Improvement in Cr Nanoparticle Content in Ni–Cr Film by Co-deposition with Combined Surfactant HPB and CTAB

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Abstract The effects of single surfactant hexadecylpyridinium bromide (HPB) and cetyltrimethylammonium bromide (CTAB) and the combination of HPB and CTAB on the Cr nanoparticle content in the Ni–Cr film prepared by co-deposition were investigated. Single HPB/CTAB addition inhibited the oxidation and amorphous transformation of the Cr nanoparticles in the plating bath and effectively stabilized the Cr nanoparticles content at approximately 10 mass% as a function of time. Moreover, the combination of HPB and CTAB formed a cylindrical micelle structure on the Cr nanoparticle surface, which prompted the formation of a layer of NiCr_2O_4 . As a result, the Cr nanoparticle content increased sharply to 20 mass%.

KEY WORDS: Co-deposition; Ni–Cr film; Cr nanoparticle content; HPB; CTAB

1 Introduction

Co-deposition of nanosized particles into a metal matrix has been used to successfully fabricate Ni–SiC [1, 2], Ni–Carbon [3], Ni– Al_2O_3 [4], Ni–Diamond [5], Ni– TiO_2 [6], Ni–Cr [7, 8] and Ni–Cr–Al [9, 10] nanocomposite films. These nanocomposites exhibit enhanced wear resistance, thermal stability and corrosion resistance compared to the pure metallic materials. In particular, the Ni–Cr [7, 8] nanocomposite shows a superior resistance to high-temperature oxidation and hot corrosion due to the rapid formation of compact, slow-growing and thermodynamically stable Cr_2O_3 oxide. To guarantee excellent performance at

high temperatures, the content of the Cr nanoparticles in the film must exceed the critical value of 9.6 mass% [8] to prompt the formation of the protective Cr_2O_3 layer and ensure the consumption of Cr during the long oxidation period.

However, many studies have proved that it is usually difficult for the nanosized particle to be co-deposited and that the content of the nanoparticles in the film is very limited compared to that of the micro-sized particle [11–14]. Numerous methods have been used to improve the content of the nanoparticles, such as adjusting the electrodeposition parameters [12, 15], changing the sediment methods [15, 16] and adding inorganic metal ions [5, 17] or organic surfactants [14, 18–21]. Optimization of the co-deposition process parameters such as the current density, particle concentration, bath composition, agitator speed gave rise to particle content fluctuation in a relatively small range. Although sediment co-deposition (SCD) where the cathode is horizontally set in the bath could attain a higher particle content in the film, the higher content could be obtained for only one side of the sample. The use of surfactants, especially cationic surfactants such as hexadecylpyridinium bromide (HPB) [18, 21, 22],

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cetyltrimethylammonium bromide (CTAB) [14] and an azobenzene group surfactant (AZATB) [19], are recognized as the most effective way to improve the content of the incorporated particles. The most remarkable characteristic of the surfactant is its participation in the solid–liquid interface with the hydrophilic head and the hydrophobic hydrocarbon chain [23]. In the co-deposition process, previous studies have shown that the aggregation of the nanoparticles can be decreased in a plating bath with surfactant [14]. Additionally, the charge of the particles can be changed to positive [21, 22] with the adsorption of a cationic surfactant that could promote electrophoretic migration of the particles toward the cathode. For example, the SiC (250 nm) content in the nickel matrix was improved to 11.5 vol% by the addition of CTAB [14]. The content of Al_2O_3 (80 nm) in the nickel matrix was improved to 14.7 vol% with the addition of HPB [18]. The synergistic behavior of binary surfactant also is exploited to reduce the total amount of surfactant used or improve the quality of film. For example, the content of Al_2O_3 (150 nm) in nickel matrix was improved by the addition of a combination of anionic SDS and cationic HPB [21]. The anionic surfactant SDS is used to decrease the pore defects of the as-deposited film. In this paper, instead of a combination of an anionic and a cationic surfactant the combination of two cationic HPB and CTAB was chosen to reduce the total amount and form the specific micelles which are a barrier of the ions adsorbed on the Cr nanoparticles surface in plating bath.

In this study, the optimum parameters of the Cr content in the Ni–Cr film were studied. Additionally, the effects of single HPB/CTAB and combined HPB and CTAB on the surface modification of the Cr nanoparticles (average size of 40 nm) and its content in the nickel matrix were studied.

