JOURNAL OF MATERIALS SCIENCE **35** (2000) 1495 – 1499

XPS, UPS and ESR studies on the interfacial interaction in Ni-ZrO_2 composite plating

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The interfacial interaction in Ni-ZrO_2 composite plating prepared by composite electrodeposition has been investigated. The results showed that no new phases were formed at the interfacial regions between matrix Ni and ZrO_2 particles, but the orbital interaction through the mutual overlap of the d orbits does exist in the interfacial regions between Ni atoms and Zr^{3+} ions. *© 2000 Kluwer Academic Publishers*

1. Introduction

Composite materials have been widely used and are playing more and more important roles. The properties of composite materials are greatly affected by their microstructure. Up to now, the knowledge about their inner structure is much limited [1–3] . The development of modern analytical methods such as XPS and UPS have made it possible to obtain more information about the build-up and microstructure. Ni-ZrO_2 composite platings (CP), comprised of matrix metal Ni and ZrO_2 particles, were prepared by composite electrodeposition (CE), and they were used as electrodes for hydrogen evolution reaction (HER). Those Ni-ZrO_2 composite electrodes showed very high electrocatalytic activity, which was many times higher than that of Ni electrode [4] although ZrO_2 itself does not display any HER ability because of its big forbidden band width ($Eg = 5.0$ eV) [5], all the experimental phenomena suggest that some kinds of interactions that benefit HER should exist between matrix Ni and ZrO_2 particles. These interactions have been systematically investigated, and the results are presented here.

2. Experimental

Ni-ZrO_2 CP was prepared by the method of CE, and the composition of the electrodepositing solution and the electrodepositing conditions are listed in Table I. Direct current was used in the electrodepositing process. Ni plating as a control was also prepared under the same conditions except that there were no ZrO_2 particles in the solution. The average diameter of ZrO_2 particles is about 2.3 μm and ZrO_2 content is 17.8% in the CP.

Morphology and structure were analyzed by HITACHI X-650 SEM and HITACHI H-700 TEM. The detailed procedures for XPS, UPS and ESR are described in reference [6].

3. Results and discussion

3.1. Results of SEM and TEM

As shown in Fig. 1, ZrO_2 particles are well-distributed in the matrix Ni, and the structure of CP is homogeneous. Pure ZrO_2 particles used in our experiment are composed of many smaller ZrO_2 monocrystals (Fig. 2), and an electron diffraction pattern is illustrated in Fig. 3. It was proved that the crystal structure of ZrO_2 particles is monoclinic. Observations and analyses have been carefully carried out in the interfacial regions to try to find out if any kind of interactions, which may lead to the formation of new compounds, exists between matrix Ni and ZrO_2 particles. TEM (Fig. 4) and X-ray results indicate that no new phases are formed in the interfacial regions, so the research was focused on the orbital interaction in the interfacial regions.

3.2. Results of XPS

The XPS spectrum of pure ZrO_2 powder shows the binding energies of 182.2 eV ($Zr3d_{5/2}$) and 184.6 eV($3d_{3/2}$) (Fig. 5a), and it proves that the valence number of zirconium in ZrO_2 powder is +4 [7]. By comparing Fig. 5b with Fig. 5a, it is found that the shape of the spectrum in Ni-ZrO_2 CP (Fig. 5b) has been changed greatly. Curve fitting has been done according to the peak shape and half-peak width of the spectrum of ZrO_2 powder, and the fitting results (Fig. 5b) coincide well with the tested one. The zirconium peak in Ni-ZrO_2 CP is composed of two groups, and their binding energies are as follows: $E_I(3d_{5/2}) = 180.3$ eV, $E_I(3d_{3/2}) = 182.9$ eV, $E_{II}(3d_{5/2}) = 181.8$ eV, $E_{II}(3d_{3/2}) = 184.6$ eV. The binding energies of $3d_{5/2}$ electron for group I and group II have decreased by 1.9 eV and 0.4 eV respectively comparing with that of pure ZrO_2 powder, while the decrease in binding energy indicates the reduction of Zr^{4+}. All these suggest that the valence numbers of zirconium for the two groups are less than +4. Considering that the reduction of Zr^{4+} in ZrO_2 particles can only take place during the process of CE, and that the reduction of $Zr^{4+} \rightarrow Zr^{3+}$ would be much easier than that of $Zr^{3+} \rightarrow Zr^{2+}$, and also that the $Zr3d_{5/2}$ electron binding energy of metal zirconium is 178.5 eV [7], it is, therefore, believed that the valence number of zirconium corresponding to group I is +3. Since the decrease in binding energy for group II

