Development of a New Electroplating Process for Hard Ni-W Alloys

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Fabrication of tools for micro-injection molding performed by electroforming of Ni-W alloy is proposed. Influences of complexing agents, which enable the Ni-W co-electrodeposition, on the process properties are critical. We optimized the complexing agents in the electrolyte for obtaining high current efficiency (>80%) and low residual stress in the deposit. The thermal stability of the Ni-W layer deposited from the new electrolyte is also investigated. Hardness of the Ni-W deposit (W=6 at. %) increased by annealing at temperatures up to 550°C. This indicates that the Ni-W material can be useful also for injection molding of polymers such as PEEK, with high glass-transition temperature. To a certain extent the Ni-W alloy could also be used as a replacement for hard chromium plating.

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1. Introduction

Micro-injection molding is foreseen to find wide future application for production of computer parts, microfluidic systems and polymer optical components. For the injection molding of high performance plastics, possessing high strength and chemical resistance, the molds must be able to withstand repeated thermal cycles at temperatures up to 350°C.

Fabrication of the molding tool is preferably performed by electroforming in order to be able to control the replication of microscale geometrical details. Nickel is a widely applied material for electroforming, but pure nanocrystalline nickel electrodeposits cannot withstand the relatively high temperature without loosing their hardness due to recrystallization. Among the metals and alloys which are expected to have a higher thermal stability than nickel, and which can be electrodeposited, Ni-W is a promising candidate. Furthermore, a Ni-W alloy is an excellent material, because it has high corrosion resistance and mechanical strength. Probably, Ni-W plating can also substitute hard Cr electroplating.

Several authors have investigated electrodeposition of Ni-W alloys [1-13]. There is a major problem of the formation of precipitates (probably $NiWO_4$) in the electrolyte for the electrodeposition of Ni-W alloys. This can be overcome by adding a suitable complexing agent. The influence of such a complexing agent on the current efficiency, the composition of the deposit and mechanical properties, etc. is critical. Actually, citrate which forms a complex with both the nickel ion and tungstate and gives stability to the electrolyte is a common complexing agent for Ni-W electroplating. However, citrate is associated with a low current efficiency. To overcome this disadvantage often ammonia is added, which raises the current efficiency, but ammonia enhances only the transport of nickel ions by complex formation and consequently reduces the tungsten content in the deposit. In the present research project glycine and triethanolamine, with a high complex stability towards both the nickel ion and tungstate, were investigated as substitution for ammonia.

Another problem with Ni-W deposits is that they suffer from relatively high tensile stress, which can give rise to crack occurrence in the electrodeposit.

We optimized the composition of the complexing agents of citrate, glycine and triethanolamine for improving current efficiency and residual stress of Ni-W electrodeposits.

2. Experimental procedure

A 1 dm^3 beaker was used as electrochemical cell for the optimization of electrolyte. The mechanical stress in the deposits was estimated from the deflection of one side deposited test strips (Specialty Testing & Development Co.) with known elastic constants. The test strip is made from a CuBe foil and is approximately 60 μm in thickness, consists of a 15 mm wide base and has two "legs" that are 76 mm long and 5 mm wide. The base and legs of the strip are covered with a deposition preventing resist layer, but on opposite sides of the legs. The cell for stress measurement has two anodes and one cathode (the test strip) which is located centrally between the anodes, such that the two sides of the test strip experience identical deposition conditions. Internal stress in the deposits makes the two legs of the strip bend in opposite directions. The distance between the deflected beams of the test strip, equaling twice the deflection of a single beam, gives an average value of deflection. The average value was converted into mechanical stress using Stoney's equation[14]. Mechanical stress values were determined 24 hours after finished deposition.