2 Experimental

Ni–Cr nanocomposite films were deposited from a nickel sulfate solution. The components of bath and the parameters of co-deposition are shown in Table 1. A certain content of the nanoparticles of pure Cr with an average size of 40 nm was added into the bath with ultrasonic stirring before the co-deposition. A reciprocating perforated plate was added in the bath during the co-deposition to maintain the suspension of the nanoparticles. Pure nickel (99.9%) with dimensions of $15 \times 10 \times 2$ mm was chosen as the substrate after being abraded using an 800-grit SiC paper. The bath temperature was 30 °C, and the pH was 5.5–6.0. Various concentrations of the Cr nanoparticles in the electrolyte and the direct current (DC) density were applied, as shown in Table 1. Additionally, the relationship between the Cr nanoparticles after different soaking times

Table 1 Parameters of the Ni–Cr co-deposition

Bath composition	NiSO ₄ ·6H ₂ O: 50–100 g/L NaCl: 10 g/L C ₆ H ₅ NaO ₇ ·2H ₂ O: 110 g/L HBO ₃ : 20 g/L
Cr nanoparticles concentration	50–300 g/L
Current density (DC)	0.5–5 A/dm ²
Plating time	1 h
pH	5.5–6
Temperature	30 °C

in bath (0, 30, 60, 90 and 120 days) and Cr content in Ni–Cr film was also investigated. Then, single surfactant HPB (250 mg/L), CTAB (200 mg/L) and a combined HPB (250 mg/L) and CTAB (200 mg/L) in analytical grade were added into bath to investigate their effect. All the co-deposition was carried within 1 h. The average thickness of these films is 15 µm.

The weight fraction of Cr nanoparticles in the Ni–Cr nanocomposite film was measured by energy-dispersive X-ray spectroscopy (EDX) connected to a Philips XL-30FEG scanning electron microscope (SEM). The microstructure of the Cr nanoparticles, especially the oxide phase, after different soaking durations in the plating bath was observed by transmission electron microscopy (TEM). Two major steps were used to prepare the samples for TEM. The given Cr nanoparticles were fully dispersed into alcohol using ultrasonic agitation, and then, a copper mesh was placed into the dispersive Cr nanoparticles alcohol bath. Finally, the samples were dried in the air to stand by service. The composition of the oxide phase of the Cr nanoparticles was tested by X-ray photoelectron spectroscopy (XPS), the samples for which were taken from the plating solution after drying prior to the measurement.

3 Results and Discussion

3.1 Co-deposition Parameter Optimization

To investigate the effect of the Cr nanoparticles concentration on the their content in the nickel matrix without surfactant, various concentrations of the Cr nanoparticles ranging from 50 to 300 g/L were added to the plating bath at the fixed current density of 2 A/dm² and the NiSO₄ concentration of 50 g/L. The result is shown in Fig. 1a. As the concentration of the Cr nanoparticles increases, the Cr content gradually increases to approximately 9.7 mass%. However, when the Cr nanoparticles concentration was as

Fig. 1 Relationship between Cr content in mass% in Ni-Cr film and **a** Cr nanoparticle concentrations in bath, **b** current density, **c** NiSO₄ concentration in bath without surfactant

high as 300 g/L, no change was observed compared to the Cr concentration of 200 g/L. This variation in Cr content with the Cr concentration in the plating bath was similar to the Langmuir isotherm adsorption phenomenon [17, 24]. A higher concentration of Cr nanoparticles could lead to more

Cr nanoparticles being transported to and adsorbing onto the surface of the cathode, so more Cr nanoparticles would be engulfed by the reduced Ni. However, when the concentration of the Cr nanoparticles was higher than 200 g/L, the adsorption of the Cr particles on the cathode surface reached the saturation with no more sites to accept more Cr nanoparticles. Therefore, no further increase in Cr content was observed.

The current density varying from 0.5 to 5 A/dm² was applied for the conditions of the Cr nanoparticles concentration of 200 g/L and NiSO₄ concentration of 50 g/L in the electrolyte without surfactant in order to investigate the relationship between the Cr nanoparticle content in the Ni-Cr film and the current density. As shown in Fig. 1b, as the current density increases from 0.5 to 5 A/dm², the Cr content increases from 8.7 mass% to the peak of 9.6 mass% when the current density reached 2 A/dm² and then decreases to 8.2 mass% at 5 A/dm². This effect can be related to the efficiency of the nickel reduction. As the current increases from 0.5 to 2 A/dm², the nickel reduction became more rapid, incorporating more particles in the Ni matrix. However, when the current density was higher than 2 A/dm², a significant amount of hydrogen was reduced, and H₂ separated out; this hindered the adsorption of the nanoparticles to the cathode and resulted in a decrease in the nanoparticles' content [25].

