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XPS study of the corrosion resisting composite alloying layer obtained by double glow plasma with the brush plating Ni interlayer

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Abstract: The Ni-Cr-Mo-Cu multi-element surface alloying with the electric brush plating Ni interlayer on the low carbon steel substrate has been investigated. By the electrochemical method in 3.5% (mass fraction) NaCl solution, the corrosion resistance of the composite alloying layer and single alloying layer is determined. The experimental results show that the corrosion resistance of the composite alloying layer is obviously better than that of the single alloying layer. The structure and composition of passive films formed on the two kinds of alloyed layers after electrochemical tests in 3.5% NaCl solution have been studied using X-ray photoelectron spectroscopy (XPS). It is concluded that the double glow plasma surface alloying of low carbon steel with the electric brush plating Ni interlayer is an appropriate technique to enhance the corrosion resistance compared with the single double glow surface alloying.

Key words: double glow; composite alloying; XPS; electric brush plating

1 Introduction

Corrosion is essentially a surface dependent degradation related to the microstructure and composition of only the near-surface region. Surface alloying technique is an effective way to enhance the surface properties of metals by applying other elements to the diffusion layer forming. The double glow plasma surface alloying technique, the Xu-Tec process, is an updated technology in the field of surface alloying [1, 2]. Comparison with the other advanced surface alloying technology, such as ion implantation and laser alloying, the double glow technique is cheaper for many potential users. The technology employs low temperature plasma produced by glow discharge. By using this technique, the alloying layer with special physical, chemical properties can be obtained on the surface of metallic materials. Much research has been accomplished over the past ten years in exploring the area of corrosion resistance with the Xu-Tec process. In stead of using bulk nickel-base alloys, the Xu-Tec process uses only a fraction of those rare and expensive elements to form the surface alloy with high resistance to corrosion. A Ni-Cr-Mo-Nb alloying layer, similar to Inconel 625, has been formed on the three kinds of substrates (304 stainless steel, low carbon steel and pure iron) [3, 4]. Recently, the Ni-Cr-Mo-Cu alloying layer formed on the two kinds of substrate (304 stainless steel and low carbon steel) has been successfully obtained by means of the double glow plasma surface alloying technique [5]. However, the experimental results indicate that corrosion resistance of the surface alloying layer formed on the 304 stainless steel substrate is better than that of the alloying layer formed on low carbon steel; namely, the carbon content in the substrate plays a very important role in the corrosion resistance of the alloying layer. To improve the corrosion resistance of the alloying layer formed on low carbon steel, the composite alloying layer with the electric brush plating Ni interlayer, which has microstructure homogeneity within the surface alloyed layer and high corrosion resistance, has been obtained. The corrosion behavior of the composite alloying layer in 3.5% NaCl solution, has been examined by electrochemical method and XPS analysis. Particular attention was paid to the effect of the composition, structure and thickness of surface films on the corrosion behavior of the composite alloying layer.

2 Experimental method

Brush plating Ni was an electroplating process that was performed with a hand-held or portable plating tool. The operator soaked the plating tool in plating

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solution and then deposited the plating material by brushing the plating tool against the base material. Plating solution was delivered to the work area by a porous, absorbent cover wrapped over the anode of the plating tool. The composition of electric brush Ni solution was: $NiSO_4 \cdot 7H_2O$, 253-255 g/L; $NH_3 \cdot H_2O$, 100-110 mL; $(NH_4)_3C_6H_5O_7$, 55-56 g/L; CH_3COONH_4, 22-23 g/L; $(COONH_4)_2 \cdot H_2O$, 0.1-0.2 g/L.

Electric brush plating was operated at a working voltage of 12-14 V. The Ni plating layer with a deposit thickness of 20 μm was obtained.

