HARDNESS OF NICKEL ELECTRODEPOSITS

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TVRDOSTI VYLOUČENÝCH NIKLOVÝCH POVLAKŮ

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Abstrakt

Byl zkoumán nekonvenční elektrolyt pro katodické vylučování niklu, tj. sulfosalicylan. Jelikož je úmyslem použít niklové vrstvy především jako funkční povlaky chránící mechanické součásti proti opotřebení, byla zkoumána hlavní mechanická vlastnost – tvrdost. Rovněž byly sledovány změny, k nimž docházelo během tepelného zpracování. Porovnání výsledků měření mikro a makro - tvrdosti ukázaly dobrou vzájemnou shodu. Proces se jeví jako perspektivní pro zamýšlené využití.

Abstract

A non-conventional electrolyte for cathodic nickel deposition, i.e. sulphosalicylate, has been investigated. As the intention of use of deposits is first of all for functional coatings protecting surface of mechanical parts against wear, the main mechanical property – hardness has been investigated. Changes occurring during heat treatment have been investigated as well. A comparison between macro and micro - hardness has shown a good relation between the gained values. The process is prospective for the intended use.

Key words: cathodic deposition, nickel, sulphosalicylate, hardness, heat treatment, wear resistance

Background

Hardness of electrodeposits does not belong to their most important properties, if the deposit is intended for exploitation as an agent protecting against corrosion. Corrosion protection is the most frequent case. Some other properties, like appearance, porosity *etc.* are more important and studied thoroughly in this case. Hardness of electrodeposited coatings is not investigated frequently. However, if the coating has to fulfill another duty, *e.g.* to protect surface of machine components, hardness becomes very important. The more hard coatings, the proper are usually for use as this type of functional coating.

From this view point only few metal being able to be deposited from aqueous solutions are acceptable. These metals are characterized by high lattice energy, *i.e.* high melting point. Thus the choice is reduced to chromium and/or iron group metals. The possible use of platinum group metals does not come into consideration owing to their high price. However,

chromium has been attacked by the environment protectors because of toxicity of hexavalent chromium compounds. Hitherto, no process of effective and practically useable chromium electrodeposition has been known without use of hexavalent chromium compounds.

The three iron group metals differ as the macrostress level of deposits is concerned. The electrodeposition of iron is the most difficult. Ferrous compounds can be easy oxidized to ferric ones. The solubility of $Fe(OH)_3$ very low (order 10^{-33}) which is the cause of growth of internal stress. Cobalt is better in this respect, but expensive. Therefore, nickel is the most commonly deposited metal of this type of coatings. It is the reason of its practical importance and hardness of nickel deposits is important as well.

The most of electrodeposits lose the hardness „as deposited" when heat treated. Nickel deposits belong to those as well [1]. The reason is recrystallization of nickel at elevated temperatures above 250°C. Deposits contain usually some part of sulphur coming from sulfur compounds in electrolyte [2]. Consequently, nickel sulphides NiS and Ni_2S_3 occur on the grain boundary, which declines coherence of grains and causes a considerable decrease in hardness and strength. As many functional coatings work at elevated temperature, it is useful to know the appropriate values of hardness at various temperatures. Actual hardness of electrodeposited layers depends on the type of electrolyte and conditions of the electrolysis. The presence of additives, especially organic compounds can affect hardness considerably as well as the type of anion used.

Experimental

Hardness is measured usually by Knoop method in overseas countries, but Vickers method is prevailing in Europe [3]. We carried out the measurements partly also by the Vickers Method in the case of thin layers. The method is based on hobbing of a diamond pyramid inside the measured metal. Hardness is determined from the length of the slant of the dinge. As the thickness of electrodeposits is often rather small, the results might be affected by the base, if the depth of the stab is more than 1/10 of the layer thickness. Hence, the power causing the dinge must be lower by three orders approximately. The results have a token „microhardness". For macrohardness measurements in the case of thick layers, Brinell method, accordingly CSN 42 0371 has been used in this work. The method is similar to the preceding one, just a hard steel bullet is used instead of pyramid. Hardness is then derived from the diameter of the dinge.

