INFLUENCE OF MANGANESE ON SULPHUR EMBRITTLEMENT OF NICKEL AND NICKEL ALLOYS ELECTRODEPOSITS.

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VLIV MANGANU NA SÍROVOU KŘEHKOST ELEKTROLYTICKÉHO NIKLU A JEHO SLITIN

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Abstrakt

V předložené práci je diskutován problém sírové křehkosti elektrolyticky vylučovaných vrstev niklu a jeho slitin. Je patrné, že nejlepším způsobem jak se tomuto negativnímu jevu vyhnout je užití manganu jako legury. Mangan však zvyšuje úroveň vnitřních pnutí (makro) povlaků. Bylo navrženo optimální řešení co se týče koncentrace manganu. V práci je rovněž uvažován problém makropnutí.

Abstract

The problem of sulphur embrittlement of electrodeposited nickel and nickel alloys has been discussed in the presented paper. Obviously, the best way to avoid negative effects of this phenomenon is alloing the deposits with manganese. However, manganese increases internal stress (macro) of deposits. An optimal solution concerning manganese concentration has been drawn out. The problem of macrostress of deposited layers has been contemplated too.

Key words: Electrodeposited nickel, nickel-cobalt alloys, sulphur embrittlement, manganese, mechanical properties, internal stress

Introduction

Electrodeposited coatings are mostly used in corrosion protection. However, functional coatings, protecting surface of machine parts against wear, are very significant and frequently used as well. They can increase durability of protected details considerably, which brings economical effects. If the parts are used at elevated temperatures, so called "sulphur embrittlement" may deteriorate the protective effect. Therefore, the ways to eliminate the harmful influence of sulphur in electrodeposits are very important.

Manganese is a very common metal in steel metallurgy. This element improves some mechanical properties of steel, especially tenacity as an alloying additive. However, it is not common in electrodeposition, as its deposition from water solutions is hardly possible, when

sound and thick layers are requested[1]. Some references show that so called "induced co-deposition" is possible with the iron group metals, similarly like in the case of molybdenum and tungsten[2-5]. The deal of manganese in deposit is low, usually less than 1% wt., but it may still influence the properties of deposited metal considerably.

Electrodeposited layers of nickel and its alloys contain always sulphur, at least in traces[6,7]. It is caused by the presence of sulphur compounds in the electrolytes for deposition. This phenomenon decreases the corrosion protection of electrodeposits. At the same time mechanical properties of deposits deteriorate, when heat treated at temperatures of few hundred °C. The sulphur content can vary from 0,001% wt. till 0,4 %wt. Deposits produced from electrolyte without organic additives have usually low sulphur content. It was discovered that sulphur compounds having four covalent bounds of sulphur, like sulphate, do not prone to adsorption at the cathode surface. It was proved by radioactive sulphur isotopes[8,9]. On the other hand, compounds containing at least one free electron doublet tend to adsorption. The sulphur content depends on the strength of adsorption. The sulphuric residua may cause some problems, as mentioned.

Interactions between manganese and sulphur

The adsorbed molecules containing sulphur decay and sulphur atoms either create molecules S_2, or react with surrounding nickel and create sulphides, either NiS or Ni_2S_3 at elevated temperatures. At higher temperatures of more than 250°C approximately, the eutectic $Ni_2S_3 - Ni$ occurs, which generates a thin film on grain boundary[10]. It is the reason of decreased coherence of individual grains and, thus, loss of basic mechanical properties in the stage "as deposited", first of all strength. The situation is similar both in electrodeposited and metallurgical nickel. Manganese reacts with sulphur easier than nickel, so that manganese sulphide MnS arises preferably at elevated temperatures. This compound is insoluble in nickel and of globular shape, which deposits on the phase boundary[11-13]. The same phenomenon was determined in the case of magnesium and calcium in the case of metallurgic nickel. Unfortunately, use of these two metals does not come into consideration in electrodeposition from water solutions and manganese is the only possibility remaining to eliminate sulphur embrittlement.

It was found that in the case of Ni-Co alloys the positive effect of manganese is more expressive[14]. Some authors insist that the presence of manganese declines internal stress of the 1.art as well. Furthermore, it improves ductility of deposits.

