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CORROSION RESISTANCE OF ION NITRIDED SINTERED STAINLESS STEELS IN 0.5 M SULPHURIC ACID SOLUTION

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ABSTRACT: The paper reports on the corrosion behaviour, in 0,5 M sulphuric acid solution, of some stainless steel grades obtained from powders: 3161 (austenitic steel), 4101 (martensitic steel), and 430L (ferritic steel), both in the initial state and after ion nitriding for 10 h at 430°C and 580°C. In order to investigate the corrosion behaviour, the polarization curves method was applied. The experimental test showed a better corrosion behaviour for the austenitic steel 316L, after ion nitriding at low temperature (430°C, 10 h).

KEYWORDS: Corrosion, Sintered Stainless Steel

1 INTRODUCTION

In the last years, the interest for fabrication by powder metallurgy of engineering components from stainless steel has grown considerably. However, the corrosion resistance of parts obtained from stainless steels powders is not comparable with that of forged stainless steels. The stainless steel powder is rather difficult to be pressed and therefore the parts present low density in the crude state. Moreover, by sintering (in H_2+N_2) the stainless steel loses its corrosion resistance. Parts from stainless steel powders are susceptible to crevice corrosion.

In the present work, the application of ion nitriding to parts from powder stainless steels was investigated, in order to obtain on the surface a compact nitride layer that should confer high hardness, high wear resistance and high corrosion resistance, comparable to that of forged stainless steels.

This desideratum comes from the requirement to obtain parts from stainless steel powders with a good corrosion resistance, but also with high tribological properties (low coefficient of friction, high wear resistance).

The application of nitriding presents many advantages: first, due to the low treatment temperature, the deformations are very small, which confers a very high dimensional stability. Secondly, the hardness of the layers is very high, reaching up to values of 1000, 1200 HV.

Of great importance in the ion nitriding process is *temperature*. At low nitriding temperatures (for instance at 350°C), the atoms substituting for iron (Cr, Ni and other) present a lower mobility, but the modification produced by them in the activity coefficient of nitrogen in iron may result in an intensification of iron nitride precipitation from the solid supersaturated solution. From the investigations of EDENHOFER [3] it follows, that ion nitriding at low temperatures is possible, following a special mechanism. Some elements from the

surface of the stainless steel are sputtered in the nitriding environment, even at low temperatures, they enter in combination with nitrogen and lead to the nitride formation.

As a result of ion nitriding, the phase composition varies in layers from the surface to the core and the following sublayers are observed:

- a compound sublayer, built up mainly from γ' and ε phases, with small amounts of γ and CrN;
- an outer diffusion sublayer with lamellar structure of γ and CrN;
- an inner diffusion sublayer made of lamellar CrN and γ, with precipitation of Cr_2N in ferrite;
- a distorted interfacial sublayer several μm thick.

For austenitic stainless steels, the presence of ferrite in the nitrided layer was observed. The mechanism of ferrite formation has not been yet clarified in literature. LEBRUN [5] suggested that ferrite is formed by a martensitic mechanism, induced by strain, because of the depletion in chromium, as a consequence of the Cr_2N precipitation. BILLON and HENDRY [1] proved that Cr_2N precipitates only in a ferrite matrix and is formed after a $\gamma \rightarrow \alpha$ transformation. The nitriding at high temperatures (over 650°C) favours the ferrite and Cr_2N transformation. At lower nitriding temperatures (under 650°C) the formation of ferrite and Cr_2N can be suppressed and thus only a single diffusion sublayer is formed where CrN precipitates in austenite and the nitrogen concentration is fairly constant in the layer. The experimental tests have not put into evidence the formation of Cr_2N.

By lowering the nitriding temperature to 400°C, the precipitation of chromium nitride is suppressed and a single-phase layer is formed. Initially this phase was identified as γ'-Fe_4N and named "S" phase. ICHHI et al. [4] showed this phase to be different from γ and γ'. It seems that the "S" phase is formed on the basis of γ-austenite and has a cfc structure and was also named "expanded austenite". Recently, MENTHE et al. [6] suggested that Fe and Cr in the "S" phase are present as nitrides, while Ni is in the free metal state, and a possible formula for the "S" phase is $(Fe_4Cr)N_2Ni$. The thermodynamics and the exact conditions for the formation of the "S" phase or of the "expanded austenite" are not clear so far.