The electrolytes consisted of 0.1 mol dm^{-3} $NiSO_4{\cdot}6H_2O$, 0.2 mol dm^{-3} $Na_2WO_4{\cdot}2H_2O$, 0.3 mol dm^{-3} complexing agent (citrate, glycine and/or TEA) and 0.44 mol dm^{-3} H_3BO_3. Agitation was conducted with a magnetic stirrer. The bath temperature was kept at 70°C during deposition.

A 25L plastic container was used as electrochemical cell for preparation of specimens for hardness measurement. The electrolyte for Ni electrodeposits consisted of 0.26 mol dm^{-3} $NiSO_4{\cdot}6H_2O$, 0.04 mol dm^{-3} $NiCl_2{\cdot}6H_2O$, and 0.44 mol dm^{-3} H_3BO_3. The electrolyte for Ni-W electrodeposits consisted of 0.26 mol dm^{-3} $NiSO_4{\cdot}6H_2O$, 0.04 mol dm^{-3} $NiCl_2{\cdot}6H_2O$, 0.6 mol dm^{-3} $Na_2WO_4{\cdot}2H_2O$, 0.3 mol dm^{-3} citrate, 0.3 mol dm^{-3} glycine, 0.3 mol dm^{-3} triethanolamine and 0.44 mol dm^{-3} H_3BO_3. Agitation was conducted with air bobbling. The bath temperature was kept at 60°C during deposition.

A copper plate cathodically degreased with an alkaline solution and pickled in a commercial acidic solution was used as substrate.

Annealing of the deposits was conducted at 100°C, 250°C, 400°C and 550°C in air atmosphere for 1 hour, respectively.

Phase characterization was conducted with X-ray diffraction (M21X TXJ-FO88, Mac Science Co. Ltd.) using CuKα radiation. The surface topography was examined with scanning electron microscopy (JSM-5900, JEOL). The depth profile of deposit composition was analyzed with glow discharge optical emission spectroscopy (JY-5000RF, Horiba Co. Ltd.). Microhardness was measured at a load of 25g. The cross-section of specimens for the measurement was polished in order to avoid influence of surface roughness on the measurement. Each value is the average of 10 independent indentations on the cross-section.

3. Results and discussion

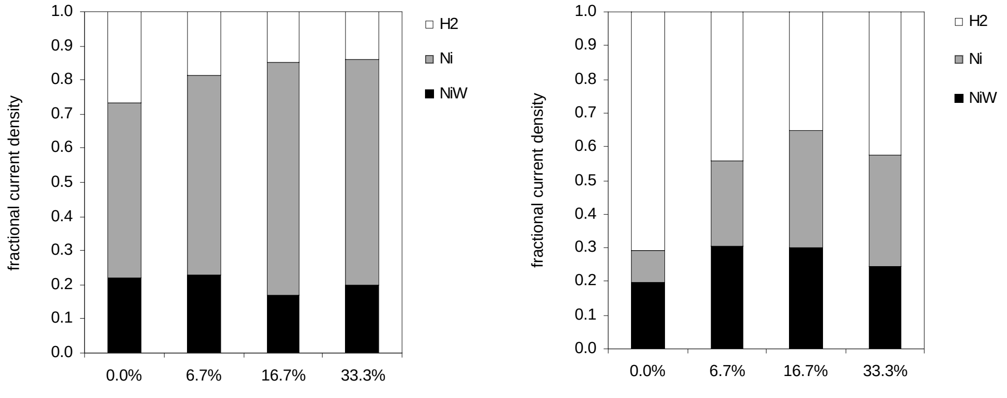
3.1 Optimization electrolyte for Ni-W electroplating [15,16]

The current efficiencies and layer compositions obtained from electrolytes mixing citrate, TEA and glycine are given in Table 1. In these experiments the total concentration of complexing agents was kept constant at 0.3 mol dm^{-3}. The ratio of glycine compared to citrate-TEA was investigated at three levels; 0.14:1:1 (6.7%), 0.4:1:1 (16.7%) and 1:1:1 (33.3%). Although the tungsten content in the electrodeposits decreases with increasing content of glycine in the electrolyte, the current efficiency is markedly improved even for the smallest addition of glycine.

