

Wear-Assisted Corrosion of Cu-Ni Alloys in HCl and NaCl Solutions

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INTRODUCTION: Corrosive wear is caused by synergistic action of stress and corrosion, which may result in significantly increased damage to the target material, compared to those caused by stress and corrosion, respectively. The total volume loss (V) includes losses caused by wear (V_w), corrosion (V_c) and the wear-corrosion synergy ($V_s = V_{w-c} + V_{c-w}$), where V_{w-c} is the corrosion-assisted wear and V_{c-w} the wear-assisted corrosion [1]. Quantifying the wear-corrosion synergy is of significance to the control of corrosive wear and in-depth understanding of the mechanism behind. V_{w-c} is usually measured, with which all other above-mentioned items can be determined. In this study, an electrochemical scratch technique was used to measure changes in corrosion current, based on which V_{w-c} can be calculated using Faraday Law.

The objective of the study is to investigate how the corrosive medium and dynamic contact affect V_{w-c} of a Cu-Ni alloy during sliding wear in 3.5wt.% NaCl and HCl (pH=3) solutions, respectively. During the tests, the rotation of disc (sample) provoked stirring the solution and thus influenced the kinetics of mass transport involved in the corrosion reaction. Corrosion caused by stirring-only was measured and compared to that caused by sliding wear in the solutions. Results of the tests and relevant analysis would help further understand the corrosion-wear synergy for effective corrosive wear control.

METHODS: Cu-Ni alloy samples with dimensions of 10 mm×10 mm×5mm were cut and mounted using epoxy resin with an exposed area of 1 cm² as working electrode. Electrochemical scratching or sliding wear tests were performed on a pin-on-disc tribometer (CSEM Instruments, Switzerland) combined with an electrochemical workstation (Gamry PC4/750). A schematic drawing of the apparatus is shown in Fig. 1. When sample/disc/working electrode rotated, the changes in the current at free potential caused by wear or stirring-only, i.e. with or without compressive force against specimen disc, were recorded. The test was performed under a normal force of 5N at a speed is 0.5cm/s over 30s.

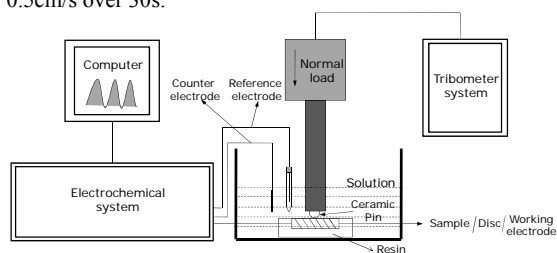


Fig. 1 Schematic illustration of the tribo-corrosion testing apparatus

In order to determine the influence of flowing condition on corrosion behaviour in HCl (pH= 3) and 3.5 wt.% NaCl solution, linear polarization and tafel plot measurements were carried out in static and agitated solutions. After the test, the morphology of corroded surfaces and the type of corrosion products were examined using SEM and XPS, respectively.

RESULTS and DISCUSSION: The current-time curve of Cu20Ni measured respectively during stirring-only and sliding wear tests in HCl and NaCl solution are shown in Fig.2. As shown, in the HCl solution the current increased rapidly to a high level as soon as stirring was started and kept at this level until the stirring

was stopped, then the current decreased gradually (Fig.2A). In NaCl solution, however, the current decreased to negative values immediately after stirring was applied. The negative current values continued until stirring was terminated, then the current returned to the initial level (approximately zero as Fig.2B illustrates).

The above phenomena are explainable. At high corrosion rates, electrochemical reactions deplete cathode reaction medium, e.g. hydrogen ion or dissolved oxygen, making the mass transfer to be a rate-determined process for the electrode reaction. When the solution is stirred, the cathodic process is facilitated by supplying sufficient hydrogen ion and oxygen. As a result, in the HCl solution in which Cu20Ni dissolves (Fig.2D), the corrosion rate can be raised as stirring was introduced, leading to an increase in current (Fig.2A). However, in the NaCl solution the current was reduced (or negatively increased) by stirring (Fig.2B). This opposite trend should be attributed to a different mechanism. Fig.2C shows that in the NaCl solution, a dense corrosion product film developed on sample surface, which reduced the mass transfer. Stirring also accelerated initial mass transfer, thus speeding up the formation of the corrosion product film, leading to a negative increase in current.

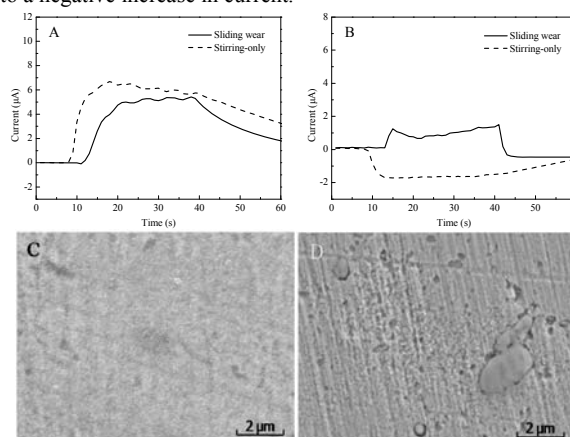


Fig.2 Current-time curves measured at free corrosion potential during sliding wear and stirring-only tests for Cu20Ni in (A) HCl and (B) NaCl solution. (C) and (D) Surface morphologies of Cu20Ni alloy after immersion in 3.5 wt. % NaCl and HCl solutions, respectively, for 10 minutes.

The situation changed when the wearing force was applied. In the HCl solution, the increase in corrosion current caused by sliding wear was not as large as that caused by stirring (Fig. 2A). This happened because, though fresh metal surface was created during by wear, the counter-face was covered the sample surface, thus resulting a smaller increase in the corrosion current compared to that caused by stirring. In the NaCl solution, however, sliding wear destroyed the corrosion product film, thus leading to a positive increase in current as Fig.2B illustrates.

In conclusion, in both HCl and NaCl solutions, sliding wear resulted in increases in corrosion current. However, stirring the solution without wearing force increased the corrosion current in the HCl solution but showed an opposite effect on the corrosion current in the NaCl solution. The mechanisms for the changes in corrosion current under different conditions are elucidated, which would be helpful to understanding the corrosion-wear synergy and control of corrosive wear.

REFERENCES:

[1] Watson S.W., 1995, "Methods of Measuring Wear-Corrosion Synergism", *Wear*, 181(4), pp.476-484