TABLE I Solution and electrodepositing conditions

$NiSO_4 \cdot 6H_2O$	AR	290.1 (g/l)
$NiCl_2 \cdot 6H_2O$	AR	50 (g/l)
H_3BO_3	AR	40 (g/l)
ZrO_2 particles	AR	3–24 (g/l)
Temperature		40 °C
pH		2.8
Anode electrode		Ni plate

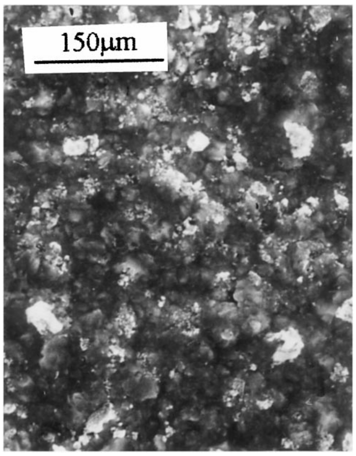

Figure 1 SEM photograph of Ni-ZrO_2 plating.

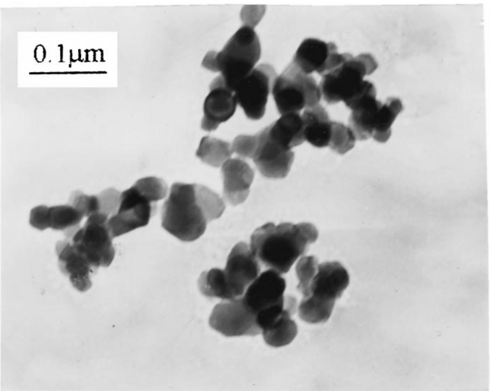

Figure 2 TEM photograph of ZrO_2 particles.

is less than 1 eV, it is thought that most of zirconium in group II possesses valence number of +4.

Since XPS information comes from a depth less than tens of atom layers, so the XPS data in our experiments

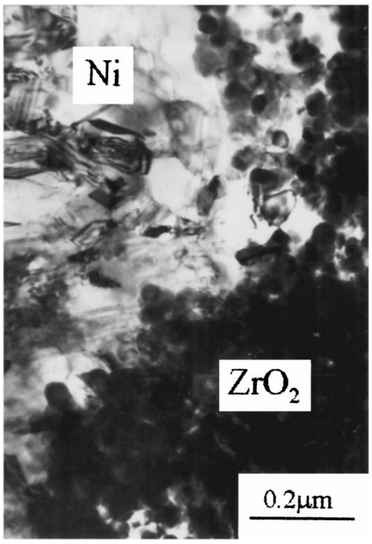

Figure 4 Interfacial structure between matrix Ni and ZrO_2 particles in Ni-ZrO_2 plating.

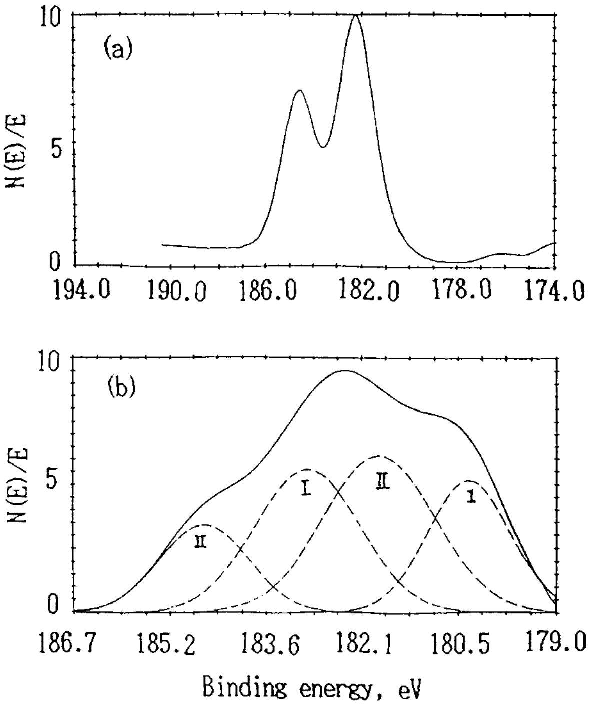

Figure 5 XPS spectra of the Zr3d region. ——: tested curves - - - -: fitting curve a) ZrO_2 powder b) Ni-ZrO_2 plating.