Sulphur embrittlement is sometimes divided into two groups. In the case of higher sulphur content, *i.e.* 0,01% wt. and more it is so called "low temperature embrittlement" and the recommended ratio manganese:sulphur is 1,7:1, while "high temperature embrittlement" needs this ratio 20:1. It concerns deposits containing 0,001% wt. S[10]. Naturally, in this case it is easier to reach the requested limit.

Experimental data

Sulfamate nickel and cobalt solutions were the base of bath, which is recommended for low level of internal stress[15,16]. Manganese was added also as pertinent sulfamate. It was produced by dissolving of sulfamic acid in manganese carbonate suspension. Two manganese concentrations were investigated – 0,3 mol/l (patterns A) and 0,6 mol/l. (patterns B).

Macrostress was decreased by supplement of commercial product EL (basically aromatic aldehyde, not containing sulphur). Macrostress (dilatometric measurements) was the main parameter investigated. At the same time the cathodic current efficiency η_k was calculated. Results gained by investigations at the lower manganese concentration are shown in the Fig.1 and Table I.
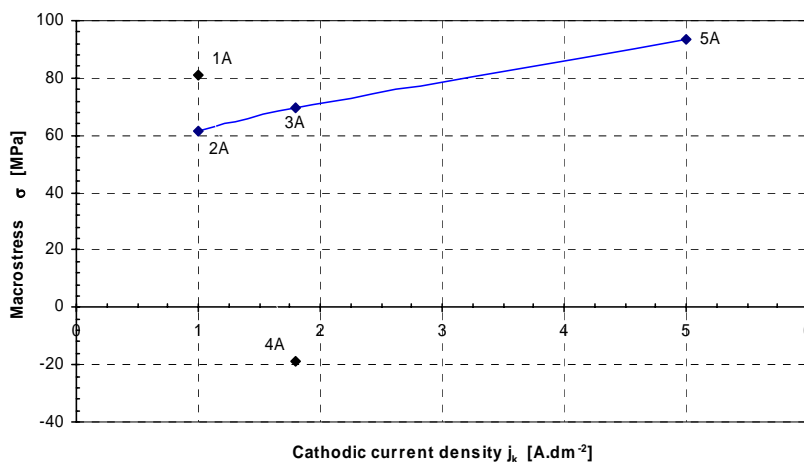

Fig.1 Dependence of macrostress on cathodic current density

Table I Results of investigations at the lower manganese concentration

Sample	Mn^{2+} [mol/l]	Supplement EL [ml/l]	j_k [A.dm^{-2}]	σ [MPa]	η_k [%]	ϕ wt Co [% wt.]	ϕ wt Mn [% wt.]	pH
1 A	0,3	0	1	81,27	94	22,158	0,05	3,4
2 A	0,3	5	1	61,32	94	20,692	0,0325	3,4
3 A	0,3	5	1,8	69,6	94,2	16,964	0,1125	3,4
4 A	0,3	10	1,8	-19,03	98,8	17,716	0,0875	3,4
5 A	0,3	5	5	93,41	92,0	9,252	0,282	3,4

The results are to be expected. Internal stress increases with the increased cathodic current density. Stress value of deposit from bath without EL supplement is higher by about 30% than in the case of mere 5 ml/l EL at the current density 1 A.dm^{-2}. The twice higher concentration EL leads as far as to the change of character of internal stress, as a compressive value was obtained at the current density 1,8 A.dm^{-2}.

The analysis of layers were carried out by x-ray spectrometry by the device EDAX 9900. The higher is cobalt content, the lower is the manganese deal. A correlation between these two values is shown in Fig.2.