Table 1. Current efficiency of electrodeposition and tungsten contents in the layer electrodeposited from electrolytes containing 0.3 mol/dm^3 complexing agents (citrate, glycine and triethanolamine)

Complexing agent in electrolyte	pH value	Current density A cm-2	Tungsten content at.%	Current efficiency %
Citrate-TEA-Glycine 1:1:0 (glycine 0%)	7.8	0.01	9	73
		0.1	26	29
Citrate-TEA-Glycine 1:1:0.14 (glycine 6.7%)	7.6	0.01	8	81
		0.1	19	56
Citrate-TEA-Glycine 1:1:0.4 (glycine 16.7%)	7.5	0.01	6	85
		0.1	15	65
Citrate-TEA-Glycine 1:1:1 (glycine 33.3%)	7.5	0.01	7	86
		0.1	13	58

Fig. 1 gives more detailed information about the effect of the combination of complexing agents on current efficiency and W content. In the figures, the fractional current density for Ni-W, Ni and H_2 respectively are given, for the purpose of examining the effect of the electrolytes on Ni-W alloy deposition precisely. In practice, though glycine seems to reduce tungsten content in Table 1, the figures show glycine raises the partial current density for Ni-W deposition owing to complex formation with tungstate.



(a) 0.01 A/cm^2

(b) 0.1 A/cm^2

Fig. 1. Fractional current densities for hydrogen, Ni and NiW depositions in electrolytes containing 0.3 mol/dm^3 complexing agents of citrate, triethanolamine and glycine {1:1:0 (glycine 0%), 1:1:0.14 (glycine 6.7%), 1:1:0.4 (glycine 16.7%) and 1:1:1 (glycine 33.3%)}

Fig.2 shows SEM micrographs of Ni-W alloys electrodeposited from electrolytes containing all three complexing agents. The surface morphology changes considerably by adding glycine. For a total current density of 0.01 A cm^{-2} the deposit becomes more needle shaped. For 0.1 A cm^{-2} the nodular appearance becomes finer with increasing glycine content, however cracks are observed in the layers deposited from all the electrolytes.

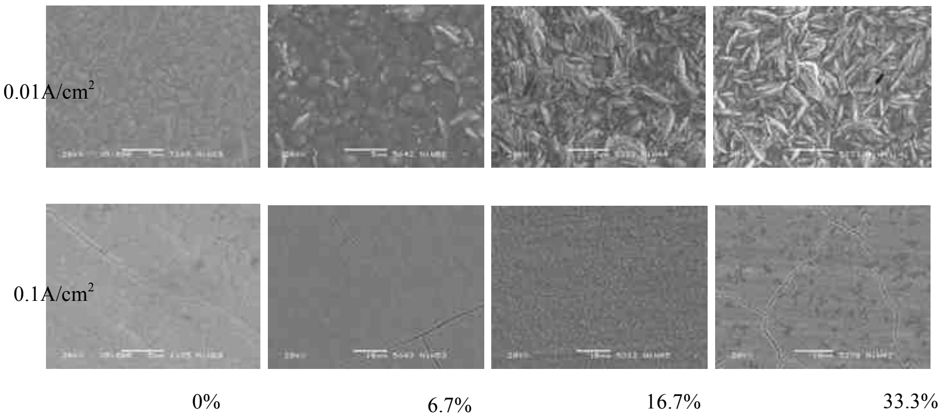


Fig. 2. SEM images of Ni-W alloy electroplated from electrolytes containing 0.3 mol/dm^3 complexing agents of citrate, triethanolamine and glycine {1:1:0 (glycine 0%), 1:1:0.14 (glycine 6.7%), 1:1:0.4 (glycine 16.7%) and 1:1:1 (glycine 33.3%)}