NiSO₄ concentration in the plating bath was another important factor influencing the content of the co-deposited particles in the nickel matrix. Ni-Cr nanocomposite film was prepared under different baths containing different NiSO₄ concentrations ranging from 50 to 200 g/L for the conditions of the Cr nanoparticles' concentration of 200 g/L and current density of 2 A/dm² without surfactant. Figure 1c shows the relationship between the Cr content in the Ni-Cr film and NiSO₄ concentration. The Cr content declined slightly from 9.6 to 7.5 mass% as the NiSO₄ concentration increased from 50 to 200 g/L. The agglomeration of the Cr nanoparticles is decreased at the lower NiSO₄ concentration due to the lower strength of ionic interactions between the nanoparticles in the bath. Good dispersion of the nanoparticles can improve the content of the co-deposited nanoparticles by facilitating the movement of the nanoparticles in the plating bath [26]. The content of Al₂O₃ nanoparticles (80 nm) in Ni-Al₂O₃ film also decreased with increasing the concentration of Ni²⁺ in the bath that has been reported by Kuo et al. [27].

Most importantly, the maximum Cr nanoparticles' content (approximately 9.7 mass%) in the Ni-Cr film can be achieved at the Cr nanoparticle concentration of 200 g/L, current density of 2 A/dm² and NiSO₄ concentration in the plating bath of 50 g/L.

3.2 Oxidation of Cr Nanoparticles in Plating Bath

Upon the repeated use of the Ni–Cr bath to fabricate the Ni–Cr nanocomposite film, Cr nanoparticles could not avoid being soaked for a long time in the plating bath. As the time of being soaked in the bath increased, Cr nanoparticles were slightly oxidized, which may further impact the co-deposited particles in the Ni matrix. According to the Celis model [28], the chemical composition and structure of the Cr nanoparticles' surface in the electrolyte determined the adsorption of the surrounding ions and further influenced the process of the particle being engulfed by the nickel on the cathode surface. Cr nanoparticles subjected to different soaking times ranging from 0 to 120 days in the plating bath were used to investigate the relationship between the Cr content and the time of soaking with plating at the optimum co-deposition parameters. As shown in Fig. 2, as the Cr nanoparticles' soaking time increased, the Cr content in the Ni–Cr film decreased. In the 0–30-day range, the Cr content decreased sharply from 9.6 to 6.0 mass%. In the subsequent 90 days (i.e., after being soaked for 120 days), the Cr content further decreased gradually to 4.1 mass%.

TEM was used to observe the morphology of the Cr nanoparticles after the different soaking times in the bath. As shown in Fig. 3, Cr nanoparticles that were soaked for 1, 30 and 120 days were gradually oxidized and transformed into amorphous state. The fresh (1 day) Cr nanoparticle shown in Fig. 1a exhibits a core–shell structure [29, 30]. The core consists of body-centered structure (bcc) Cr metal. The shell was the epitaxial passive face-centered cubic structured (fcc) oxide Cr_2O_3 film (approximately 2.5 nm thick) that was formed due to the oxidation during the fabrication process. However, the oxide shell became thicker with increasing soaking time. At 30 days,

Fig. 2 Relationship between Cr content in mass% in Ni–Cr film and soaking time without surfactant

the thickness of the oxide shell grew to 3 nm and was approximately 5.6 nm on the 120th day, as shown in Fig. 3b, c. It is important to note that the structure of this

Fig. 3 Morphologies of Cr nanoparticle after soaking for **a** 1 day, **b** 30 days, **c** 120 days

shell did not preserve the crystalline state and apparently changed into an amorphous state.