The alloying process of as-deposited samples was performed in a double glow surface alloying device. A superalloy Hastelloy C-2000 (the composition is Cr, 23; Mo, 16; Cu, 1.6; Ni, 59 (mass fraction in %)) plate (130 mm x 50 mm x 4 mm) was used as source electrode materials for supplying alloying elements. Low carbon steel plates (80 mm x 25 mm x 3 mm) were used as substrate materials. The processing parameters were: the source electrode voltage, 1050 V; the substrate voltage, 250 V; the working pressure, 35 Pa; the parallel distance between the source electrode and the substrate, 15 mm.

The chemical compositions in the surface layer and the microstructure were analyzed by scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (XEDS). The phase structure identification was conducted by X-ray diffraction (XRD) with Cu-K_α radiation.

The electrolyte used was 3.5% NaCl solution (mass fraction) open to air at 25°C. The potentiodynamic anodic polarization curves were measured at the scan rate of 20 $mV \cdot min^{-1}$ when the open circuit potential becomes steady after the immersion of the specimen for about 10 min. A saturated calomel electrode and a platinum sheet were used as reference and counter electrodes, respectively. The X-ray photoelectron spectra were measured by PHI 1600 ESCA System using Mg K_α radiation with the energy of 1253.6 eV. The pressure in the chamber was 10^{-8} Pa. The hydrocarbon contamination C1s peak at 284.6 eV binding energy (BE) was used as charge reference for all spectra. The depth profiles were achieved by etching with argon ions of 4 keV energy. During the depth profiling experiment, the current of the measured sample was 25 mA, and the etched area was 1 mmx1mm. Data were acquired for Ni2p (846-885 eV), Cr2p (572-589 eV), Mo3d (225-240 eV), Fe2p (704-716 eV) and C1s (276-294 eV) regions. The deconvolution of the spectra was achieved by fitting the data with a Gaussian/Lorentzian-combination peak shape with variation in peak full width at half maximum, position and height being determined by an iterative program. The peak identification was performed by reference to an XPS database [6].

3 Results and discussion

3.1 Chemical composition of the composite surface alloying layer

The distribution of alloying elements in the composite surface alloying layer and the compared alloying layer without the electric brush plating Ni interlayer are shown in **figures 1** and **2**, respectively. It is evident that the contents of Ni, Cr, Mo and Cu in two kinds of alloying layers decrease as the distance from the surface increases. The gradient alloying layers are identically composed of the alloying elements (Ni, Cr, Mo, Cu)-enriched layer, in which the composition is similar to that of Hastelloy C-2000, and the transition layer to the substrate. But there is difference between the composite alloying layer and single alloying layer. Comparing with the composite alloying layer, the distribution of elements in the single alloying layer is sharper and the thickness of the alloying layer is about 10 μm thinner than that of the composite alloying layer.

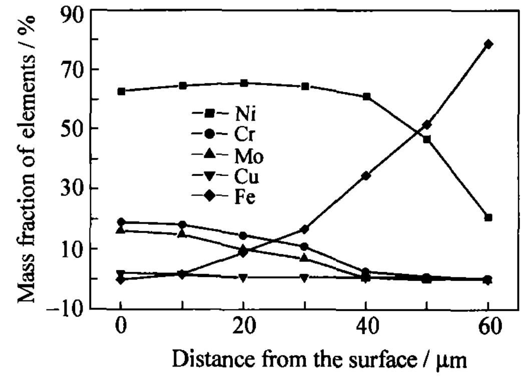

Figure 1 Chemical composition of the composite alloying layer.

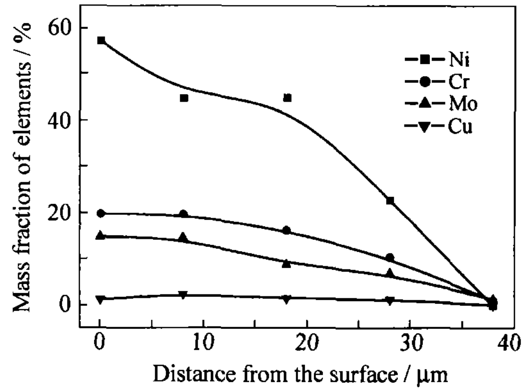

Figure 2 Chemical composition of single alloying layer.

