Combined Aluminizing with Nitriding Process of Structural and Tool Steels in a Low-Pressure Arc Discharge Plasma[1]

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Abstract – Investigations of surface modification of structural and tool steels treated in low-pressure arc discharges plasmas have been carried out. The complex treatment in single vacuum cycle involved a sequence of operations: ion cleaning of the surface and heating the sample, diffusion surface alloying with aluminum and nitriding. The sample temperature was not over 620 °C at all stages of the process and the total time of treatment was approximately 2 h. The structure, phase and element constitution, and microhardness of the surface layer have been investigated. It has been established that the significant increase in microhardness from 2–2.5 in the original state to 10–13 GPa in the modified layer after complex diffusion saturation in an arc discharge is due to the formation of iron nitride containing dispersed particles of aluminum nitride.

1. Introduction

The nitriding process of structural and tool steels with the goal of enhancing the corrosion resistance and hardness is of great utility in mechanical engineering.

Alloyed steels containing Al, Cr, Mo, and V are generally used for the nitriding process. The alloying element content is in general 1.5÷2%. Nitrogen diffuses into the iron to form solid nitrides such as AlN, CrN, MoN, etc. At this takes place, the surface hardness of steel articles increases to 10–15 GPa [1]. Nitriding is more efficient for steels containing Al (about 2%).

This paper presents the results of experimental investigations on the surface modification of types both 1045, 5140, 5340 low-alloy structural steels and W6Mo5 tool steel by Al diffusion saturation and nitriding in low pressure arc discharges.

2. Experimental

Steels 1045 (0.45% C, 0.17 – 0.37% Si), 5140 (0.4% C, 1.0% Cr, 0.17 – 0.37% Si), 5340 (0.4% C, 13.0% Cr, 0.8% Si) and W6Mo5 (0.85% C, 6% W, 5% Mo, 4.0% Cr, 0.5% Si) were used as the test material.

Samples of diameter 20 mm and height 10 mm were previously mechanically grinded and were washed with organic solvent in ultrasonic bath before placing in vacuum chamber.

The complex treatment was performed on a setup shown schematically in Fig. 1. The test sample was placed on a holder in the central part of the vacuum chamber evacuated by a turbo-molecular pump to a pressure of 10^{-3} Pa. The Al cathode was evaporated using an ordinary vacuum arc with a dc discharge current of up to 100 A. An additional gas-discharge plasma was generated in the chamber by a hot-cathode gas arc [2, 3]. The vacuum chamber served as an anode both for the vacuum and gas arcs.

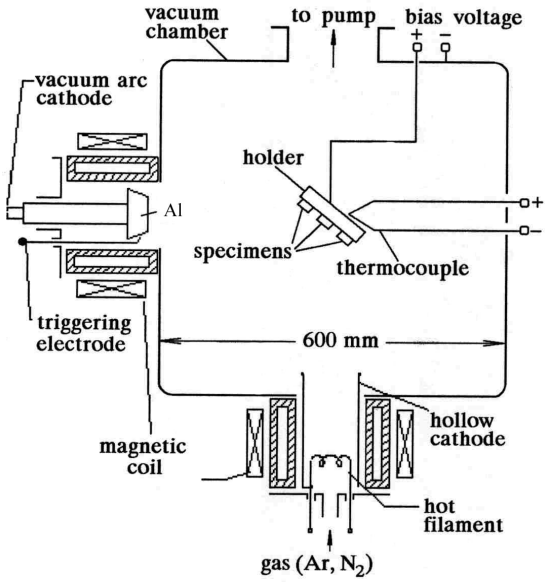

Fig. 1. Schematic of the experimental setup

The gas arc with a discharge current of 80 A produced a homogeneous plasma with a density of 10^{10} cm^{-3} and a saturation ion current of up to 10 mA/cm^2 in the chamber. The gas (Ar, N_2) was fed through the gas-arc cathode. This allowed a control of the reactive gas ion density near the surface over a wide range.

