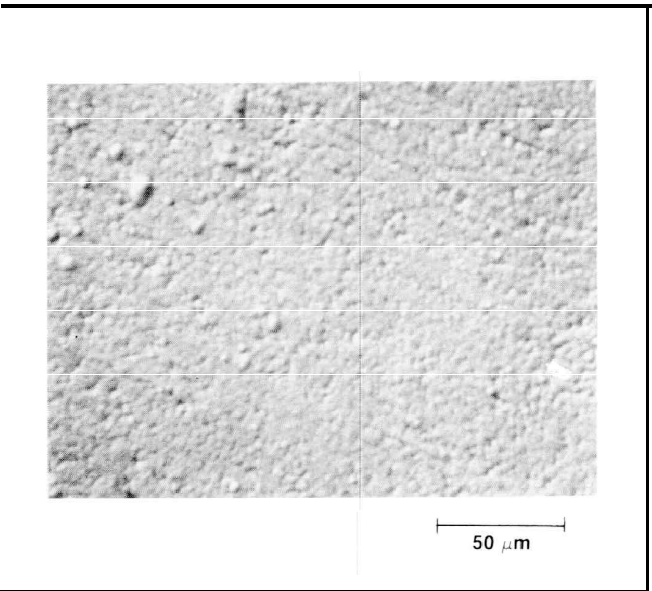Fig. 5—SEM photograph of Ni-P-Cu deposit from experiment 20.

Fig. 7—SEM photograph of Ni-P-Cu deposit from experiment 30.

experiments 1, 5, 10, 16, 20, 25 and 30 were selected for monitoring the deposition rate using a quartz resonator'. Sample deposits from these experiments also were subjected to the accelerated corrosion test.

Results and Discussion

Figures 1 to 7 show photomicrographs of the surfaces of electroless nickel alloy deposits obtained during experiments 1, 5, 10, 15, 20, 25 and 30. The experiment 5 deposit appears to have the smoothest surface; the surface from experiment 30, which shows large hemispherical micronodules, appears to be the roughest. Figure 8 data indicate increasing micro roughness with bath use. The P-V values for the first two deposits were less than the P-V value of 800 angstroms for the surface-ground aluminum alloy, indicating that the nickel alloy deposit had a slight smoothing influence. However, the first and second deposits in the series selected for surface roughness measurements had about the same rms values (100 angstroms) as the aluminum alloy substrate.

Photomicrographs of the surfaces of a deposit from experiment 1 after 2, 5 and 10 days of exposure in the corrosion chamber are shown in Figs. 9, 10 and 11, respectively. Liquid droplets were observed on the surface after the first day of exposure. he droplets grew in size and number with time of exposure. Fringes observed within the droplets indicated that they were also increasing in height. Solid corrosion products were apparent in the liquid drops after 8 days. Blisters at the edges of the plated samples also appeared after 8 days. These blisters were a result of aluminum alloy substrate corrosion through pinholes in the electroless nickel alloy.[4]

Figure 12 shows the weight gain as a function of exposure time for six plated samples from experiments 1,5, 10, 16, 25 and 30. After 2 da s, weight gains increased linearly with increasing exposure time. Weight gain after 10 days of exposure ranged from bout 0.24 to 0.28 $\mu g/cm^2/hr$ in Fig. 13. The amount of corrosion corresponding to weight gain appears to correlate with surface roughness, based on a comparison of data points in Figs. 8 and 13. For
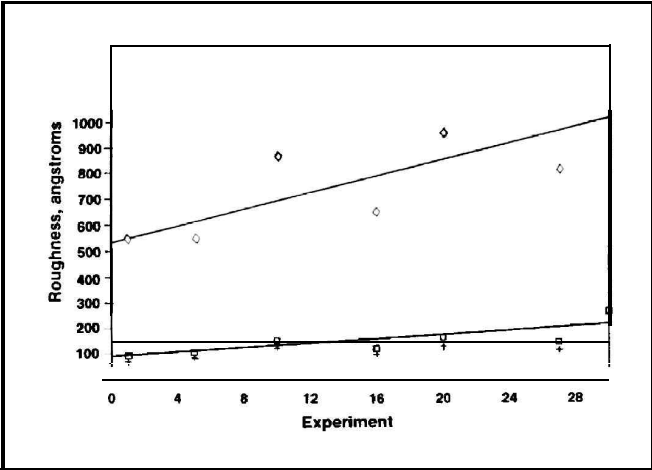