The electrolytes used for nickel functional coatings deposition are characterized by low macrostress level in the deposits, otherwise no sound thick layers could be deposited. Sulphamate electrolyte is the most frequently used for this purpose. This bath has an disadvantage in hydrolysis of the sulphamic anion, which proceeds accordingly the equation

$$NH_2SO_3^- \quad = \quad NH_4^+ \; + \; SO_4^{2-}$$

This process is irreversible. The hydrolysis velocity increases with increasing temperature and sinking pH value. The both ions resulting from hydrolysis are the cause of increase of internal stress. Thus, durability of the bath is limited.

Therefore, new processes have been searched, having more stable electrolyte. Nickel (and other) salts of 5-sulphosalicylic acid are one of the possibilities [4, 5]. This electrolyte is able to deposit low-stressed layers including cobalt alloys [6, 7]. Lower solubility of sulphosalicylic salts are possibly the only shortcoming of this bath. The electrolyte is very

simple, based on the sulphosalicylate and a part of halogenide, which is an unavoidable component of any iron group electrodeposition. There are two grounds for it. Firstly halide increases solubility of anodes. On the other hand, it increases internal stress. Secondly it is a part of activated complex, the charge transfer passes through [8]. Bromide seems to be the most proper one [9]. Therefore, the optimal concentration has been searched [10]. Dependence of internal stress on bromide concentration is introduced in Fig. 1. Obviously, internal stress does not exceed the level of 100 MPa, if Br$^-$ concentration is less than 0,05.
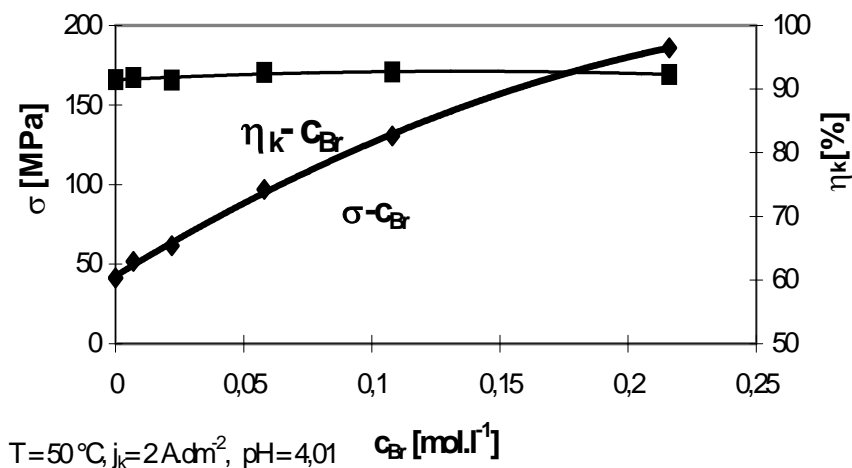

Fig.1 Dependence of cathodic current efficiency and internal stress on cathodic current density

Nickel sulphosalicylate is a product of neutralization of suspension of nickel carbonate by solid 5-sulphosalicylic acid, similarly to the process of sulphamate production. Solubility of nickel sulphosalicylate is 1 mole/l approximately.

A sulphosalicylate electrolyte containing 0,85 mole/l Ni^{2+} and 0,05 mole/l Br$^-$ has been used for deposition of samples, about 1mm thick on a brass sheet of sizes 90 x 100 mm. Cathodic current densities were 1, 3 and 5 A.dm^{-2} respectively, temperature 50 °C ± 0,5°C, pH values 2,6 and 4 respectively. The specimens were shred by a water beam cutter on pieces proper for hardness measurements to avoid heat affects on the structure of deposits which might be cause by other types of cutting.

