Effects of Cu addition on the corrosion behavior of NiCoCrMo alloys in neutral chloride solution

The influence of Cu addition on the corrosion behavior of Ni-30Co-16Cr-15Mo alloy in neutral chloride solution is investigated by electrochemical measurements. The results indicate that alloy with 0.5 mass% Cu shows inferior corrosion resistance compared to Cu-free alloy under open-circuit potential, which is possibly ascribed to the galvanic corrosion from the insufficient coverage of Cu on passive film; higher fraction of Cu exhibits significant improvement on corrosion resistance.

Due to the exceptionally high heat resistance and corrosion resistance, Ni-based alloys are widely used in a variety of severe environments. Among them, Ni-Cr-Mo alloys demonstrate outstanding corrosion resistance, primarily attributed to Cr and Mo elements: Cr promotes the formation of a compact Cr_2O_3 passive film; Mo significantly enhances the localized corrosion resistance by blocking the dissolution of passive film and acts as the effective barrier against the diffusion of ions through the film via precipitating on the external film. Mo (Ⅳ) (as hydrated MoO_2) on the outermost film can be oxidized into Mo (Ⅵ) forming soluble MoO_4^{2-}. The dissolved MoO_4^{2-} anions are cation-selective, resisting the penetration of Cl^- and other ions, which facilitates the growth of inner oxide film.

In spite of the aforementioned merits, the low wear resistance of Ni-Cr-Mo alloy due to the low hardness greatly limits its further application in the injection moulding of fluorine-containing resin or plastic. Recent study indicates that substituting Co for Ni greatly increases the wear resistance of Ni-16Cr-15Mo (NiCrMo) alloy without sacrificing its corrosion resistance to aqueous HF solutions, although with the cost significantly increasing. This can be ascribed to the reduced stacking fault energy (SFE) of alloy by Co addition, leading to higher work hardening on surface during friction. The hardness of Ni-30Co-16Cr-15Mo (NiCoCrMo) alloy can be further enhanced by plastic deformation, although the corrosion resistance of deformed alloy is greatly reduced compared to that of NiCrMo alloy. More recent studies show that further addition of 2 mass% Cu yields a tremendous improvement on corrosion resistance of NiCoCrMo alloy in aqueous HF acid solution, even after severe plastic deformation.

Cu is widely used as an alloying element to enhance the corrosion resistance of alloys in various conditions. For instance, a compact Cu film formed in the alloy/solution interface impedes the dissolutions of alloy elements and dramatically increases the corrosion resistance of AISI304 stainless steel in 30 mass% H_2SO_4 at 50 °C. Similar result by Hong et al. suggests that the passive film of Cu-containing steel mainly consists of Cu compounds in a 10 mass% H_2SO_4 solution. Cu addition alters the passivation from a Mo-dominated into a Cu-dominated passive film in HF solution. Despite the aforementioned efforts devoted to investigate the effect of Cu on corrosion resistance, the effects of Cu addition on the passivation mechanism of NiCoCrMo alloy in common corrosive media such as brine solutions have not been clarified clearly yet. Therefore, in the present research, the influence of Cu addition on the corrosion behavior and passivation mechanism of NiCoCrMo alloys in 3.5 mass% aerated NaCl solution is investigated systematically in detail for the first time.

Electrochemical measurements were conducted to investigate effects of Cu addition's increasing from 0 to 4 mass% on corrosion resistance of Ni-30Co-16Cr-15Mo alloy in neutral chloride solution. Among them, LSV from 300 mV more negative than open-circuit potential (E_{ocp}) up to 1.5 V (vs. saturated calomel electrode, SCE) at a scan rate of 0.167 mV/s were measured. Corresponding results are shown as Fig. 1.