Fig. 8–Microroughness of Cu-P-Cu alloy deposits on samples from experiments 1, 5, 10, 16, 20, 25 and 30. ❑ rms + Ra; ° P-V.
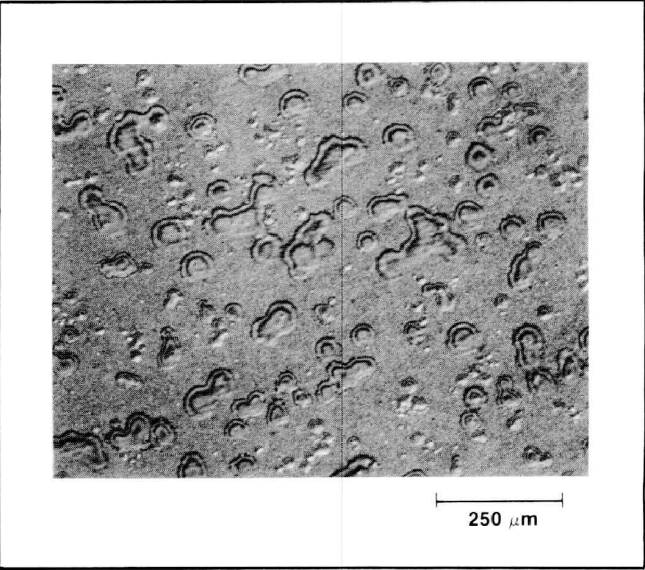

Fig. 10—Corrosion products on the Ni-P-Cu deposit from experiment 1 after 5 days of exposure in the corrosion chamber.
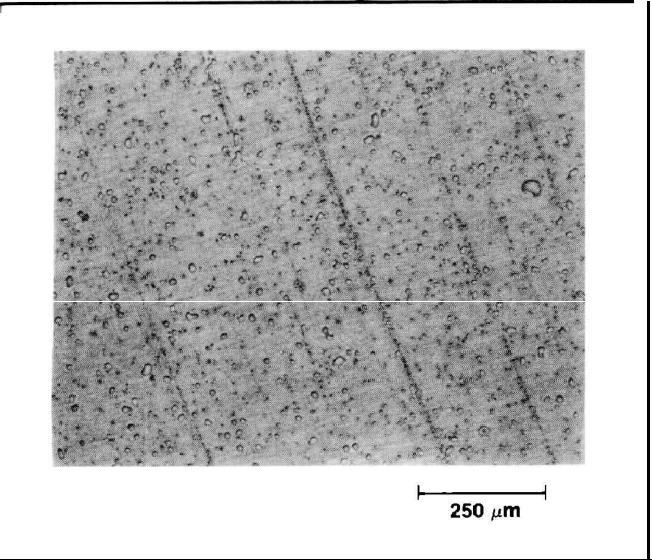