3.2 Microstructure and phase analysis of the surface alloyed layer

Typical microstructures of the composite alloying layer, and the alloying layer without the electric brush plating Ni interlayer (single alloying layer) are shown in **figures** 3(a), and (b), respectively. The two kinds of alloying layers are continuous and compact. The X-ray diffraction spectra (**figure 4**) show that the phase structure of the composite alloying layer consists of single γ phase, but the single alloying layer without the predeposited Ni interlayer (by brush plating) consists of γ matrix and several precipitates (M_6C and μ phase). More carbide precipitated in the single alloying layer on the substrate of low carbon steel, because of its higher carbon contents. The results show that the electric brush plating Ni interlayer as a barrier layer to carbon is effective to decrease the carbon content in the composite alloying layer.

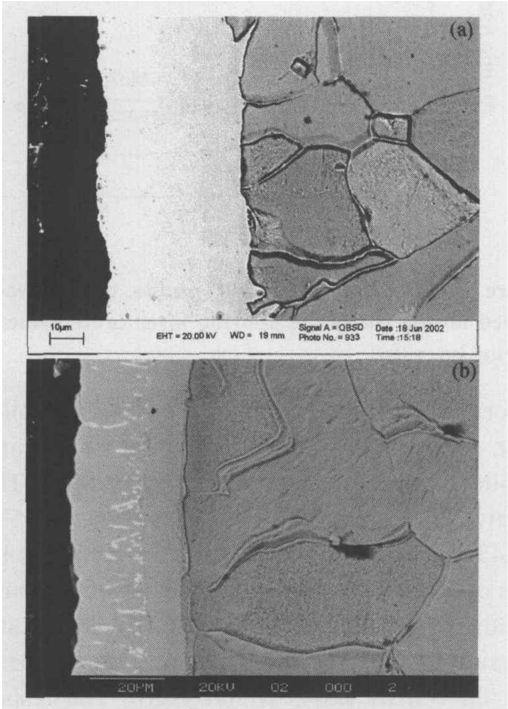

Figure 3 SEM photographs of the composite alloying layer (a) and single alloying layer (b).

3.3 Corrosion test results

Figure 5 and **table 1** show the potentiodynamic polarization curves of the composite alloying layer measured in 3.5% NaCl solution open to air at 25°C. The polarization curve of the alloying layer without the electric brush plating Ni interlayer (single alloying layer) is shown for comparison. In 3.5% NaCl solution, the pitting potential E_b of the composite alloying is 710 mV higher than that of the single alloying layer without the predeposited Ni layer. The passive current density i_p of the composite alloying layer is also lower than that of the single alloying layer.

3.4 XPS analysis

In order to gain further insight into the nature of passive films, XPS is employed to analyze the chemical composition and structure of electrochemically passive films of the alloying layers. The XPS survey spectra of two kinds of alloying layers after the anodic polarization tests are shown in **figures 6**(a) and (b), respectively. It shows that there are Ni, Fe, Mo, Cr, O, and C on the surface of the specimen after the contamination is cleared away, but Cu does not exist, which needs to be investigated further. The composition and thickness of the passive films were determined by XPS depth profiling using argon ion.

