MICROSTRUCTURE AND HARDNESS OF VACUUM OXYNITROCARBORIZED ELECTROLYTIC IRON

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Abstract
This study deals with the microstructure and lattice parameters of vacuum oxynitrocarborized pure electrolytic iron. The vacuum oxynitrocarborization treatment is performed to improve the wearing-out and corrosion resistance of pure electrolytic iron and AISI 1045 (C45, DIN1.1191) steel as a reference. The vacuum oxynitrocarborization has been carried out for a period of 7 hours at 550°C in ammonia and carbon dioxide atmosphere. The pressure in the vacuum chamber has been 8.10⁴ Pa for the first 5 hours and 1.10⁵ Pa during the last 2 hours. The micro-structural and micro-hardness changes in the iron and in the steel are studied. Compound and diffusion layers in the oxynitrocarborized electrolytic iron and AISI 1045 steel are observed. The phase composition and structure of the both zones are discussed. A higher diffusion activity of the penetrating elements in the iron as compared to that of the steel is found out. The amount of the Fe₄N phase in the surface layers of the iron is proved by X-ray diffraction analysis to be increased as compared to that in the steel. The ε-Fe₂₋₃(N,C) phase formation is not influenced by the carbon content in the AISI 1045 steel. The presence of impurities could not cause alteration in α- and ε-phase parameters or it could not be detected by the X-ray diffraction analysis due to their low concentration. The iron hardness measured on the surface remains unchanged after the process (before oxynitrocarborization HV₁=600, after - HV₁=630), while the steel hardness remains medium. However, iron gains a corrosion resistance

Keywords: oxynitrocarborization, vacuum, ε-Fe₂₋₃(N,C), Fe₄N.

1. INTRODUCTION

Nitrocarborization is a gaseous diffusion process in which the surface of the metal or alloy is saturated mainly with nitrogen and a few quantities of carbon. The process of oxynitrocarborization is also gaseous but the gas phase includes oxygen containing gas. The phase structure after the process shows an increased surface hardness, wear-, heat- and corrosion-resistance.

It is known that the main disadvantage of the electrolytic iron use is its low corrosion resistance. In other hand, the iron is easily and inexpensively obtained, its structure is porous and ultrafine which makes it an excellent subject to study. A vastly used for machine elements carbon steel - AISI 1045 (C45, DIN1.1191) is examine as a reference for the diffusion processes that take places.

2. EXPERIMENTAL PROCEDURE

Lamella samples of an AISI 1008 steel with electrolytic iron coating (overall about 2 mm thin) and an AISI 1045 steel sample with an average size of 10 x 10 mm are used for the metallographic study (Olympus BX41M, Neopfot 2), the X-ray diffraction analysis (ДРОН-2), the hardness and microhardness measurements in depth of the oxycarbonitrided layer. The vacuum oxynitrocarborization has been carried out in an industrial equipment for a period of 7 hours at 550°C in ammonia and carbon dioxide atmosphere.
The pressure in the vacuum chamber has been $8 \times 10^4$ Pa for the first 5 hours and $1 \times 10^5$ Pa during the last 2 hours [1]. The surface hardness is measured by a Vickers tester "Krautkramer" (before and after the oxycarbonitration) under a load of 1 kg. The microhardness is measured on a microhardness tester ПМТ-3 under a load of 0.05 kg according to a chess-board order 4...5 times for each sample. The microstructure is etched by 4%-solution of HNO₃ in ethyl alcohol.

3. RESULTS AND DISCUSSION

Figure 1 shows a comparison of the depth profile of the microhardness results of the electrolytic iron and the substrate before (a) and after (b) vacuum oxynitrocarborization as well as their cross-section microstructures.

![Fig.1. Microhardness and microstructure (x200) of pure electrolytic iron after piling (a) (600HV₁), and microhardness and microstructure (x200) of the oxynitrocarborized electrolytic iron (b) (630HV₁).](image)

The compound layer on the surface of the oxynitrocarborized electrolytic iron is white looking with a 10 μm thickness and microhardness of 790 HV₀,₀₅. The hardness of the electrolytic iron before (a) and after (b) vacuum oxynitrocarborization remains merely unchanged (350 – 400 HV₀,₀₅). Partial relaxation of the high III⁻ type structural stresses could explain the insignificant microhardness reduction in the oxynitrocarborized electrolytic iron. In the other hand the ultra thin nitride phases in the latter that change its color increase the iron's hardness. The presence of these nitrides could not be light – microscopically detected but it is registered by the XRD analysis and the dark color of the layer. The main difference is found out in the substrate hardness which shows enrichment of the diffusive elements. There is an electrolytic iron intermediate zone. It is obtained at a low density asymmetric alternate current in the electrolytic bath, used in order to increase the adhesion between the iron and the substrate. The density of this zone as compared to the electrolytic iron is higher and its structure is less stressed. The figure shows that these zones tend to have opposite trends to microhardness. The color of this intermediate zone resembles that of the compound
layer. Perhaps, the zone is a “barrier” against the passing nascent atoms, and thus resulting in their local concentration increase. The Fe₄N needles are found out near the intermediate white zone as well as in the depth of the substrate. Figure 2 illustrates the structural difference of both substrates before and after the vacuum oxynitrocarborization. The substrate microhardness decrease near the intermediate zone compared to the measured values deeper in it is due to the grains’ recrystallization as it is show on figure 2.