Table 2. Residual stress in the Ni-W layer electroplated at 0.01 A/cm^2 from electrolytes containing 0.3 mol/dm^3 complexing agents of citrate, triethanolamine and glycine {1:1:0 (glycine 0%), 1:1:0.14 (glycine 6.7%), 1:1:0.4 (glycine 16.7%) and 1:1:1 (glycine 33.3%)}

Complexing agent in electrolyte	pH value	Current efficiency %	Residual stress MPa
Citrate-TEA-Glycine 1:1:0 (glycine 0%)	7.8	73	270
Citrate-TEA-Glycine 1:1:0.14 (glycine 6.7%)	7.6	81	190
Citrate-TEA-Glycine 1:1:0.4 (glycine 16.7%)	7.5	85	120
Citrate-TEA-Glycine 1:1:1 (glycine 33.3%)	7.5	58	97

The mechanical stress values in electrodeposits with a thickness of about 4 μm are given in Table 2. Hydrogen dissolution in the deposit and its subsequent release is assumed to be the origin of the occurrence of tensile stress[16]. Although all the current efficiencies and W contents are similar, the residual stress level in Ni-W deposits is strongly influenced by the composition of complexing agent use. The tensile stress decreases with increasing the content of glycine in the electrolyte. The tensile stress level in the deposit depends also on the applied current density. Even though the current efficiency is almost constant at about 80%, the stress level increases with current density. The cracks observed in the layer deposited at high current density of 0.1 A cm^{-2} are caused by relaxation of the internal tensile stress in the deposits.

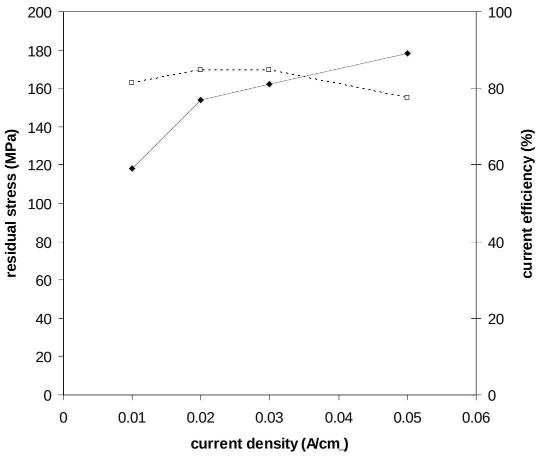


Fig. 3. Residual stress (solid line) and current efficiency (dotted line) depending on current density for electrolyte containing 0.3 mol/dm^3 complexing agents of citrate, triethanolamine and glycine {1:1:1 (glycine 33.3%)}

3.2 Hardness of Ni-W alloy deposits

We investigated the hardness of Ni-W alloy layers electrodeposited from an electrolyte containing equal amount of citrate, glycine and triethanolamine.

The hardness of pure Ni deposits decreases with annealing. In contrast, the hardness of the Ni-W deposits from an electrolyte containing complexing agents increases with annealing. (Fig. 4) The hardness of the Ni-W deposit before annealing is about 400 MPa, irrespective of tungsten content in the deposit. Hardness of the annealed deposit for 0.05 A cm^{-2} is higher slightly compared to 0.01 A cm^{-2}.

In the diffractograms of the Ni-W deposits shown in Fig. 5, almost all of the peaks, except peaks at about 41° (2θ) and 90° (2θ), are presumed to be assigned to solid solution of tungsten in nickel; as compared to W-free nickel, the peaks shifted to lower angles as a function of increased tungsten contents in layers. (Fig. 5) The dissolution of W in Ni leads to lattice expansion, because there is a difference in atom size between Ni and W (Ni: 2.492Å, W: 2.741Å). The peak intensity of the Ni-W layers is lower compared to the Ni layer. The peak width of the Ni-W layer annealed at 550 °C is still larger compared to the Ni deposit before annealing. Yamasaki et. al reported [8-10] the hardness of Ni-W electrodeposits increased with annealing, even though the crystalline size increased. Inverse Hall-Petch relation of nanocrystalline materials has been reported by a number of authors. In this study the increase in hardness with annealing indicates that the Ni-W deposits, even with a low tungsten content of 6 at.%, are also nanocrystalline with high thermal stability. Thus both low residual stress and high thermal stability could be realized by applying the new electrolyte and low current density of 0.01 A cm^{-2}.