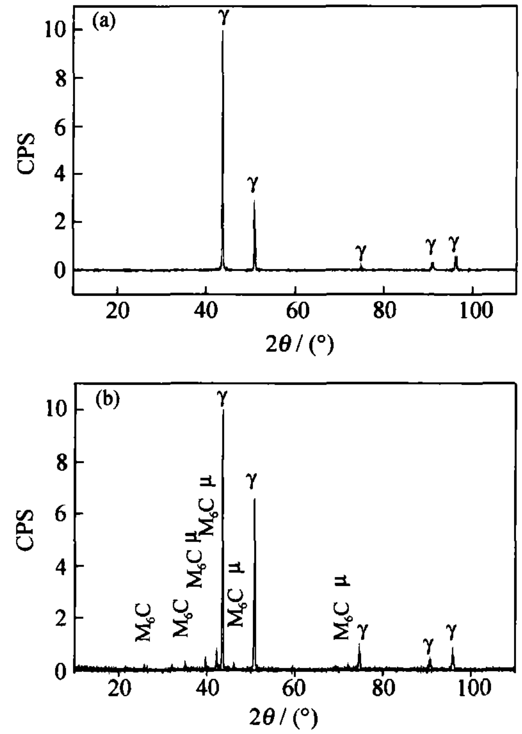

Figure 4 XRD patterns of the composite alloying layer (a) and the single alloying layer (b).

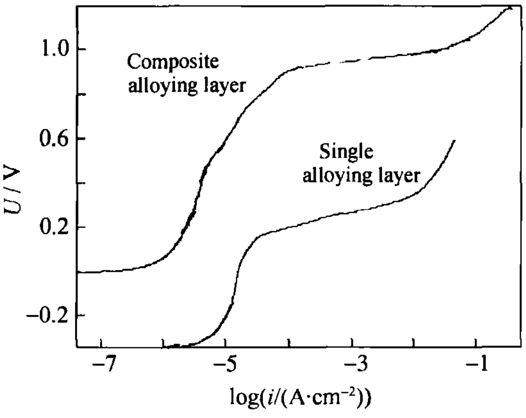

Figure 5 Polarization curves of the surface alloying layers in 3.5% NaCl solution.

Figure 7 shows the depth distribution of all elements in the two kinds of layers as registered by XPS analysis. Their contents have been calculated from the intensities of Ni2p, Cr2p, Fe2p, Mo3d, O1s and C1s peaks. It is shown in figure 7(a) that the atomic fractions of O and Mo are very steady or decreases slowly with increasing the sputtering time; and before sputtering, Cr, Fe and Ni content amount to 12.67%, 9.64% and 11.47% (atomic fraction, so as the follows), respectively; and after sputtering for 10 min, increasing slightly to 14.25%, 11.02% and 15.53%, respectively. The analysis of passive films formed on the single alloying layer (figure 7(b)) shows that the atomic fractions of O, Cr and Mo are obviously lower than those of the composite alloying layer, and the contents of Ni and Fe are higher than those of the composite alloying layer. It must be noted that the thickness of O in the passive films represents the thickness of the passive films. Therefore, the thickness of the passive film formed on the composite is thicker than that on the single alloying layer. The valence state spectra of Cr, Fe, Ni and Mo after sputtering for 2 min were fitted, and a valence state analysis was conducted. The curve fitting of Cr2p, Fe2p, Ni2p and Mo3d high-resolution spectrum after sputtering for 2 min are shown in **figures 8** and **9**, respectively.

Table 1 Electrochemical properties of different surface alloying layers in 3.5% NaCl solution

Specimen	3.5% NaCl solution	
	U / mV	*i* / (μA·cm^{-2})
Composite alloying layer	900	12.589
Single alloying layer	190	31.622

Note: *U*—pitting potential; *i*—passive current density.