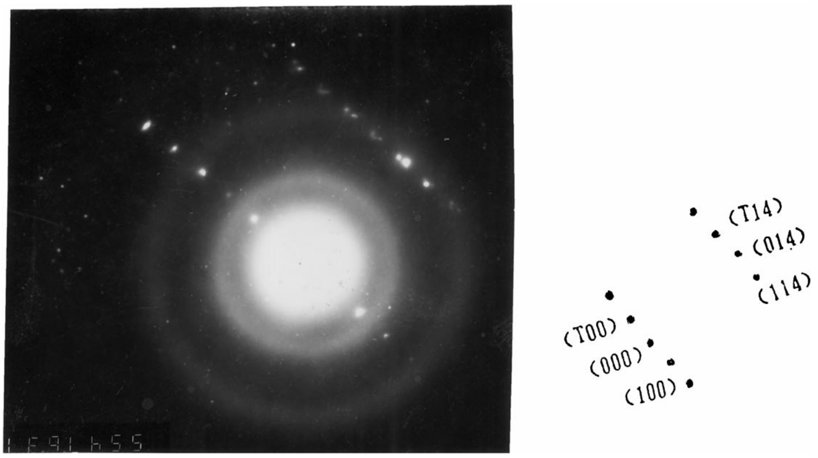

Figure 3 Electron diffraction pattern of ZrO_2 particles.

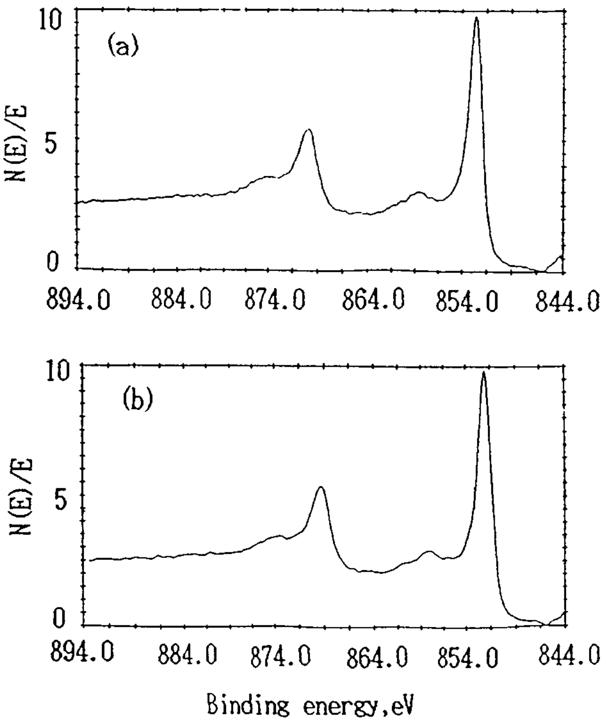

Figure 6 XPS spectra of the Ni2p region a) Ni plating b) Ni-ZrO_2 plating.

mainly reflect the state of the interfacial regions between matrix Ni and ZrO_2 particles. From the results, it can be concluded that Zr^{4+} on the surface of ZrO_2 particles may be partially reduced to Zr^{3+} during the process of CE, and the zirconium ions in the interfacial regions of Ni-ZrO_2 CP possess a different valence number such as +3, +4, or between +3 and +4.

A quantitative analysis has been done according to the O1s and Zr3d XPS peak areas of ZrO_2 powder that was not sputtered by Ar^+ before the measurement. The result showed that the atomic ratio of Zr to O is 1 : 1.978, which is bigger than the value calculated from the chemical formula of ZrO_2. This indicates that the cavities of O^{2-} exist on the surface of ZrO_2 particles.

The XPS spectrum of Ni plating (Fig. 6a) shows the normal binding energy of 852.7 eV ($Ni2P_{3/2}$) and 870.0 eV ($Ni2P_{1/2}$). Comparing the two XPS spectra showed in Fig. 6, it can be found that the peak positions of Ni2P are different although their peak shapes are almost the same. The binding energies of Ni in CP are 852.1 eV ($Ni2P_{3/2}$) and 869.4 eV ($Ni2P_{1/2}$), and the binding energy of $Ni2P_{3/2}$ electron has shifted by 0.6 eV towards the negative direction comparing with that of pure Ni plating. The resolution of the XPS measurements is within the limits of 0.2 eV, so the notable negative shift of the binding energy shows that a bonding action has been generated between matrix Ni and ZrO_2 particles, and Ni atoms prefer to obtain electrons during the bonding process. Since the chemical shift is less than 1 eV, this explains that the bond possesses a mixed property of covalent bond and ionic bond.