![Fig.2 Substrate microstructure before (a) and after (b) vacuum oxynitrocarborization (x200).](image1)

The microhardness of the substrate at a distance of 150 μm from the “white” zone towards the core of the oxynitrocarborized electrolytic iron maintains unchanged - figure 3. However there are nitride needles in the ferrite grains at a distance twice greater than that (over 300 μm in depth) which is obvious from the microstructural analysis. The diffusive zone of the carbon steel reaches up 250 μm in depth (figure 4). Therefore the overlying porous and ultrafine electrolytic iron enhances saturation of the substrate with N and C as compared to the carbon steel. It is known that this saturation is strongly influenced by the preliminary structure of the metal or alloy [2]. The electrolytic iron is probably an “accelerant” for the active nitrogenous atoms. The equal depth of the diffusive layers in the AISI 1045 steel, determined by the microhardness, and in the substrate under the electrolytic iron layer, determined by the microstructure, is evident. It has to be also pointed that the ultra thin structure accelerates significantly the diffusion of nascent...
N and C in low carbon steels [3, 4]. Furthermore the substrate grains in depth remains plastically deformed, their boundaries are enlarged and thus, the structure is undoubtedly more defective. That's the reason why the grains near the surface of the substrate recrystallize. Due to the nitride needles in the oxynitrocarburized ferrite grains their microhardness is increased.

The annealed and air cooled AISI 1045 steel is vacuum oxynitrocarburized. Its surface hardness after this process is 400HV1. The microhardness values become stable (about 300HV0.05 ) at a distance of 250 μm (figure 4). The compound zone microhardness was not measured because this layer is thin and fragile.

Figures 5 shows a comparison of the X-ray results of the vacuum oxynitrocarburization electrolytic iron and the pure electrolytic iron. According to the Fe – phases’ 100% peaks of both, the difference in d/n ratio is insignificant. Due to the diffusion of the elements mainly through the grain boundaries the ferrite saturation with nitrogen is low. The quantity of Fe4N phase is more than that of Fe3N phase according to their 100% and 50% peaks – figure 5. The highest Fe3N phase peak is twice smaller than those of the Fe4N. A high nitrogen diffusive activity in the electrolytic iron as well as a low surface potential of the element at a low environmental pressure could explain that fact. The Fe4N phase d/n ratios are merely the same as theoretical ones. That proves the participation only of the Fe and N in this phase formation. At the same time the differences in the Fe3N d/n ratios from the theoretical ones prove its oxy-carbo-nitride structure.

1 The X-ray analysis is carried out by eng. M. Balcheva.
Fig. 6. X-ray diffraction patterns of the oxynitrocarborized AISI 1045 steel.

The α – phase d/n ratios of the oxynitrocarborized AISI 1045 steel are almost the same as theoretical ones - figure 6. Due to the low concentration of the impurities in this steel, they could not cause alteration in the α-phase parameters or this could not be detected by the X-ray diffraction analysis. In contrast to the electrolytic iron, the Fe3N phase quantity is more than that of the Fe4N phase. The Fe3N d/n ratios are not quite different from the oxynitrocarborized electrolytic iron ones. So, N, C and probably some oxygen from the gas phase participate in this phase formation. The steel’s carbon plays role in the Fe3N phase stabilization [5].

4. CONCLUSIONS

1. The diffusion layer overall thickness of the system "oxynitrocarborized electrolytic iron - AISI 1008 steel substrate" is twice greater as compared to that of AISI 1045 steel at equal conditions of obtaining. This proves the higher diffusion activity of the nascent atoms in the electrolytic iron;

2. The iron’s and the steel’s oxynitrocarborized layers have different composition in quantity and quality because of the different crystal structure, chemical and phase composition of both type samples;

3. The diffusion rate in different in structure electrolytic iron layers varies significantly. Although the thin intermediate iron layer is dense and have non-defective structure it acts like a “barrier” for the passing nascent atoms. Their local concentration increases and causes a higher microhardness;

4. Except a high corrosion-resistance, the vacuum oxynitrocarborized compound layers has also increased heat-resistance due to which their ultra thin structure and high hardness are saved up to 570 °C;

5. An electrolytic iron affords faster and more effective penetration of the active N, C and O atoms in the different steel substrates. Since the high diffusive activity of the nascent atoms in the iron and the substrate, an electrolytic iron layer could be an eligible coating for lots of parts and tools. This is a subject for future investigations.

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