Fig. 9—Droplets of corrosion products on a Ni-P-Cu deposit from experiment 1 after 2 days of exposure in the corrosion chamber.
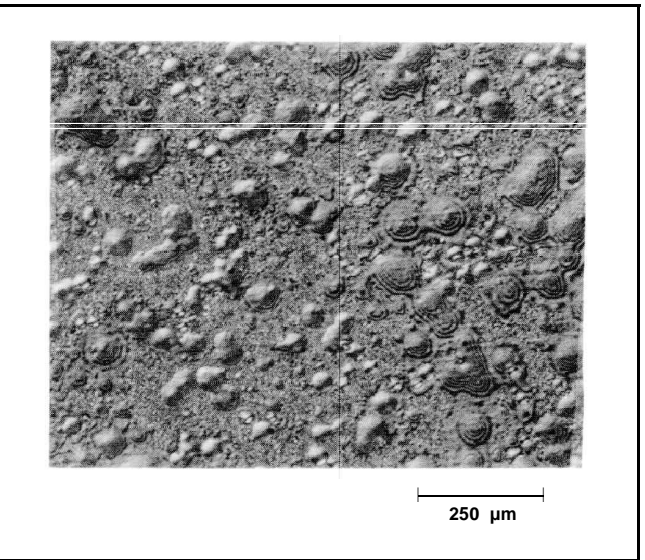

Fig. 11 —Corrosion of the Ni-P-Cu deposit from experiment 1 after 10 days of exposure in the chamber.

example, the deposit from experiment 16 not only was smoother than the experiment 10 deposit, but also had a smaller weight gain.

A direct correlation between corrosion weight gain and surface roughness is evident from the data in Fig. 14. Using a first order approximation by taking a linear regression of the data between experiments 1 to 25 for best fit, a straight line could be plotted for weight gain as a function of roughness. From the slope of this line, weight gain was normalized and the effect of roughness was factored out. When the roughness effect was eliminated, corrosion rate proved to be independent of the sequence of experiments. Figure 15 shows this independence.

Surface roughness contributes to corrosion because more surface area is available for attack. Thus the corrosion rate in terms of weight gain was higher for rougher surfaces, by comparison with smoother ones.

Chloride, nitrate and sulfate ions were the only anions detected by liquid chromatography in the water extractions from the surfaces of corroded plated samples. Extractions from deposits produced in experiments 5,10,16,20,25 and 30 contained 68 ±2 mole percent sulfate ions, 17 ±2 mole percent chloride ions and 16 ±2 mole percent nitrate ions. The extraction of the corroded deposit from the first experiment contained a little less sulfate, slightly more chloride and slightly more nitrate ions. Although the ratio of SO_2 to HCl in the gas flow into the corrosion chamber was approximately 100:1, the concentration of sulfate ions in the water extractions was only four times the chloride ion concentrations. Thus the chloride ions reacted more aggressively with the Ni-P-Cu alloy than with SO_2. The reaction rate of NO_2 was even lower, in view of its high concentration (500 ppb) in the gas flow.

Other than nickel and phosphorus, sulfur was the only element detected by EDXS on a deposit produced during experiment 20, after immersion in water to remove soluble products. The spectrogram is shown in Fig. 16. The sulfur exists in the form of water insoluble nickel sulfide compounds.

Deposits obtained during experiments 1, 5, 10, 16, 20, 25 and 30 contained 88 or 89 percent nickel, 11 or 11.5 percent phosphorus and up to about 1 percent copper. Variations within these ranges did not correlate with experiment number.