Results and discussion

Samples were heat treated in an electric chamber oven LAC, type L 15 S at temperatures 100, 200, 300, 400, 500 and 600 °C respectively. The time of processing was 30 min. Marking of particular samples is in Table 1.

Every sample was treated twice, once for macro-, once for microhardness measurements. Every specimen was analyzed on sulphur content too. Analysis was carried out by device LECO, type CS 444. The metod is based on combustion of specimen in flow of oxygen. Sulphur dioxide is product of combustion and its amount is detected by infrared radiation absorption. The sulphur content value was the same in all cases, *i.e.* 0,003 % wt. This value is very low in a comparison to other nickel electrodeposits /2/.

Table 1 Variables of nickel deposition for particular samples

číslo vzorku	j_k [A.dm^{-2}]	I [A]	pH lázně [1]
1	3	5,4	
2	1	1,8	4
3	5	9	
4	1	1,8	
5	3	5,4	2,6
6	5	9	

The results of measurements of microhardness HV 0,7 on samples 1-3, *i.e.* at pH = 4, are presented in Fig.2. A remarkable decrease of hardness can be observed even at 300°C. The decrease is more intense in the case of sample deposited at cathodic current density 3 A.dm^{-2} also owing to the highest hardness at the „as deposited" state.

On the other hand the samples deposited at pH = 2,6 keep hardness up to 300°C, and this   tendency is obvious even up to 400°C at higher current densities – Fig.3.
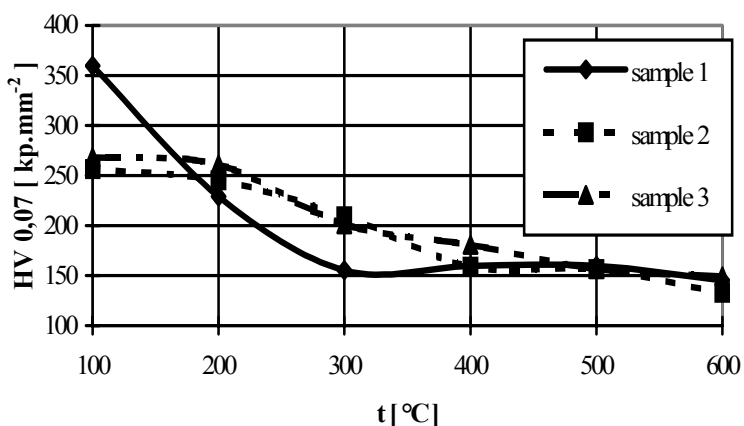

Fig.2 Dependence of Vickers microhardness HV 0,07 of Ni coatings, deposited from a sulphosalicylate bath at pH = 4, on heat treatment
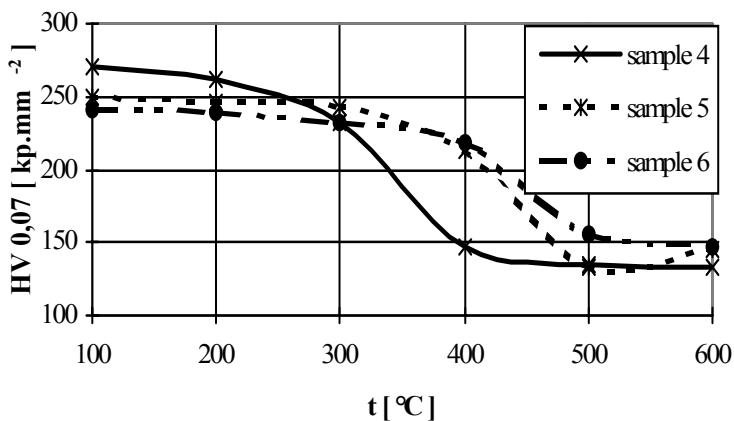

Fig.3 Dependence of Vickers microhardness HV 0,07 of Ni coatings, deposited from a sulphosalicylate bath at pH = 2,6, on heat treatment