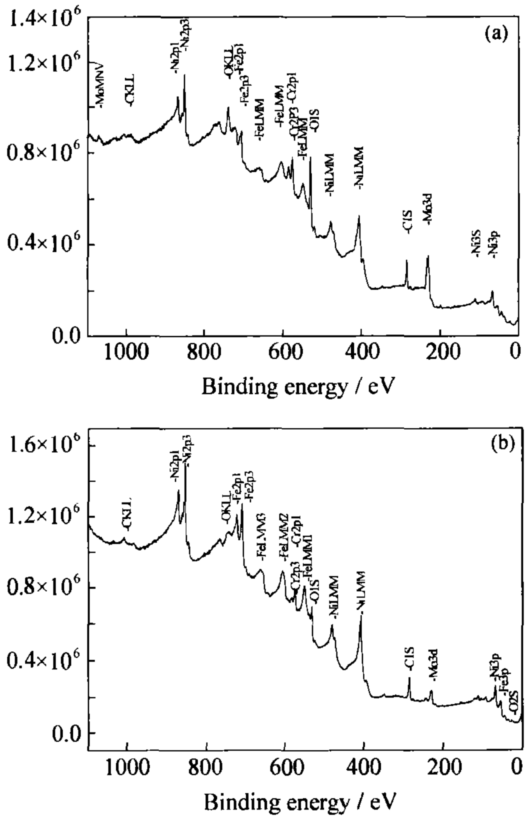

Figure 6 XPS survey spectra of passive films formed on the composite alloying layer (a) and the single alloying layer (b).

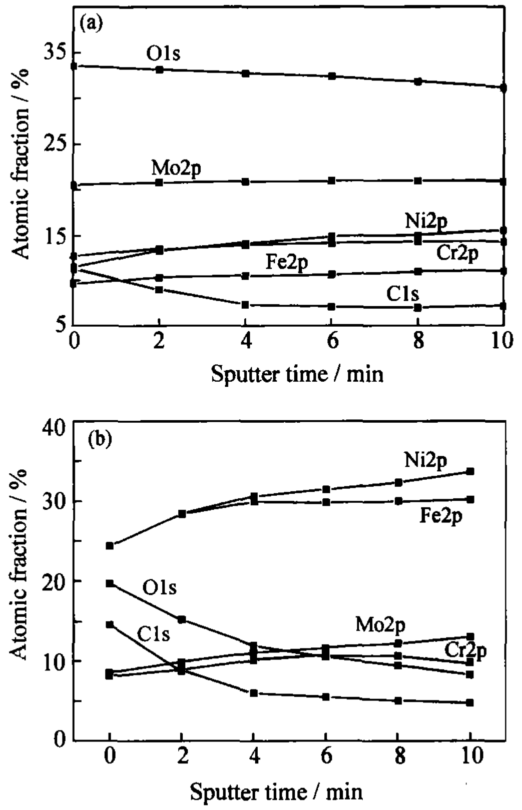

Figure 7 Depth composition profile of passive films formed on the composite alloying layer (a) and the single alloying layer (b).

For passive films formed on the composite alloying layer, after sputtering for 2 min, the Cr spectrum can be fitted with three main peaks (figure 8(a)). The respective binding energies at approximately 574.14, 576.43 and 578.50 eV with corresponding contributions of 17.10%, 60.26% and 22.64% are attributed to metallic Cr, trivalent Cr oxide (Cr_2O_3) and hexavalent Cr oxide (CrO_3). The Mo spectrum also can be fitted with three main peaks (figure 8(b)). The respective binding energies at approximately 228.33, 230.43 and 232.44 eV with corresponding contributions of 50.87%, 27.12% and 21.99% are attributed to metallic Mo, quadrivalent Mo oxide (MoO_2), and hexavalent Mo oxide (MoO_3). The Fe spectrum can be fitted with three main peaks (figure 8(c)). The respective binding energies at approximately 706.86, 709.02 and 711.54 eV with corresponding contributions of 42.39%, 39.19% and 18.42% are attributed to metallic Fe, divalent Fe oxide (FeO) and trivalent Fe oxide (Fe_2O_3). It can be seen from the figure 8(d) that Ni is in form of metallic Ni.

Figure 9 shows the high resolution XPS scans from the passive film formed on the single alloying layer, Cr2p region. After electrochemical tests, three main peaks observed at 574.11, 576.25 and 578.13 eV (figure 9(a)) with corresponding contributions of 50.22%, 33.38% and 16.64% are attributed to metallic Cr, trivalent Cr oxide (Cr_2O_3) and hexavalent Cr oxide (CrO_3). Same as that of the passive film formed on the composite alloying layer, Ni is in form of metallic Ni (figure 9(b)), Fe region. The respective binding energies at approximately 706.96, 709.08 and 711.54 eV with corresponding contribution 40.06%, 37.74% and 22.20% are attributed to metallic Fe, divalent Fe oxide (FeO) and trivalent Fe oxide (Fe_2O_3) (figure 9(c)). But different from the passive film formed on the composite alloying layer, Mo is in form of metallic Mo (figure 9(d)).