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Complex modification of the sample surface was performed in one cycle in the following way: The first stage was cleaning and heating of the surface with the low-temperature argon plasma produced by the gas arc. To intensify the cleaning process and to heat the sample additionally by the ions accelerated in the space charge layer near the sample surface, a negative bias of up to 600 V was applied to the sample. Cleaning was carried out for 20 min at an argon pressure of ~ 10^{-1} Pa. During this time the sample temperature, which was measured by a thermocouple, increased to 620 °C. The next stage was plasma-assisted arc vapor deposition of an Al coating on the heated substrate for 40 min. During this stage the sample surface was subjected to bombardment with Al and Ar ions simultaneously. This stage corresponds to surface alloying of the sample with aluminum. The final stage was nitriding of the sample in the gas arc plasma for 90 min at a temperature of 520 °C. This operation was aimed at obtaining a nitride layer based on iron and aluminum. For this purpose, nitrogen with a pressure of 0.5 Pa was used instead of argon.

The properties and performance of the layer produced were investigated with the use of X-ray diffraction analysis, optical metallography, Secondary Ion Mass Spectrometry (SIMS) and Transmission Electron Microscopy (TEM) methods and by measuring the microhardness.

The microstructure of the samples surface and samples cross sections was investigated using metallographic microscope of the MMR-4 type by examining cross sections etched in a 4-% HNO_3 solution in alcohol. The microhardness was measured both at the sample surface and in its bulk for sample cross sections on the PMT-3 instrument at a load of 1.0 N with a step of 10 μm. The element composition was investigated by the SIMS method on a MS-7201M mass spectrometer. The phase composition was determined by X-ray diffraction analysis using the DRON-1 diffractometer. The structure of the diffusion-saturated layer and the phase constitution of its surface and cross section were investigated by TEM method on an EM-125 instrument.

3. Results and Discussion

Figure 2 shows photos of the modified steel surfaces received with a magnification of 210 times in a microscope. As shown in the figure, due to low-energy ion bombardment the surface of samples is strongly etched; there is large number of inequalities and roughnesses.

In the original state, the structural steels were ferritic-pearlitic in structure; their hardness is 200–220 kgf/mm^2. The microstructure of a cross section of structural steel samples subjected to complex treatment revealed by metallography method has shown that depending on a type of steel the three-layered structure are formed: a surface white layer of width ~ 10–20 μm, under which there is an intermediate grey layer of width ~ 8–20 μm, and an extensive (150–300 μm) zone is similar to the original structure beneath this sublayer (Table). Fig. 3 illustrates this three-layered structure by the example of type 5140 steel.

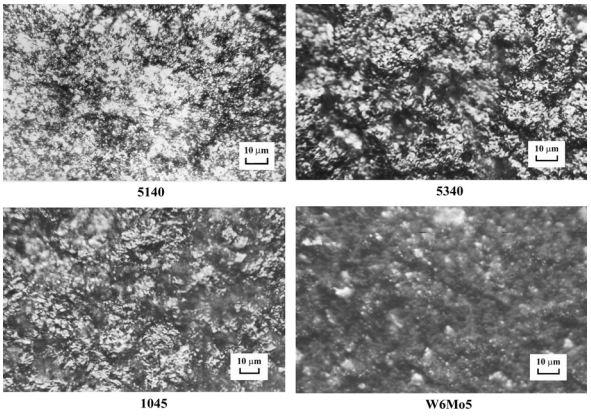

Fig. 2. Topography of the modified steel surfaces after Al diffusion saturation followed by plasma nitriding

Table. The influence of steel type on thickness of the modified layer

No	Type of steel	Thickness of the nitrided layer (Fe_4N), μm	Thickness of the intermediate layer, μm	Thickness of the diffusion layer, μm
1	5140	15–20	8	300
2	5340	10	–	200
3	1045	20	20	150
4	W6Mo5	10	150	30

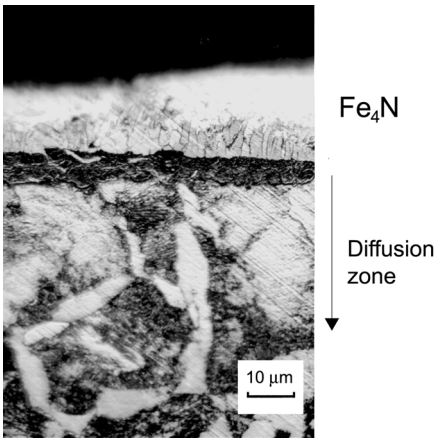

Fig. 3. Structure of modified layer in 5140 steel after complex surface treatment including diffusion saturation with Al followed by plasma nitriding in a low pressure arc discharge

The microstructure of type W6Mo5 tool steel is shown in Fig. 4. It is clearly seen that an uniform grey layer of width ~ 10 μm is formed on the surface. Beneath the modified surface layer there is an extensive zone up to 150 μm.