Summary

An increase in surface roughness was observed as the nickel-phosphorus-copper alloy plating bath was aged. This roughness contributed to an increase in the rate of corrosion when plated aluminum was exposed in the
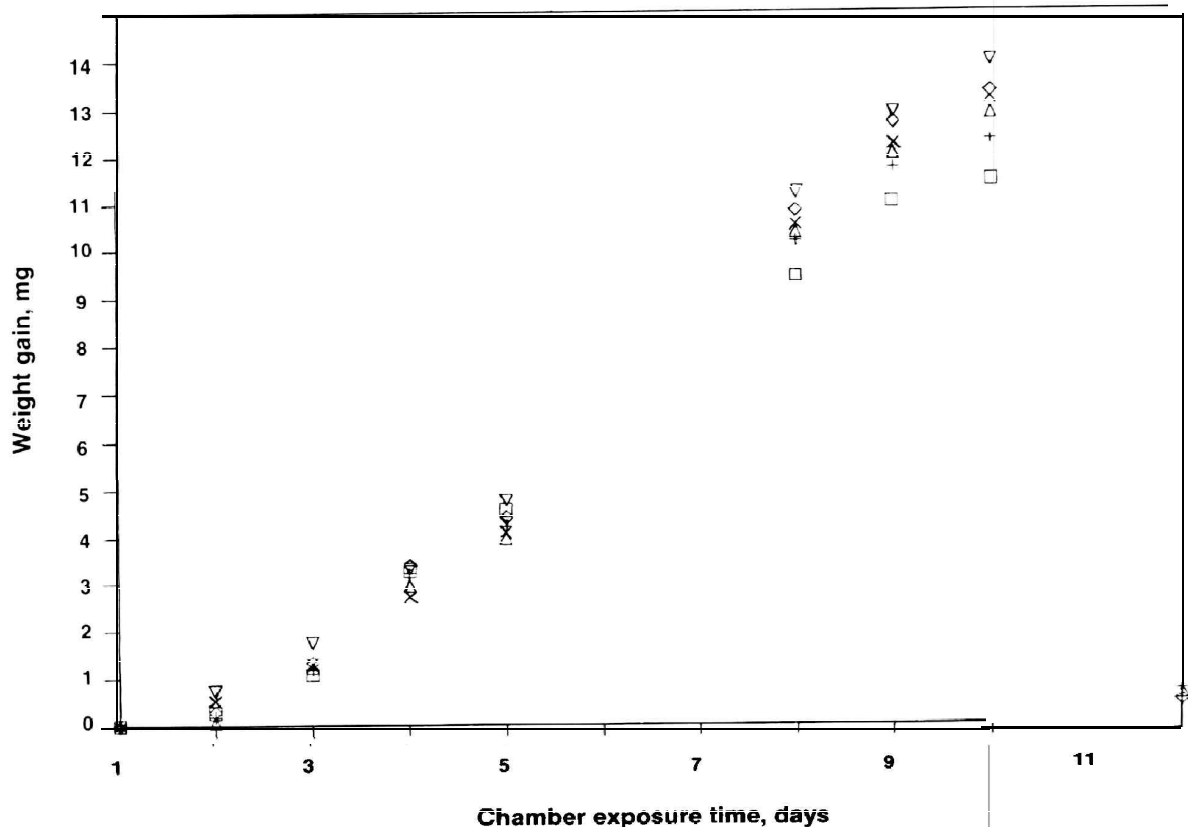
Fig. 12—Weight gain resulting from corrosion as a function of exposure time in the corrosion chamber. □ = experiment 1, beginning of first metal turnover + = experiment 5; ◊ = experiment 10; ◊ = experiment 16; X = experiment 25; ▽ = experiment 30, end of third metal turnover.
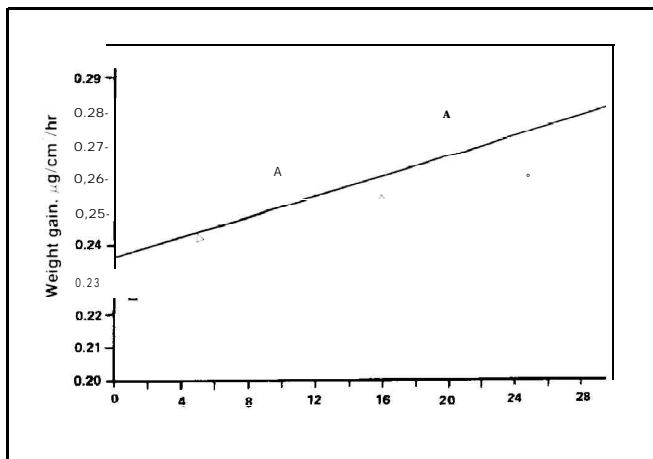
Fig. 13— Weigh t gain resulting from corrosion after 9 days of exposure of samples from experiments 1, 5, 10, 16, 20, 25 and 30.
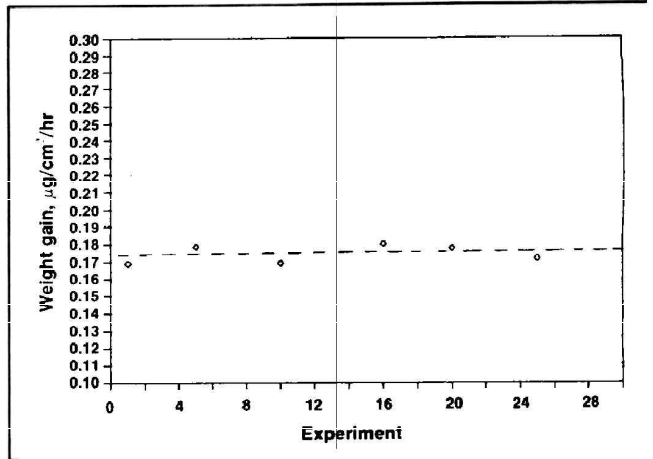