3.3. Results of UPS

UPS technique was used to investigate the difference in the electronic structures of nickel in Ni plating and CP.

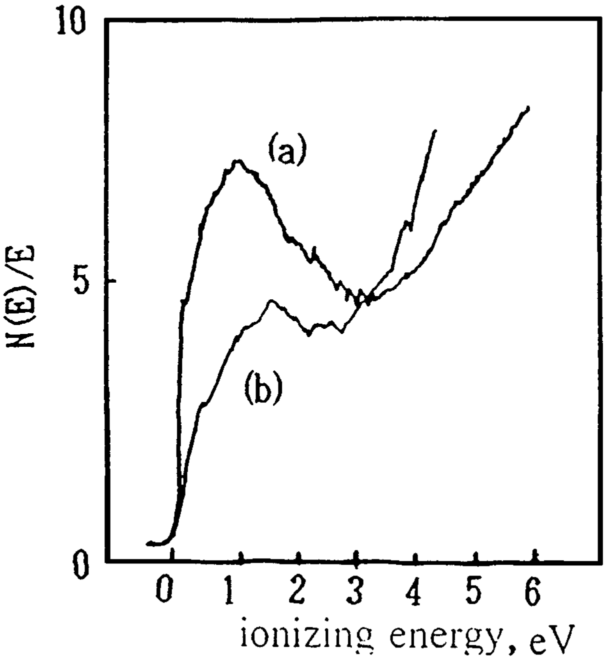

Figure 7 UPS spectra of Ni plating (a) and Ni-ZrO_2 plating(b).

The peaks near the Fermi level in Fig. 7 come from the d band of Ni, and the ionizing energies for Ni plating and CP are 1.0 eV and 1.6 eV, respectively. The 0.6 eV increase in the ionizing energy for CP means that the ionization of the d electrons of Ni is more difficult in CP than in Ni plating. This also proves that Ni atoms in CP participate in the bonding action. Fig. 7 also shows that the peak height of CP has clearly decreased comparing with that of Ni plating. This indicates that the emissive intensity of d electrons of Ni in CP has greatly decreased. The decrease in emissive intensity can also be taken as evidence that the d electrons of Ni atoms located at the interfacial regions participate in the bonding action with ZrO_2.

3.4. Results of ESR

As illustrated in Fig. 8, Ni produces an ESR spectrum and ZrO_2 powders do not produce an ESR spectrum. It was also found that the peak shapes and peak widths for Ni plating and CP are the same, but their peak heights are not equal. The calculated relative intensities of ESR peak for Ni plating and CP are 4.16/mg and 3.80/mg, respectively. The decrease in the ESR relative intensity of CP can be explained as the decrease of single electron numbers in matrix Ni, and the decreased numbers of electrons can be considered as those electrons which have participated in the bonding action. So the orbital interaction between matrix Ni and ZrO_2 particles was also verified by ESR.

3.5. Model of interfacial orbital interaction in CP

XPS results have proved that the valence number of zirconium in pure ZrO_2 powder is +4, but the valence number of zirconium in Ni-ZrO_2 CP has several different values such as +3, +4, even between +3 and +4.

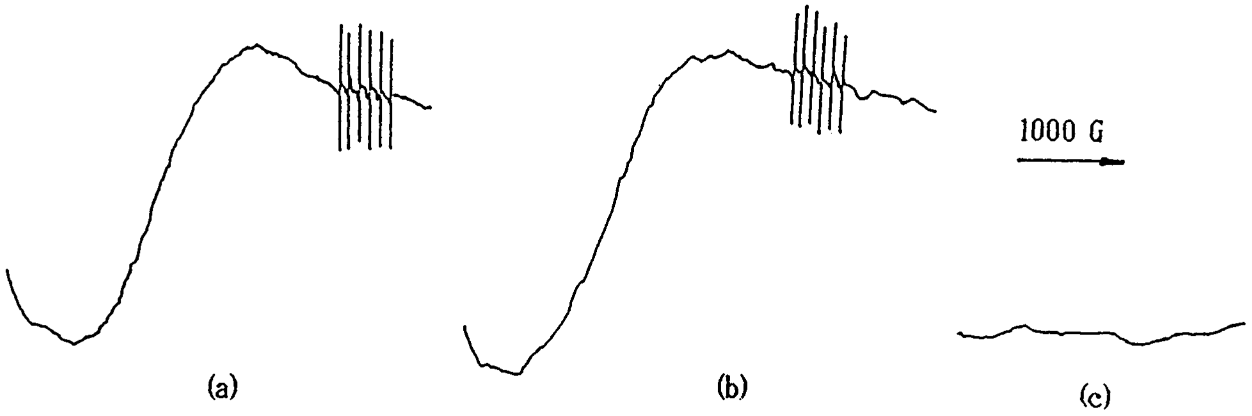

Figure 8 ESR spectra of Ni plating a), Ni-ZrO_2 plating b) and ZrO_2 powder c). (Mn^{2+} was used as standard).