Moreover, Fig. 4 shows the XPS results for the fresh (1 day) Cr nanoparticle and the Cr nanoparticle after soaking for 120 days. The XPS survey spectra of these two kinds of Cr nanoparticles contained C 1s, O 1s and Cr 2p lines in Fig. 4a. The peak fitting of the Cr 2p_{3/2} spectra

Fig. 4 XPS spectra of Cr nanoparticle after soaking for 1 day and 120 days **a** survey spectrum, the Cr 2p_{3/2} spectra of Cr nanoparticle after soaking for **b** 1 day and **c** 120 days

of the different Cr nanoparticles was conducted using the commercial XPSPEAK41 software to examine the composition of the oxide shell. Figure 4b shows the peak fitting results for the fresh Cr nanoparticle, where Cr, Cr₂O₃ and CrOOH [31] were observed at 573 eV (Cr) and 574 eV (Cr), 575.7 eV (Cr₂O₃) and 577 eV (CrOOH) as presented in Table 2. Thus, the shell of the fresh Cr nanoparticles consists predominantly of Cr₂O₃. The formation of CrOOH was due to the H₂O adsorbed during the sample preparation process. However, after soaking for 120 days CrO₃ was observed [31] (578 eV in Table 2), as were the peaks of Cr, Cr₂O₃ and CrOOH in Fig. 4c. The existence of CrO₃ indicates that some Cr³⁺ were oxidized to Cr⁶⁺ bonding with O²⁻ to form CrO₃ in the electrolyte.

In conclusion, as the soaking time was extended from 1 day to 120 days, the oxide shell of the Cr nanoparticles grew and gradually changed from a crystalline state to an amorphous state, accompanied by the oxidation of some of the Cr₂O₃ shell into CrO₃. The decrease in the Cr content in the Ni–Cr film could be attributed to the amorphous transformation of the Cr nanoparticles' oxide shell. Celis [28] proposed that the particles on the cathode were incorporated by the reduction in the surrounding ion layer. Moreover, the amount and type of ion adsorbed on the particles were determined by the surface state of the particles. Compared to crystalline state, there is no existence of the defects, such as dislocation, grain boundary, because their atomic arrangements are disorderly, which is the same reason of why amorphous coating has excellent corrosion resistance. These defects (steps, kinks, edges and corners) are known as the active sites with high energy levels that have been proved by other authors [32, 33], where adsorption and reactivity are improved. So, in the co-deposition of Ni–Cr, the amorphous oxide shell on the surface of the Cr nanoparticles significantly reduced the amount of active sites for ion adsorption compared to the crystalline state. Therefore, less Ni ion absorption around the Cr nanoparticles resulted in decreasing incorporation of the Cr nanoparticles in the Ni matrix.

3.3 Effect of Single Surfactant HPB/CTAB

Single surfactant HPB (250 mg/L)/CTAB (200 mg/L) was added into the bath. Similarly, for the optimal co-deposition parameters, the relationship between the content of the Cr nanoparticles in the Ni–Cr film and soaking time was investigated, as shown in Fig. 5. Compared to the case without the surfactant, the addition of HPB or CTAB makes the content of Cr gradually increase from 2.3 mass% on the 1st day to approximately 10 mass% on the 90th day. Furthermore, as the soaking time increased to 120 days, no obvious decreasing trend was observed, making Cr content stable at approximately 10 mass%. Generally, a surfactant

Table 2 Binding energies for peak fitting of Cr2p3/2 spectra

Type of nanoparticle	Cr	Cr ₂ O ₃	CrOOH	CrO ₃	C–Cr–H	NiCr ₂ O ₄
Fresh Cr	573/574	575.7	577	–	–	–
Cr soaking for 120 days	574	575.7	577	578	–	–
Cr with HPB	573/574	575.7	577	–	–	–
Cr with CTAB	573/574	575.7	577	–	–	–
Cr with HPB and CTAB	574	575.7	577	–	574.6	575.2

Fig. 5 Relationship between Cr content in mass% in Ni–Cr film and soaking time with the addition of HPB/CTAB

molecule has two different ends: hydrophilic head and hydrophobic chain. In solution, HPB or CTAB molecules may have been adsorbed on the surface of the particles with their cationic charged hydrophilic head to the surface and the hydrophobic chain outward to the solution or vice versa. Additionally, according to Chen et al. [34], the adsorption process of cationic surfactant onto a metal oxide surface is a function of time. For the first several days after adding HPB/CTAB into the plating bath, the surfactant molecules are adsorbed onto the Cr nanoparticles surface through dipole–dipole bonds [34]; this adsorption is not very strong. Most surfactant molecules could reversibly desorb and became free in the electrolyte. During the plating process, free surfactants would like to be adsorbed onto the cathode surface, highly decreasing the number of sites of the nickel reduction and blocked the Cr nanoparticles with the surfactant molecules close to the cathode. This leads to the decrease from 9.7 to 2.3 mass% on the first day. It would take several days or even months for the surfactant molecules and ions (i.e., Ni^{2+}) in the electrolyte to rearrange on the particle surface and bind to the surface more strongly via Coulombic (ionic) bonds rather than the dipole–dipole bonds [34]. At this time, most surfactant molecules are adsorbed on the Cr nanoparticles, and only