Dependences of Brinell macrohardness on heat treatment are shown in Fig.4 for samples deposited at pH=4 and Fig.5 for samples deposited at pH = 2,6. The picture is rather similar, but the dependences are more stepless. This can be explained by more or less bigger fluctuations of mictrostress values caused by small depth of dinges. Obviously, sample 1 exhibits considerably higher hardness "as deposited". Generally, samples deposited at lower pH values exhibit higher hardness.
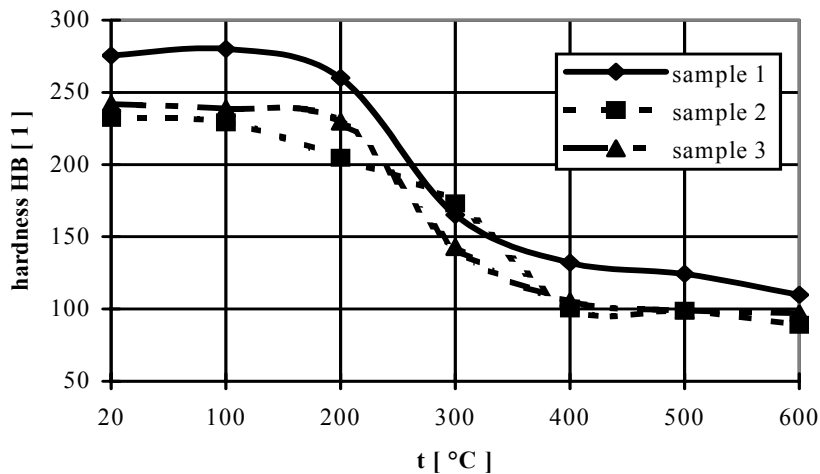

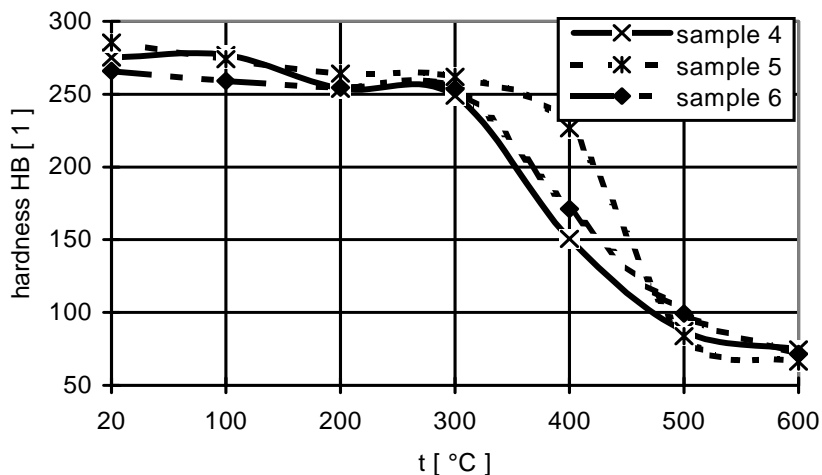Fig.4 Dependence of Brinell Hardness on heat treatment (samples 1 - 3)

Fig.5 Dependence of Brinell Hardness on heat treatment (samples 4 - 6)

Conclusions

Hardness of nickel electrocoatings deposited from a sulphosalicylate bath is slightly bigger than hardness of those deposited form a sulphamate bath (which vary in the range 200/230 HV approximately [11]). However, the tendency to decrease at elevated temperatures is less expressive than in the case of the other nickel electrocoatings. It can be attributed to very

fine structure (see Fig.6) and recrystallization starting at higher temperatures only. Very low sulphur content is a positive of the process. The sulphosalicylate bath can be recommended for nickel electrodeposition in engineering applications.