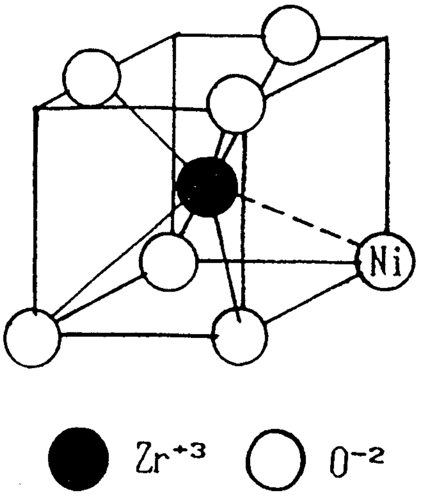

Figure 9 Schematic view of the bonding between Ni atoms and Zr^{3+} ion in Ni-ZrO_2 plating.

The differences indicate that the Zr^{4+} ions on the surface of ZrO_2 particles may be partially reduced to Zr^{3+} during the process of CE under high cathodic over-potential. The quantitative XPS analytical result of pure ZrO_2 powder has shown that O^{2-} cavities exist on the surface of ZrO_2 particles. All these make it possible that Ni atoms were preferentially absorbed to the O^{2-} cavities and approached to Zr^{3+} so sufficiently to bond with Zr^{3+} when Ni atoms contacted with ZrO_2 particles during the process of CE. The XPS results of CP have also shown that the binding energy of Ni $2P_{3/2}$ electrons has a negative chemical shift less than 1 eV comparing with that of Ni plating, and that zirconium ions with valence numbers between +3 and +4 have also been found. It can be concluded that during the bonding process, Zr^{3+} ions tend to give out electrons and Ni atoms tend to obtain electrons, and the bonds formed between them probably possess a mixed properties of covalent bond and ionic bond.

The UPS results have shown that it is the d orbit of Ni atoms that participates in the bonding process. Since the outer electronic structure of Zr atom is $4d^2$ $5S^2$, the bonding process can only take place among the d orbits of Ni atoms and Zr^{3+} irons, and their d orbits overlap mutually to bond. The molecular model of the interfacial orbital interaction in CP can be schematically shown in Fig. 9.

3.6. Effect of the orbital interaction between Ni and ZrO_2 particles on the electrocatalytic activity for HER

The electrocatalytic activity of transient metal for HER is greatly affected by the electron distribution in the outer d orbit of the atom. The fuller the d orbit is filled with electrons, the higher the electrocatalytic activity showed [8]. As indicated above, the d orbit of Ni atoms in the composite plating is more filled up with electrons through the orbital interaction between matrix Ni and ZrO_2 particles. The more filled up d orbit of Ni atoms would decrease the adsorptive heat of hydrogen atoms adsorbed on Ni during the process of HER, and makes the adsorbed hydrogen atoms desorb more easily. The HER mechanism of composite plating used for electrodes belongs to a recombination-desorption mechanism [4]. It is believed that the important reason for the high electrocatalytic activity of composite plating for HER is the more filled-up d orbit of Ni atoms caused by the orbital interaction between matrix Ni and ZrO_2 particles.

4. Conclusions

1) No new phases at the interfacial regions of matrix Ni and ZrO_2 particles in CP are found by either TEM observation or electron diffraction analysis.
2) XPS analyses indicate that Zr^{4+} ions on the surface of ZrO_2 particles were partially reduced to Zr^{3+} ions when ZrO_2 particles were embedded in Ni-ZrO_2 CP during the composite electrodepositing process under high cathodic over-potential.
3) XPS quantitative analysis shows that O^{2-} cavities exist on the surface of ZrO_2 particles.
4) The analyses of XPS, UPS and ESR have shown that the orbital interaction by the overlap of the d orbit between Ni atoms and Zr^{3+} ions exists at the interfacial regions in Ni-ZrO_2 CP.

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Received 14 October 1997
and accepted 24 June 1999