Experimental tests proved that low temperature, short maintenance times and low nitrogen potentials favour the formation of the single-phase layer of "S" phase.

For stainless steels, the most common forms of corrosion are pitting corrosion and crevice corrosion. The most frequent cause of pitting corrosion is the selective attack of the metal where there is a scratch on the surface or other mechanical damages of the protecting film. For this reason, electrochemical techniques were used in the study of the breaking of the passivating film. In the study of the corrosion behaviour of nitrided surfaces, the method of polarization curves was used, and these were compared with those of the basis material.

2 EXPERIMENTAL TESTS

In the present study three classic grades of steels from powders were used: 316L - austenitic steel; 410L - martensitic steel; 430L - ferritic steel.

Due to the sintering conditions, the martensitic steel 410L modified its structure, finally reaching a ferrito-martensitic structure. The test pieces from stainless steel powders were prepared and sintered by the firm HOEGENES.

The samples for ion nitriding were previously degreased and polished with 1 μm diamond paste and then degreased again with acetone before being subjected to ion nitriding. For the experimental tests performed at the Technical University of Cluj-Napoca, the ion nitriding treatment of of the stainless steel samples was

carried out in an ion nitriding equipment "NITRION 10", represented schematically in Fig.1.

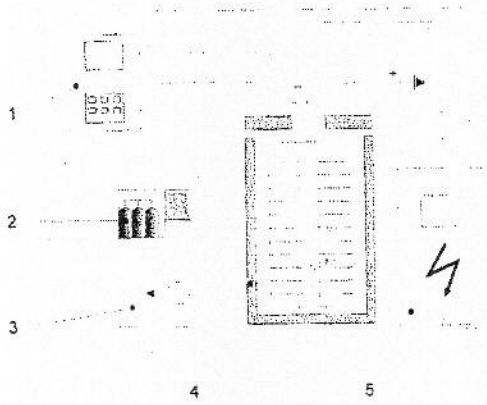

Fig.1. Block diagram of the ion nitriding equipment NITRION 10;
1-parameters control system; 2- gas supply system; 3-void system;
4-container; 5-electric power supply system.

After nitriding, samples were sectioned with a diamond disk in order to preserve as good as possible the nitrided layer. Then, some of the samples were prepared for structure investigations by optical and electron microscopy. In order to fill as good as possible the pores, the samples were mounted in a special resin using a Struers device.

The experimental tests were performed for a great number of nitriding regimes, where the temperature was varied in the 400-600°C range and the duration from 5h to 50h. The longer nitriding times (50h) were chosen in order to obtain deep nitided cases, because the diffusion coefficient of nitrogen at 400-450°C is low.

The use of the low temperature regime had in view the formation of "S" phase, respectively of a diffusion layer, without white layer, in order to see if the corrosion resistance remained the same after those nitriding regimes.

The corrosion tests were made in 0,5 M H_2SO_4 solution. A saturated calomel electrode (SCE) was used as a reference electrode, and the scanning rate for the determination of the polarization curves was 1 mV/min. Before the immersion in the solution, the edges of the samples were coated with resin, in order to minimize the effect of crack corrosion. The electrode potential and the current were recorded on a computer and then plotted.

The measurements were made at 20°C in media with open surfaces in static conditions. The stirring of the medium was achieved only by the releasing of the gas bubbles resulted from the corrosion reaction. The samples (the working electrode) were placed so that the releasing of gases was allowed and the immersion depth in the medium was the same. The Luggin capillary was fastened so that the opening of the capillary was as close as possible to the working electrode surface in order to overcome the resistance of the corrosive medium and to remove the ohmic drop in the medium.