The microhardness profiles for these samples are given in Fig. 5. As a result the microhardness meas-

urements it has been obtained that the maximal hardness corresponding to 1000–1300 kgf/mm^2 is achieved in the white hard-etching layer. In going from the white layer deeper into the bulk sample, the microhardness decreases and becomes equal to the original state hardness at a depth of ~ 150–300 μm. It should be noted that the hardness of the white layer is invariable throughout its width.

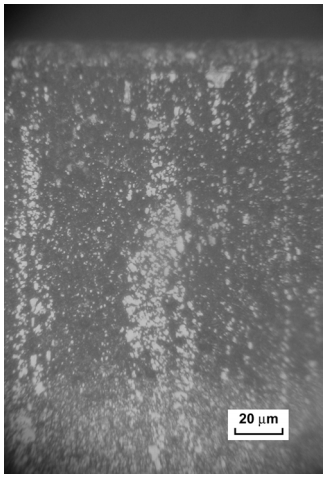

Fig. 4. Structure of modified layer in W6Mo5 steel after complex surface treatment including diffusion saturation with Al followed by plasma nitriding in a low pressure arc discharge

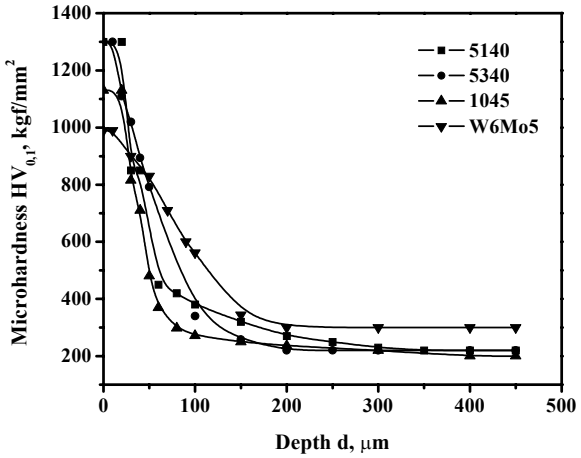

Fig. 5. Microhardness profiles in the layers modified in steels by a low pressure arc discharge

X-ray diffraction analysis carried out for a sample of type 5140 steel (with an analyzed layer of width 10 μm) has revealed that the surface white layer was constituted by iron nitride (Fe_4N, fcc) (Fig. 6, *c*). No other phase was found. This may testify to the fact that, these phases might make up no more that 3–5% by volume or they were nonuniformly distributed throughout the modified layer. It should be noted that the compound Fe_4N is characterized by microhardness values lying in the range 650–850 kgf/mm^2, which are about twice the values estimated for our case (Fig. 5).

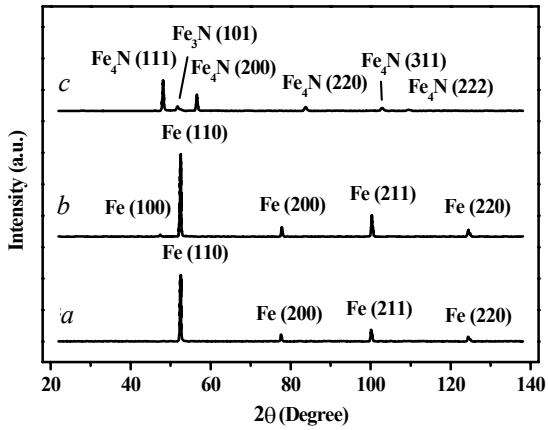

Fig. 6. X-ray diffraction patterns of the surface layer of 5140 Steel: in the original state (*a*), after Al diffusion saturation (*b*), after Al diffusion saturation followed by plasma nitriding (*c*)

Further examination of the surface of the sample subjected to complex treatment was performed by the SIMS method (Fig. 7). Along with the original elements (Fe, Si, Cr), Al has been detected on the sample surface. It should be noted that the technical capabilities of the instrument we used gave no way of detecting secondary ions of nitrogen, carbon, and oxygen. In the alloyed layer, Al may either be present in the Fe_4N-based solid solution, or be in a free state, or be a constituent of second-phase particles (aluminum nitrides, aluminum carbonitrides, and intermetallic compounds with iron).