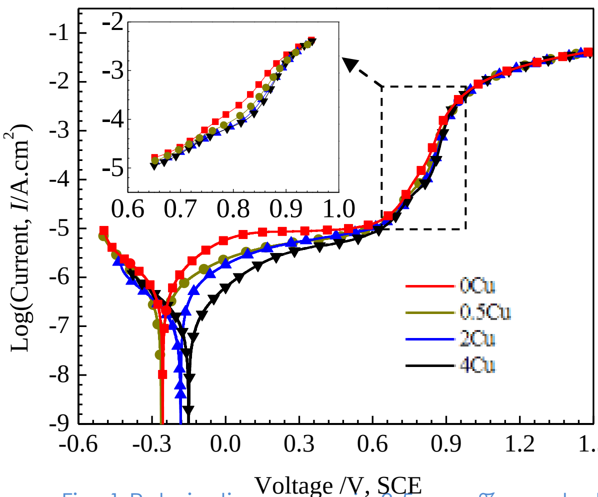

Fig. 1 Polarization curves in 3.5 mass% aerated NaCl solution at room temperature of: 0Cu, 0.5Cu, 2Cu, and 4Cu.

It's obvious that higher fraction of Cu, 4 mass% in this study, exhibits significant improvement on corrosion resistance, with the noblest corrosion potential (E_{corr}) and the lowest corrosion current density (I_{corr}). Moreover, our studies also show slight addition of Cu to Ni-30Co-16Cr-15Mo alloy will be detrimental to alloy's corrosion resistance around E_{ocp}. This is probably related with galvanic corrosion from the insufficient coverage of Cu on passive film.

A new galvanic corrosion model has been set up based on anterior works, to study the effects of Cu content's increasing on corrosion current density. The corrosion galvanic model is shown as Fig. 2. Our theoretical results can be concluded as following equation:

$(\partial \log \alpha I)/(\partial S_C)=1/((b_a+b_c)*\ln 10)*[((b_a+b_c)*S_C-b_c)/(S_C(S_C-1))]$

I represent the apparent current density. S_C express cathodic (Cu) area fraction. b_a and b_c stand for Tafel slope for anodic and cathodic reaction.

A maximum for for log I, or I, will occur at $S_C=b_c/(b_a+b_c)$. From above equation, a pronounced tendency can be found that corrosion current density will be increased as Cu content increases firstly from 0, while decreased gradually as S_c exceeds $b_c/(b_a+b_c)$. This is greatly consistent with our experimental results. Sufficient coverage of Cu layer will improve NiCoCrMo alloy's corrosion resistance.

No more discussions are displayed, considering the limitation of space.

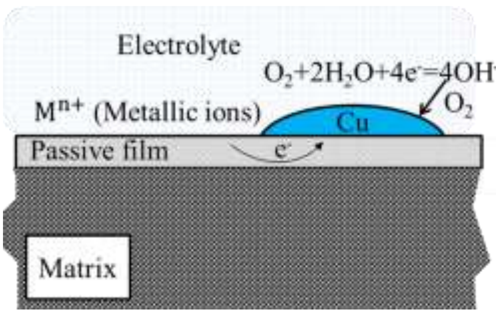

Fig. 2 Schematic illumination of galvanic corrosion on Cu-containing alloys with supposing that Cu will segregate at the outermost surface around open-circuit potential.

The main conclusions are summarized as follows:

Corrosion resistance of the alloys studied is greatly dependent of Cu element. 0.5Cu demonstrates lower corrosion resistance at low potential around E_{ocp}, and improved corrosion resistance at higher potential. The improvement of corrosion resistance becomes more significant with increasing Cu content.

Cr plays a key role in forming the passive film in NiCoCrMo alloys. Meanwhile, the presence of Cu will hinder the extensive dissolution of Cr, ascribed to the rapid formation of a Cu-rich layer on the outmost Cr_2O_3 oxide film. Mo exerts its role by hindering the dissolution of metals by segregating to the surface in transpassive region.

References

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Keywords: alloy; corrosion; passivation;
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