3 RESULTS AND DISCUTIONS

After various ion nitriding regimes a nitride layer was obtained, with very high hardness. In this paper we report only on the corrosion behaviour of the nitride layers. The best results were reached after ion nitriding at low temperature (430°C/10h). This regime led to the formation of the "S" phase

Fig.2. The structure of the samples from 316L stainless steel, ion nitrided at 430°C/10h.

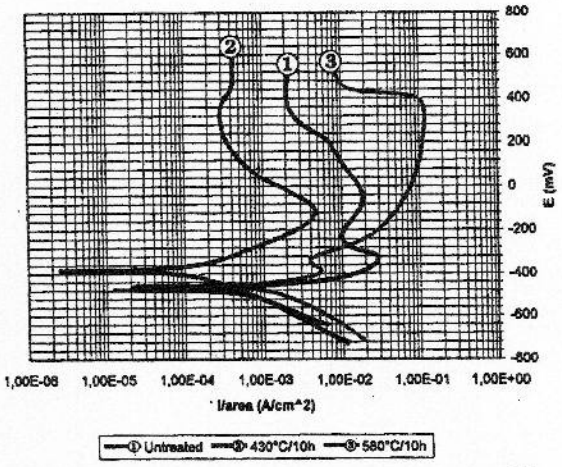

Fig.3. The corrosion behaviour of the 316L steel in 0.5M H_2SO_4 solution.

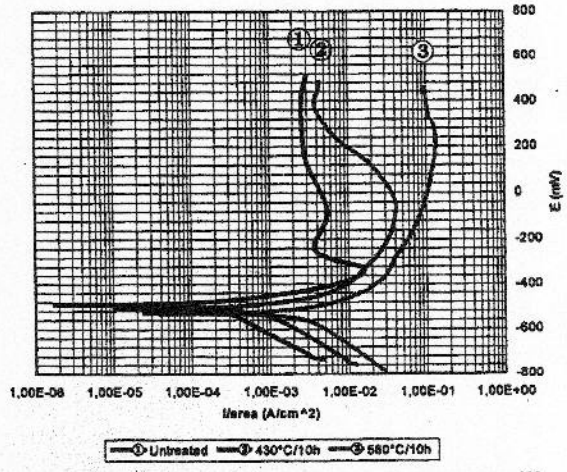

Fig.4. The corrosion behaviour of the 410L steel in 0.5M H_2SO_4 solution.

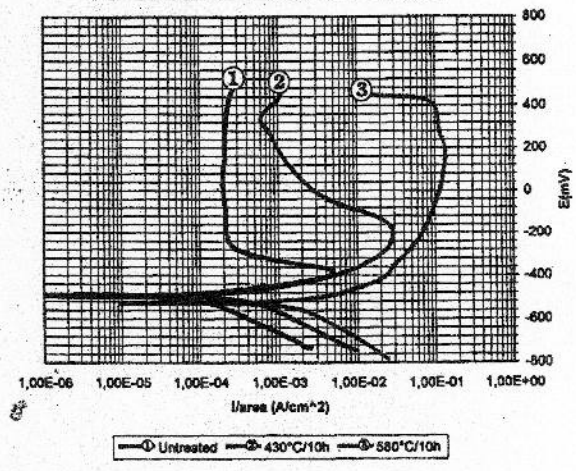

Fig.5. The corrosion behaviour of the 430L steel in 0.5M H_2SO_4 solution.

on the surface of the austenitic steel (316L) samples. In Fig.2 is presented the microstructure of the layer obtained after ion nitriding at low temperature

The results of the corrosion test were presented by means of polarization curves. The polarization curves for the three grades of steels in 0,5M H_2SO_4 solution, for various nitriding regimes, are plotted in Fig.3, 4 and 5.

For the untreated 316L steel (Fig.3) the free corrosion potential is established roughly at -450 mV, afterwards the potential is increased until it reaches an instability zone. After ion nitriding it is obvious that the 430°C/10h regime improves the corrosion resistance, while the high temperature nitriding brings about a decrease in corrosion resistance, as compared to the untreated sample. This confirms that during low temperature nitriding the "S" phase is produced (the X rays analysis of the layer also confirms this fact).