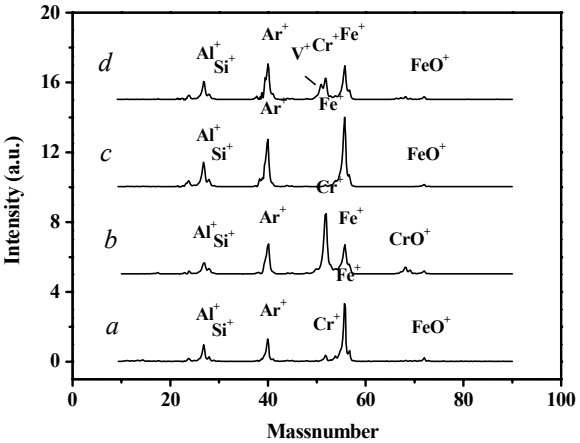

Fig. 7. Mass spectrum of the steel surfaces after Al diffusion saturation followed by plasma nitriding, measured by SIMS method. 5140 steel (*a*), 5340 steel (*b*), 1045 steel (*c*), W6Mo5 (*d*)

This problem was solved by TEM method with the use of the extract replica method to perform a structure-phase analysis of the white layer for a sample of type 5140 steel. It was found that after nitriding process the thin layer with nanocrystalline structure (Fig. 8, *a*, *b*) is forming on a surface. It is explained by typical "speckled" contrast on dark field image (Fig. 8, *a*) and by ring-type structure of the microe-

lectron diffraction pattern (Fig. 8, *b*). The mean sizes of crystallites are varied from 20 to 40 nm. It is necessary to note, that nanocrystalline state is not formed at diffusive saturation of a steel surface by aluminum (Fig. 8, *c*, *d*). The indexing of microelectron diffraction patterns has allowed to show that together with iron nitrides the aluminum-containing phases, namely, $(Fe,Al)_3C$ and AlN (Fig. 8, *a*, *b*) are being detected. Moreover, it can be expected that Al will be present at lattice defects (dislocations) and at intraphase and interphase boundaries. In sample on intermediate treatment stage, along with the phases present in the original state (α-Fe, Fe_3C), free Al has been detected.

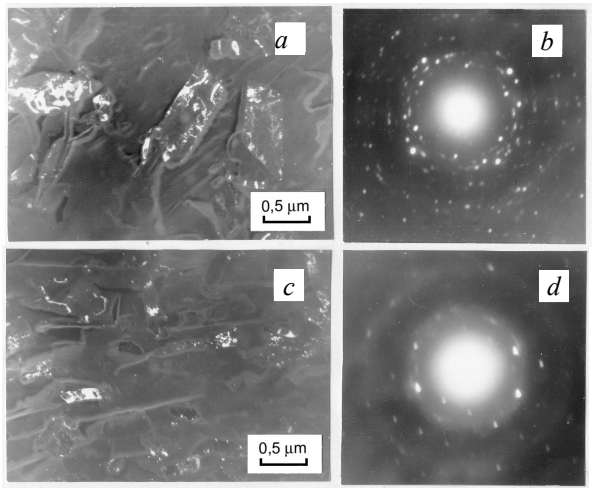

Fig. 8. TEM dark field images (*a*, *c*) and area diffraction patterns (*b*, *d*) of the surface layer in 5140 steel after Al diffusion saturation (*c*, *d*) after Al diffusion saturation followed by plasma nitriding (*a*, *b*).

Consequently, the comparatively high values of microhardness that we have found for the samples subjected to complex vacuum ion-plasma treatment are due to the formation of a precoat with nanocrystalline structure based on aluminum nitrides and carbides of iron and aluminum.

4. Conclusion

1. An original technique for the surface modification of structural and tool steels, based on the use of low-pressure arc discharges, has been developed.

2. With this technique a modified surface layer of width from 10 to 20 μm has been obtained that has a high hardness (~ 1000–1300 kgf/mm^2), an intermediate sublayer of width from 8 to 20 μm which possesses increased microhardness has been achieved and is followed by an extended (150–300 μm) zone of diffusion saturation showing an increased hardness.

3. It has been found that the near-surface region of the modified layer has nanocrystalline structure and it consists of the nitrides and carbides of iron and aluminum. The high microhardness of the modified layer is due to the presence of AlN nanoparticles.

4. The proposed simple and effective treatment method can be used to improve the performance characteristics of articles made of low-alloy and/or unalloyed structural steels and also tool steels such as W6Mo5.

References

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