A similar picture was found in the electrolyte containing more manganese (samples B). The dependence of macrostress on cathodic current efficiency is shown in Fig.3 and Table II.
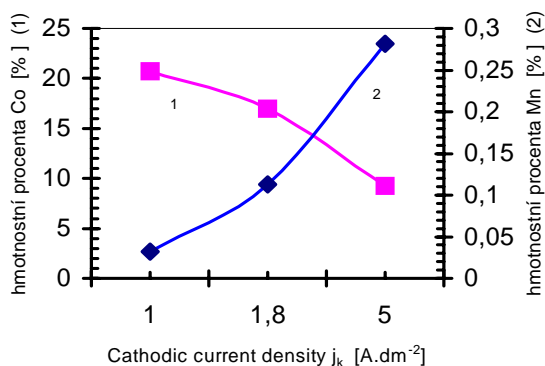
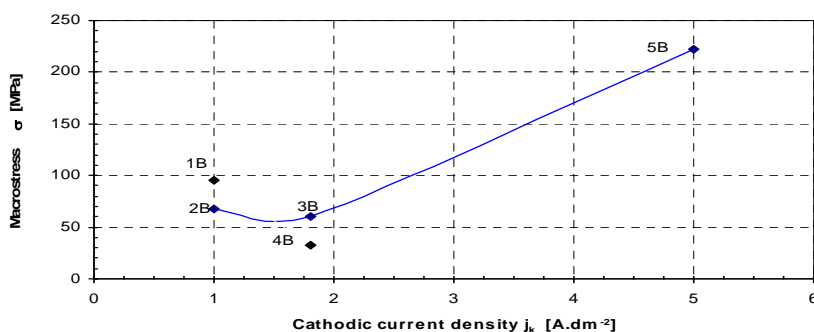Fig.2 Dependence of percentage by weight (Co, Mn) on cathodic current density

Fig.3 Dependence of macrostress on cathodic current density

Table II Results of investigations at the lower manganese concentration

Sample	Mn^{2+} [mol/l]	Sumpplement EL [ml/l]	j_k [A.dm^{-2}]	σ [MPa]	η_k [%]	ϕ wt Co [% wt]	ϕ wt Mn [% wt]	pH
1B	0,6	0	1	95,4	95,52	22,906	0,047	3,55
2B	0,6	5	1	67,07	93	22,348	0,01	3,55
3B	0,6	5	1,8	60,23	95,7	16,474	0,0625	3,55
4B	0,6	10	1,8	33,176	95	17,084	0,045	3,55
5B	0,6	5	5	222	100	8,76	0,74	3,55

The dependence has a similar character like at the foregoing case, but the values of internal stress are considerably higher. While at the manganese concentration 0,3 mol/ macrostress does not exceed 100 MPa, the higher manganese content increases the value even over 200 MPa. From practical point of view, there is no reason to use that higher manganese concentration, as the share of manganese in deposits in the case of samples A can fulfil the role of elimination of sulphur hardness. Addition of EL substance lowers the internal stress again, but decreases to process of induced codeposition of manganese.

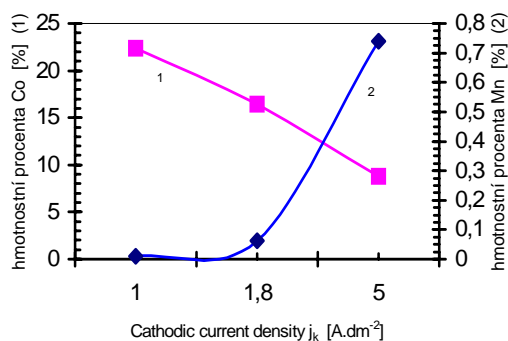Corelation between the cobalt and manganese content is shown in Fig.4.

Fig.4 Dependence of percentage by weight (Co, Mn) on cathodic current density

The dependence is of a similar character again. It can be deduced that the electrodeposition of pure nickel enables to reach higher concentrations of manganese in the deposits.

Conclusions

It is possible to produce nickel and its alloys electrodeposits alloyed by manganese up to 074 %wt. of Mn. However, the higher content of manganese in electrodeposit is the cause of its higher macrostress. The value of macrostress can even exceed 200 MPa in the investigated process, *i.e.* sulphamate solution, alloy nickel-cobalt. Conclusions, coming from practical experience of the authors, are that for deposition of thick sound layers the level of macrostress should not exceed 100 MPa. Because the amount of necessary amount of manganese depends on sulphur content and a proper ration has been found by other authors, there is no need to keep the manganese content as high as the cited limit obviously. Therefore, electrolytes with a content around 0,3 mol/l Mn are acceptable and recommendable. This process fulfils the conditions for sulphur embrittlement elimination.

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