Structure of Ni deposited from a sulphosalicylate bath :

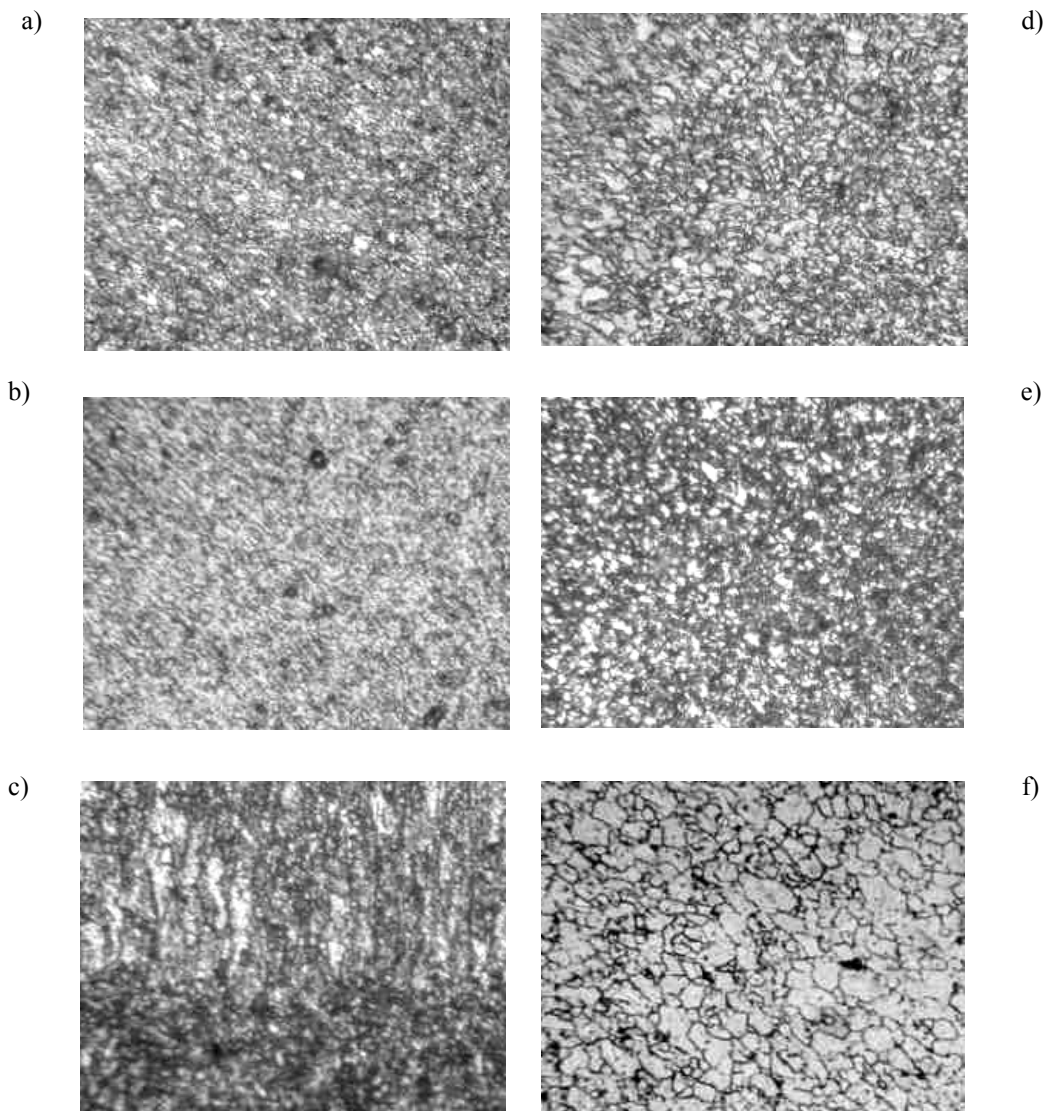a)   d)

Fig.6 Influence of heat treatment on structure of nickel electrodeposits produced from a sulphosalicylate bath at pH = 4 a j_k = 3 A.dm^{-2}. (a) 100°C, (b) 200°C , (c) 300°C, (d) 400°C, (e) 500°C a (f) 600°C, (Magnification 500x)

Acknowledgement

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