学 位 論 文 の 要 旨

Study on Electrochemical Deposition of Ni-P-Cr Alloy Coatings and Brazability of Deposit
(Ni-P-Cr 合金膜の電気化学析出とろう付性に関する研究)

氏 名　　劉 澍彬　　印

This study focused on the fabrication of Ni-P-Cr alloy coatings as a brazing filler metal by electrochemical deposition method. A novel Ni-P-Cr plating bath was developed to form the Ni-P-Cr alloy coating with good appearance and properties. The electrodeposition mechanism of Ni-P-Cr alloys was studied. In addition, the brazing of SUS304 stainless steel using the electrodeposited Ni-P and Ni-Cr-P alloy coatings were performed, and the microstructures and shear strength and fracture mode of the brazed joints were investigated. The corrosion behaviors of the brazed Ni-P and Ni-Cr-P alloy coatings were also investigated. The main conclusions of this study are as follows:

In Chapter 1, the background and purpose of this study was described. Besides, the development status of the electrodeposition of Ni-P alloys as well as the electrodeposition of trivalent chromium and its alloys was reviewed. Finally, the implementation process of this study was presented.

In Chapter 2, as a comparison, a Ni-11P (mass%) alloy coating of 20 μm thickness was deposited on the surface of SUS304 in the case of 0.4 M H_3PO_3 in the plating bath, a current density of 2.0 A/dm^2 and a plating time of 90 min. Afterwards, the brazing test was conducted with the deposited Ni-11P alloy coating. Microstructure analysis results showed that the brazing filler metal was homogeneously distributed between the SUS304 plates and no defects were observed, indicating that the deposited Ni-11P alloy coating can be used as a brazing filler metal for SUS304. Shear test results showed that the average of the shear strength of the brazed joints was 47.3 MPa. In addition, the galvanic current measurement result indicated that the brazed Ni-11P alloy coating preferentially dissolves in the SUS304/Ni-11P couple at 60 ºC in a 0.06 M NaCl solution.

In Chapter 3, a novel Ni-P-Cr plating bath was developed. The optimized bath formulation is as follows: 0.4 M $CrCl_3 \cdot 6H_2O$, 0.25 M $NiCl_2 \cdot 6H_2O$, 0.14 M $NaH_2PO_2 \cdot H_2O$, 0.5 M glycine, 0.5 M NH_4Cl, 0.5 M NaCl, 0.2 M sodium citrate, 0.145 M NaBr, 0.5 M

H_3BO_3, 0.6 g/L $C_7H_4NO_3SNa \cdot 2H_2O$ and 0.1 g/L SDS. Using this optimized plating bath, Ni-5.8Cr-11.1P (mass%) and Ni-13.4Cr-11.6P (mass%) alloy coatings with good appearance were obtained at current densities of 10 A/ dm^2 and 15 A/dm^2, respectively. Brazing of SUS304 was conducted with the deposited Ni-13.4Cr-11.6P alloy coating via conventional brazing method. The shear strength of the brazed joint was low and a large number of green powder was found adhered to the fractured surface. XRD analysis revealed that the green powder is Cr_2O_3 formed by the reaction of Cr and O in the deposited coatings.

In Chapter 4, the electrochemical reduction mechanism of Ni-Cr-P alloys were investigated by linear sweep voltammetry and cyclic voltammetry techniques. Both Cr(III) and Ni(II) ions are electroreduced to metallic state in two steps. Adding Ni ions to Cr solution makes the onset reduction potential of Cr(II)→Cr(0) significantly positively shift, which can be associated with a catalytic effect of initial Ni deposit on Cr deposition, so that it induces underpotential deposition of Cr on Ni atoms, and form the Ni-Cr alloys. At a low pH value of 1.8, adding $NaH_2PO_2 \cdot H_2O$ to a Ni solution inhibited the electroreduction of Ni, while a complete Ni-P alloy deposit was obtained at a relatively negative potential. However, the presence of $NaH_2PO_2 \cdot H_2O$ in Cr solution reduced the polarization of Cr deposition, which in turn promoted Cr-P codeposition. Although the addition of $NaH_2PO_2 \cdot H_2O$ changed the electroreduction behavior of Ni and Cr, the actual reduction potential difference between them remained unchanged, thus ensuring the occurrence of Ni-Cr-P codeposition.

In Chapter 5, the brazing of SUS304 with the electrodeposited Ni-13.4Cr-11.6P and Ni-5.8Cr-11.1P alloy coatings was successfully realized by a stepwise brazing method. Excellent joints with shear strength of 59.0 MPa (brazed with Ni-13.4Cr-11.6P alloy coating) and 63.0 MPa (brazed with Ni-5.8Cr-11.1P alloy coating), respectively, were obtained at 1020 ºC for 30 min. Microstructure analysis results showed that the P-containing phases mainly concentrated in the brazed filler zone. Fracture mode observation showed that the cracks extended along the interface between the brittle P-containing phases and the primary phase, resulting in fracture. In addition, the corrosion behaviors of the brazed Ni-13.4Cr-11.6P alloy coating was investigated by galvanic current measurement. Galvanic current measurement results showed that the brazed Ni-13.4Cr-11.6P alloy coating has a better corrosion resistance than that of the brazed Ni-11P alloy coating, which can be attributed to the formation of a large amount of Ni-Fe solid solution and Cr-P rich phase in the top layer of the brazed Ni-13.4Cr-11.6P alloy coating.

In Chapter 6, this study was summarized.