For the martensitic steel (Fig.4) both nitriding regimes worsen the corrosion resistance. This is visible also on the surface of the parts after ion nitriding. For the ferritic steel (Fig.5) both nitriding regimes have negative effects on the corrosion resistance. The sample surface shows extended areas covered with deep corrosion spots.

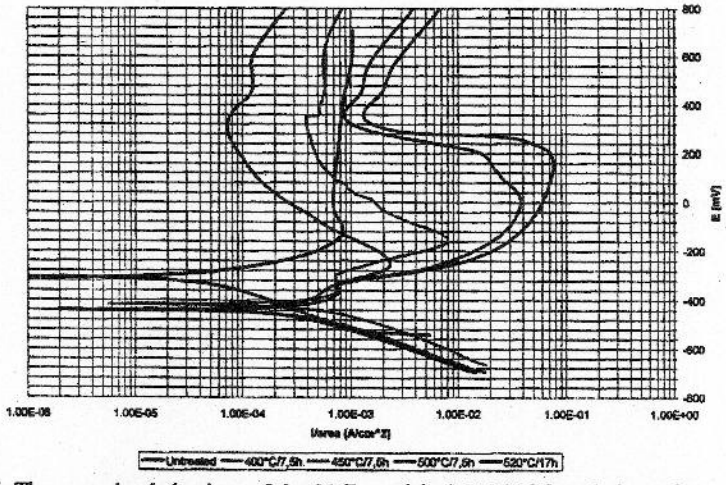

Fig.6. The corrosion behaviour of the 316L steel in 0.5M H_2SO_4 solution, after various regimes of ion nitriding.

Finally, different ion nitriding regimes and various maintenance times were tested (Fig.6). The results showed that the 400 °C/7.5 h regime produced a layer with a good corrosion resistance, while the 520 °C/17h led to the formation of a thicker layer, but with a low corrosion resistance.

The results of this study supported the idea that by ion nitriding layers with high hardness can be obtained, with a reasonable good corrosion resistance, on stainless steels obtained by powder metallurgy. But the problem with ion nitriding of stainless steels from powders remains that of the compactness of the nitrided layer. The nitrided layer had a better compactness compared to the sample in its initial state, but nevertheless, but some cracks in the layer are steel present.

4 CONCLUSIONS

From the experimental tests, the following conclusions were inferred:

1. The sintered samples from stainless steel present a very low corrosion and wear resistance, thus it is quite necessary to find out technologies for improving these characteristics.
2. The experimental results confirmed that by ion nitriding a layer with high hardness is obtained. The thickness of the layer depends mainly on the nitriding temperature and duration.
3. The corrosion behaviour of the 316L steel, after ion nitriding at 430°C/10h, was better than that of the untreated steel, which shows that the layer obtained under this regime presents also a good compactness and a good corrosion resistance.
4. By controlling the parameters of ion nitriding, layers with improved corrosion resistance, can be obtained at the surfaces of sintered stainless steels.

REFERENCES

1. BILLON,B.; HENDRY,A. - Nitriding of stainless steel in amonia: 2 Kinetics of nitriding, Surface Engineering, 1985, vol.1, No.2. p 125-129.
2. DESHAYES,S. - Etude de la nitruration a basse température d'aciers inoxydables austénitiques.
3. EDENHOFER,B.; BEWLEY,T.J. - Low - temperature ionic nitriding : nitriding at temperatures below 500 C for tools and precision machine parts. Heat treatment 1976, The metals society, No.181, p 7-14.
4. ICHII, K.; FUJIMURA,K.; TKASE,T. - Pitting corrosion Behavior of Ion Nitrided stainless Steel. Plasma Surface Engineering, 1981, p 1187.
5. LEBRUN,J.P. - La nitruration ionique, Traitements thermiques nr.176-1983, p 17-24.
6. MENTHE,E.; RIE,K.; SCHULTZE,J. - Structure and properties of plasma nitrided stainless steel, Surface and CoatingsTechnology, 74-75, 1995, p 412-416.