trace amounts were still free. Therefore, on the 90th day, most HPB/CTAB molecules would not further influence the nickel reduction, and the Cr content remained stable at 10.2 and 8.9 mass% for the additions of HPB and CTAB, respectively. Most importantly, the addition of the single surfactant HPB/CTAB stabilized the Cr content at approximately 9 mass% and no decreasing trend was observed despite the long soaking time in the bath.

Single surfactant HPB/CTAB added in the bath tended to adsorb on the surface of the Cr nanoparticles and self-assemble forming monolayers, bilayers, spherical or rod-like micelles [35–37], when the concentration of the surfactant is near or above the critical micelle concentration (CMC). In this work, the HPB and CTAB concentrations were near CMC. Therefore, a full monolayer was formed on the particle surface that occupied the active sites on the surface. The full monolayer of the surfactant blocked the adsorption of O_2 in the bath and inhibited the oxidation and amorphous transformation of the Cr nanoparticles. TEM results of the Cr nanoparticles soaked for 120 days with the addition of HPB and CTAB presented in Fig. 6 show that the thickness of the oxide shell of the Cr nanoparticles did not change and was obviously still approximately 2.5 nm. The lattice of the oxide shell of the Cr nanoparticles is still crystalline. Furthermore, Cr 2p3/2 spectra of two kinds of Cr nanoparticles with HPB/CTAB were fitted and analyzed as shown in Fig. 7. Cr, Cr_2O_3 and CrOOH peaks [31] are observed that are same as the peaks for the fresh nanoparticles (Table 2). It was obvious that Cr nanoparticles had not been oxidized with HPB/CTAB, despite being soaked for 120 days in the plating bath.

Furthermore, the addition of HPB increased the Cr nanoparticle content to 10.2 mass% at 90 days, which was slightly higher than ordinary 9.7 mass%, and the addition of CTAB stabilized the Cr content at 8.9 mass%. Thus, the addition of HPB to the bath not only inhibited the oxidation of the Cr nanoparticles but may also improve the net positive charge of the particles. However, the addition of CTAB may not improve the net positive charge of the Cr nanoparticles. Instead, the remaining free CTAB impacted the nickel reduction slightly and decreased the Cr content.

Fig. 6 Morphologies of Cr nanoparticle after 120 days of soaking in the bath with the addition of **a** HPB, **b** CTAB

3.4 Effect of Combined HPB and CTAB

Combined HPB (250 mg/L) and CTAB (200 mg/L) was added to the bath to study the effect of combined HPB and CTAB on the Cr content in the Ni–Cr film. Figure 8 shows that the Cr mass% gradually increased from approximately 2. to 7.9 mass% with the extension of the soaking time from 1 day to 60 days, and the Cr mass% increased dramatically to 19.8 mass% at 90 days.

The morphology of the Cr nanoparticles soaked for 120 days with the addition of the combination of HPB and CTAB is shown in Fig. 9. It shows that the oxide shell of the Cr nanoparticle was still approximately 2.5 nm thick and was in the crystalline state. No obvious oxidation and amorphous transformation occurred. However, there are four atomic layers on the particle surface, for which the lattice was different from the oxide shell of the

Fig. 7 XPS spectra of Cr 2p_{3/2} of Cr nanoparticle after 120 days of soaking in the bath with the addition of **a** HPB, **b** CTAB

Fig. 8 The relationship between Cr content in mass% in Ni–Cr film and soaking time with the addition of combined HPB and CTAB

nanoparticles described above. In addition, the aggregation of the surfactant at the height of approximately 4 nm was present on the surface of the Cr particle. Cr nanoparticles were further examined in detail by XPS. The XPS survey spectrum shown in Fig. 10a contains C 1s, O 1s, Cr 2p and

Fig. 9 Morphology of Cr nanoparticle after 120 days of soaking in the bath with the addition of combined HPB and CTAB