Fig. 15 —Weight gain resulting from corrosion during 9 days of exposure of samples from experiments 1, 5, 10, 16, 20, 25 and 30, after factoring out the effect of surface roughness.
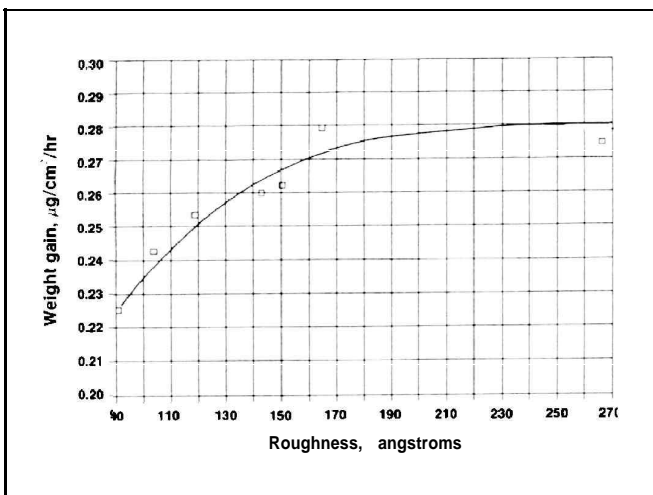

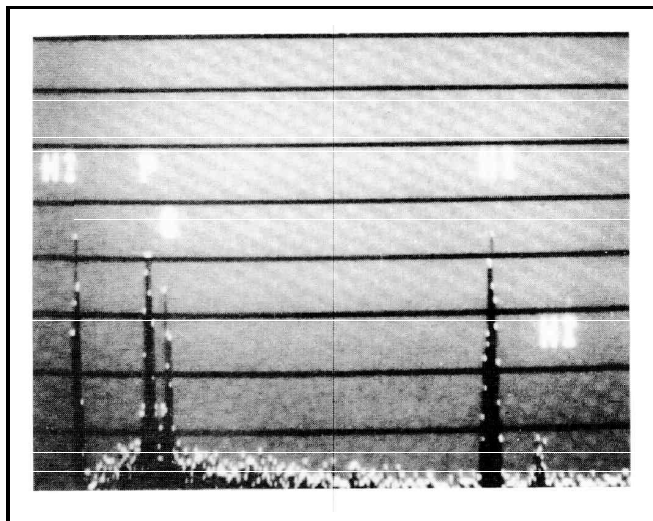Fig. 14—Weight gain resulting from corrosion as a function of surface

Fig. 16 —EDXS of Ni-P-Cu alloy deposit after extraction of water-soluble corrosion products.

corrosion chamber, but the difference between the highest and lowest corrosion rate was insufficient to be of any concern. The average corrosion rate was 0.26 µg/cm^2/hr, which was less than that of permalloy (0.33 µg/cm^2/hr).

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