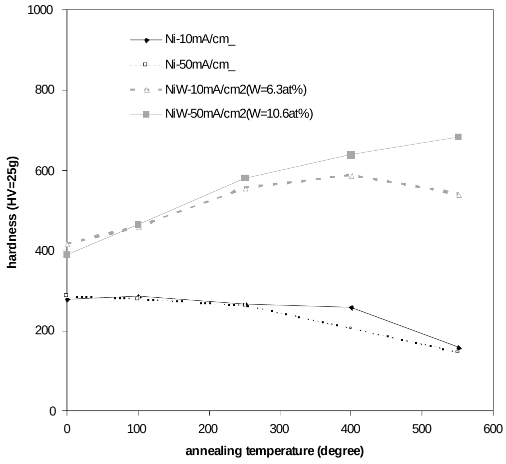


Fig. 4. Hardness of Ni and Ni-W electrodeposited layers as a function of annealing temperature

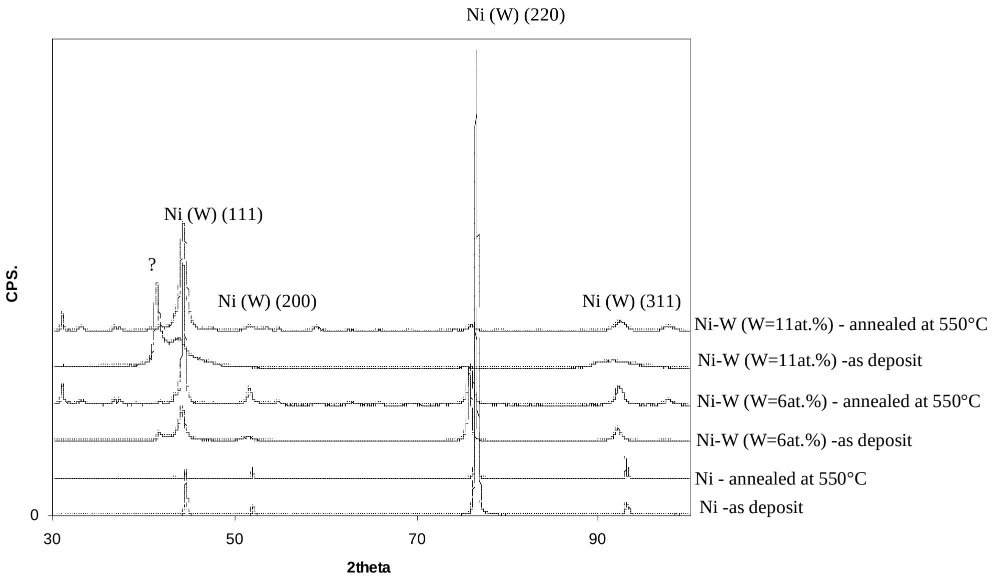


Fig. 5. X-ray diffraction patterns of Ni and Ni-W as-deposit layers and the layers annealed at 550°C

4. Conclusion

Influences of complexing agents, which enable the Ni-W co-electrodeposition, on the process properties are critical. We optimized composition of the complexing agents of citrate, glycine and triethanolamine in the electrolyte for obtaining high current efficiency (>80%) and low residual stress in the deposit. The thermal stability of the Ni-W layer deposited from the new electrolyte is also investigated. Hardness of the Ni-W deposit (W=11 at. %) increased by annealing at temperatures up to 550°C.

5. References

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