摘要

本研究以「同時添加微量 Cu 與 Sn」與「微量添加 Ge」，微合金化肥粒鐵不鏽鋼，利用線性極化法 LSV、阻抗頻譜法 EIS、循環伏安法 CV、開路電位法 OCP 等電化學量測，觀察合金的抗蝕行為；利用浸泡前後的金相及成分分析，觀察腐蝕後合金微結構與腐蝕液中的元素溶解量；再利用 ESCA 及 AES，分析合金鈍化膜組成；綜合評估微合金化後 Fe-Cr 合金(以下簡稱本合金)的抗蝕行為。

本合金在硫酸中的 LSV 結果顯示，Cu-Sn 微合金化，雖然可以提升活性區抗腐蝕能力，促進鈍化膜生成，但卻使鈍化電流上升；Ge 微合金化，則可以提升鈍化膜穩定性。硫酸中的 EIS 顯示，Cu-Sn 微合金化，使鈍化膜厚度下降，阻抗值變小；Ge 微合金化，使鈍化膜厚度下降，但阻抗值變大，顯示鈍化膜型態有因 Ge 添加而改變。硫酸中的 OCP 顯示，添加 Cu-Sn 對於合金鈍化膜穩定性沒有明顯趨勢；添加 Ge 對於鈍化膜穩定性則有明顯提升。腐蝕後金相與成分分析，顯示合金在硫酸中屬均勻腐蝕，添加 Cu-Sn 使合金腐蝕更為嚴重；添加 Ge 使鉻氧化層的緻密度提升，不易腐蝕。硫酸鈍化膜的 ESCA 與 AES 分析，顯示鈍化膜主要由 Fe_3O_4, FeO/Fe_2O_3, Cr_2O_3, CuO, SnO_2,

GeO_2等氧化物組成，無論添加 Cu-Sn 或 Ge，皆會使鈍化膜厚度減少，組成結構改變。

在氯化鈉中的 LSV 顯示，Cu-Sn 添加對合金抗腐蝕行為影響不明顯；Ge 使跨壓增大、孔蝕電位上升、腐蝕電流密度降低、鈍化電流密度降低，因此提升合金耐蝕力。氯化鈉中的 EIS 顯示，添加 Cu-Sn 沒有明顯趨勢；添加 Ge 提高鈍化膜阻抗，且當添加量超過一定值後，會有離子擴散現象。氯化鈉中的 CV 呈現正遲滯環，顯示有孔蝕現象，鈍化膜修復能力較差。添加 Cu-Sn 後，使合金鈍化膜修復能力變差；添加 Ge 後，合金鈍化膜修復能力變好。氯化鈉浸泡後，浸泡液成分分析顯示，添加 Cu-Sn 後，僅 Cu 有明顯腐蝕溶解，Sn 則沒有；添加 Ge 使腐蝕現象，轉變成均勻腐蝕。

在氫氧化鈉中的 LSV 顯示，添加 Cu-Sn，僅降低活性區電流密度；添加 Ge，則同時降低活性區與鈍化區的電流密度。氫氧化鈉的 EIS 顯示，添加 Cu-Sn，使鈍化膜阻抗上升；添加 Ge，使鈍化膜阻抗上升更明顯。

綜合以上評估，Ge 微合金化後的 Fr-20Cr 合金，是一個創新型耐腐蝕合金。

Abstract

This study is to evaluate the anticorrosion behaviors of alloyed Fe-20Cr ferritic stainless steels with microaddition of Cu-Sn and Ge, by means of LSV, EIS, CV, OCP, microstructure and composition analysis of etchant after immersion, as well as by use of ESCA and AES analyses of the passive film of the alloys.

Although LSV results in H_2SO_4 for alloys of Cu-Sn addition show improved corrosion resistance at the alloy active corrosion region, which promotes the passive film formation, the passivation corrosion current density increases. For Ge-alloyed, LSV results in H_2SO_4 show improved stability of passive film. EIS data in H_2SO_4 for the Cu-Sn-alloyed have a decreased passive film thickness and lower impedance, while for the Ge-alloyed, data not only show a decreased film thickness, but also show increased impedance, indicating that the Ge-alloyed changes the type and property of the passive film. Data for OCP in H_2SO_4 manifest the Cu-Sn-alloyed has no obvious trend for added amount of Cu-Sn, while the Ge-alloyed has improved stability for increasing the content of Ge addition. Microstructure and composition analyses on corrosion surface show general corrosion behavior for both the Cu-Sn- and the Ge-microalloyed cases. However, the Cu-Sn-alloyed has deteriorated corrosion resistance vs the non-alloyed, while the Ge-alloyed has superior behavior. Data for ESCA and AES analyses of passive film in H_2SO_4 show the passive film for both kinds of alloys is principally composed of Fe_3O_4, FeO/Fe_2O_3, Cr_2O_3, CuO, SnO_2, and GeO_2. As mentioned above, no matter what the Cu-Sn- or Ge-microalloyed, the passive film thickness decreases, and the composition of the film changes. Data from the LSV in NaCl have no obvious effect on the corrosion behavior for the Cu-Sn-added, while for the Ge-added, the cross-over voltage for passivation corrosion enlarges, pitting corrosion voltage increases, and passivation corrosion current density drops, mentioning its improved corrosion behavior. Data from the EIS in NaCl also show no obvious trend in results for the Cu-Sn-added, while for the Ge-added there is a rise in impedance for passive film, and as the amount of Ge addition increases to a specific amount, ionic diffusion occurs. CV data in NaCl show an inferior effect of Cu-Sn, while there is a superior effect of Ge. The NaCl solution after alloy immersion of Cu-Sn-alloyed shows an obvious Cu dissolution but without Sn content. It shows general corrosion behavior for the Ge-added in NaCl.

Results of the Cu-Sn-added for LSV in NaCl observe only a lower corrosion current density in its active region, while for the Ge-added, both active and passive corrosion current densities are lowered. EIS results in NaCl demonstrate a rise in impedance for the Cu-Sn-added, and even a more rise for the Ge-added.

Therefore it is concluded that the Fe-20Cr microalloyed with Ge is an innovative corrosion resistance alloy.