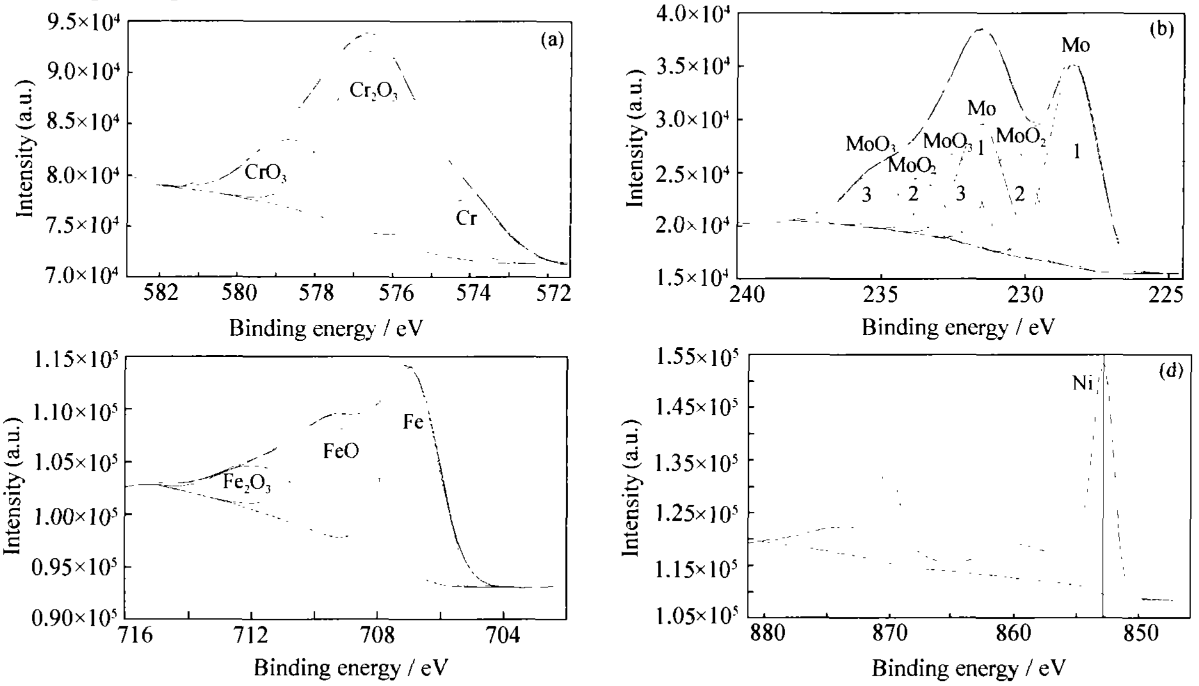

Figure 8 XPS spectra from the passive film formed on the composite alloying layer, (a) Cr2p; (b) Mo3d; (c) Fe2p; (d) Ni2p.