Ni 2*p* lines. An extra Ni 2*p* line is present compared to the spectrum of the fresh nanoparticles and nanoparticles with the addition of either HPB or CTAB. The peak fitting for the Cr 2*p*_{3/2} and Ni 2*p*_{3/2} spectra is presented in Fig. 10b, c. Cr, Cr₂O₃, CrOOH, NiCr₂O₄ [38] and C–Cr–H [39] is observed at binding energies of 573 eV(Cr), 575.7 eV(Cr₂O₃), 577 eV(CrOOH), 575.2 eV(NiCr₂O₄) and 574.6 eV(C–Cr–H), in Fig. 10b and Table 2. The formation of C–Cr–H is caused by the chemical adsorption of the hydrocarbon chains of the surfactant. NiCr₂O₄ and NiO are also observed at 853.8 eV (NiCr₂O₄) and 855 eV (NiO) with the core and satellite line structure [40] in the Ni 2*p*_{3/2} spectra shown in Fig. 10c. Combined with the morphology of the Cr nanoparticle, the Cr₂O₃ phase of the Cr nanoparticles was not further oxidized, but a thin layer of NiCr₂O₄ and NiO was formed on the particle surface.

According to the XPS and TEM results, the combination of HPB and CTAB not only protected the oxidation of the Cr nanoparticles but also improved the formation of NiCr₂O₄ and NiO on their surfaces. Generally, a combination of two kinds of cationic surfactants is applied to lower the CMC in the solution [41]. Compared to the addition of either HPB or CTAB only, the CMC of the combination of these surfactants is lower than a single surfactant [42]. As a result, the self-assembling shape of their mixture may have transformed from monolayers to cylinders as a function of the time in the solution [33, 43]. The sharp increase in the content of the Cr nanoparticles in the Ni–Cr film to approximately 20 mass% could also be attributed to the cylindrical micelles structure. On the one hand, the cylinder micelles structure is considered to provide a higher surface charge of the particles through the absorption of a large amount of the surfactant molecules, thereby promoting

Fig. 10 **a** XPS spectra, **b** Cr 2*p*_{3/2} spectra, **c** Ni 2*p*_{3/2} spectra obtained from Cr nanoparticle 120 days of soaking in the bath with the addition of combined HPB and CTAB

electrophoretic migration of the suspended particles. On the other hand, Ducker and Wanless [43] found that CTAB formed stable cylindrical micelles in the KBr solution at two times of CMC. The formation of cylindrical micelles greatly slows the adsorption of H⁺ on the surface, whereas the rate of K⁺ adsorption is not noticeably affected. This illustrates that the adsorbed film of the surfactant on the

surface acted as a barrier and was ion selective. In our study, the cylindrical micelles of mixed HPB and CTAB on the Cr particle surface could be an obstacle for the absorption of H^+ , but some of Ni^{2+} traversed cylindrical micelles and directly adsorbed on the active sites. The selective adsorption of Ni^{2+} and not H^+ could significantly improve the chance of the Cr nanoparticles being incorporated in the nickel matrix. Importantly, the formation of $NiCr_2O_4$ and NiO leads to the exposure of more nickel atoms on the surface of the Cr nanoparticles. These nickel atoms could act as the nucleation sites of nickel to enable easier nickel reduction. The formation of $NiCr_2O_4$ and NiO could be attributed to the chemical adsorption of the surfactant. The chemical adsorption of the hydrocarbon chains of the surfactant resulted in the formation of C–Cr–H and the electrons transferred to the oxide phase of the Cr nanoparticles [44–46]. Absorbed Ni^{2+} may get electrons and change to Ni and then react with Cr_2O_3 to change to NiO . Some regions of NiO further reacted with Cr_2O_3 to form $NiCr_2O_4$.

4 Conclusions

1. 9.7 mass% Cr nanoparticle content can be achieved in the conditions of 200 g/L Cr nanoparticle content in the bath, 2 A/dm² current density and 50 g/L $NiSO_4$ concentration in the plating bath.
2. Cr nanoparticles were oxidized, and the oxide shell was in an amorphous state as the soaking time of the Cr nanoparticles in plating bath was increased. This leads to the Cr nanoparticle content sharply decreasing to 4.1 mass%.
3. Single surfactant HPB and CTAB can be adsorbed on the surface of the Cr nanoparticles and inhibit their oxidation, eventually stabilizing the Cr nanoparticle content at approximately 10 mass%.
4. A combination of HPB and CTAB not only inhibited the oxidation of the Cr nanoparticles but also promoted the formation of a thin layer of $NiCr_2O_4$ on the Cr nanoparticle surface. This highly improved the Cr nanoparticles content to approximately 20 mass%.

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