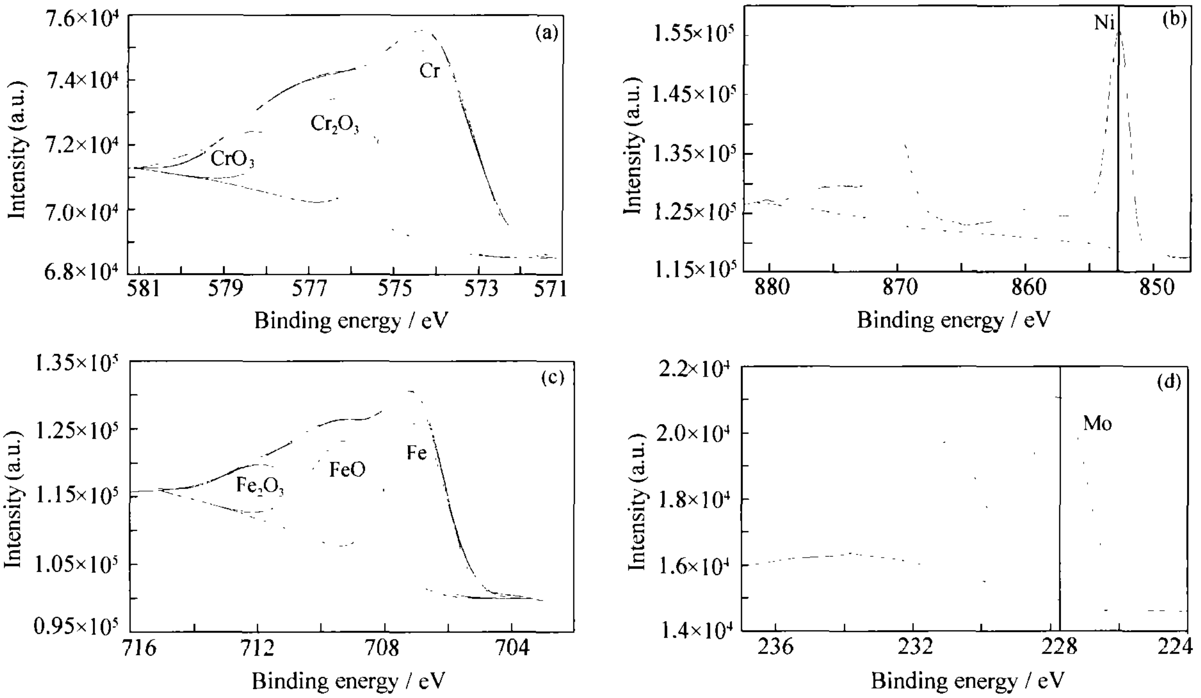

Figure 9 XPS spectra from the passive film formed on the single alloying layer, (a) Cr2p; (b) Ni2p; (c) Fe2p; (d) Mo3d.

It can be concluded that the passive film formed on the composite alloying with the electric brush plating interlayer consists of Cr_2O_3, CrO_3, MoO_3, MoO_2, FeO and Fe_2O_3 and the passive film formed on the single alloying layer without the electric brush plating interlayer consists of Cr_2O_3, CrO_3, Fe_2O_3 and FeO. The amount of the oxide and the thickness of oxide film of the former are greater than that of the latter, which is very important for providing effective protection of the materials surface from corrosion. The poor corrosion resistance of single alloying layer is due to the higher amount of the carbide precipitation and μ phase.

The passive film near the detrimental phase is prone to be assaulted by aggressive ion. The composite alloying layer possesses an excellent corrosion resistance as a result of microstructure homogeneity.

4 Conclusions

(1) The electric brush plating Ni interlayer as a barrier layer to carbon is effective to decrease the carbon content in the composite alloying layer. The structure of the composite alloying layer consists of single γ phase, but the alloying layer without the predeposited Ni interlayer (by brush plating) consists of γ matrix and several precipitates (M_6C and μ phase).

(2) The composite alloying layer has better corrosion resistance than the alloying layer without the electric brush plating Ni interlayer in 3.5% NaCl solution. Thus, it is concluded that the double glow plasma surface alloying of low carbon steel with the electric brush plating Ni interlayer is an appropriate technique to enhance the corrosion resistance compared with single surface alloying layer.

(3) The passive film formed on the composite alloying consists of Cr_2O_3, CrO_3, MoO_3, MoO_2, FeO, Fe_2O_3 and metallic Ni and the passive film formed on the alloying layer without the electric brush plating interlayer consists of Cr_2O_3, CrO_3, Fe_2O_3 and FeO and metallic Ni and Mo, but the thickness of the passive layer is obviously thinner than that of the composite alloying layer and the amount of Cr_2O_3, MoO_3, MoO_2, Fe_2O_3 and FeO of the former is notably higher than that of the latter.

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