CORROSION RESISTANCE OF NANOSTRUCTURED 67SiMnCr6-6-4 BEARING STEEL

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Abstract

The subject of the study was to determine the corrosion resistance of the bearing steel 67SiMnCr6-6-4 with a nanocrystalline structure compared to those with the conventional structure of tempered martensite. In order to obtain a nanocrystalline structure one set of steel samples was subjected to heat treatment consisting on quenching and austempering at 240°C. This treatment produced a homogenous nanobainitic structure composed of nanometric plates of carbide-free bainite separated by thin layers of retained austenite. The microstructures formed were investigated by use of transmission electron microscopy techniques. For comparison a conventional quenching and tempering at 350 °C for 1 h was applied to second set of steel samples. Time and temperature of tempering was chosen so that the hardness of both samples (nanostructured and quenching and tempered) was similar. The microstructure obtained was a tempered martensite.. The corrosion resistance studies of both kinds of steels with different microstructures were carried out in Na_2SO_4 acidic and neutral environment using potentiodynamic and electrochemical impedance spectroscopy (EIS) methods. The obtained results indicate, that the nanobainitic structure produced in bearing steel 67SiMnCr6-6-4 does not affect the corrosion resistance of the steel as compared with conventional quenching and tempering treatment in both acidic and neutral environment.

Keywords: Bearing steel, austempering, nanocrystalline structure, corrosion resistance

1. INTRODUCTION

One of the most promising directions of development in the field of crystalline materials is the reduction of their grain size down to the nanometric scale. This nanocrystalline structure encompasses grains of a size smaller than 100 nm [1] in at least one direction. Nano-sized grains rectifies or modifies material properties and hence broadens the scope of their usage.

In recent years, works on steel nanostructuring have been extensively developed, as steel is the most commonly used metallic structural material. Nanostructured steels are produced by various methods. Among others, the most promising method is to develop a nanocrystalline structure by subjecting a material to subsequent phase transitions leading to the formation of nano-bainite structures. Such structure can be formed in finished components with diversified shapes and dimensions, thus improving functional properties of the initial material.

The functional properties of currently used steels with a typical structure are not satisfactory in many cases. Such properties as high mechanical strength, corrosion resistance and resistance to wear by friction are highly demanded from materials used in applications like valves, gas turbine blades, cutting tools or medical instruments. Steels with nano-bainite structure may provide an excellent solution in relation to inflated requirements.

The present study attempts to determine the influence of formation of the bainite-like nanostructure on the corrosion resistance of the 67SiMnCr6-6-4 bearing steel.

2. EXPERIMENTAL METHODS

67SiMnCr6-6-4 bearing steel of composition presented in **Table 1** was subjected to nanostructuring treatment consisted of austempering with an isothermal quenching at 240°C for 61 h. In order to determine austempering parameters, the studies of characteristic parameters of phase transformations in steel were carried out using the quenching dilatometer Bähr DIL 805L. The austempering parameters was chosen so that the temperature was above Ms temperature and time ensured the end of the bainitic transformation at this temperature. A cooling medium in which the treatment was carried out was liquid Sn-Ag alloy heated to a temperature of austempering. Microstructure of the samples after heat treatments was observed using light microscope, scanning electron microscope and transmission electron microscope (TEM) operating at 120 kV.

Table 1 Chemical composition of 67SiMnCr6-6-4 bearing steel

	C [%]	Si [%]	Mn [%]	Cr [%]	Mo [%]	Ni [%]	P [%]	S [%]
67SiMnCr6-6-4	0.65÷ 0.7	1.45÷ 1.6	1.35÷ 1.55	1.00÷ 1.2	0.23÷ 0.27	max 0.25	max 0.025	0.015÷ 0.02

The corrosion resistance was examined by the potentiodynamic and Electrochemical Impedance Spectroscopy (EIS) methods in an acidic (pH4) and neutral (pH7) aqueous 0.1 M Na_2SO_4 solution. Changes in pH of the solution were made with use of sulfuric acid. The impedance measurements were made at a corrosion potential with the frequency ranging from 10^{-3} Hz to 10^4 Hz. The amplitude of the pulse of the alternating current (sinusoidal) was 20 mV. The spectra obtained were analyzed using the 3.0 Boukamp computer program. The results are presented in the form of the Bode diagrams, showing the relationship between log $|Z|$ (where Z is a vector length on complex plane corresponding to the impedance) or an angle θ (formed by the vector "z" of the real axis) as a function of the logarithm of frequency F. In the potentiodynamic method the samples were polarized towards the anode from the potential 200-250 mV lower than the corrosion potential to the potential of -200 mV. The potential variation rate was 0.3 mV/s. Prior to the measurements, the samples were immersed in the corrosion solution to let the corrosion potential to stabilize. After examinations of the corrosion resistance, the surfaces were observed in a Hitachi S-3500N scanning electron microscope. The corrosion resistance study of bearing steel 67SiMnCr6-6-4 after nanostructuring treatment was carried out with compare to the steel after a quenching and tempering on a similar hardness.

3. RESULTS

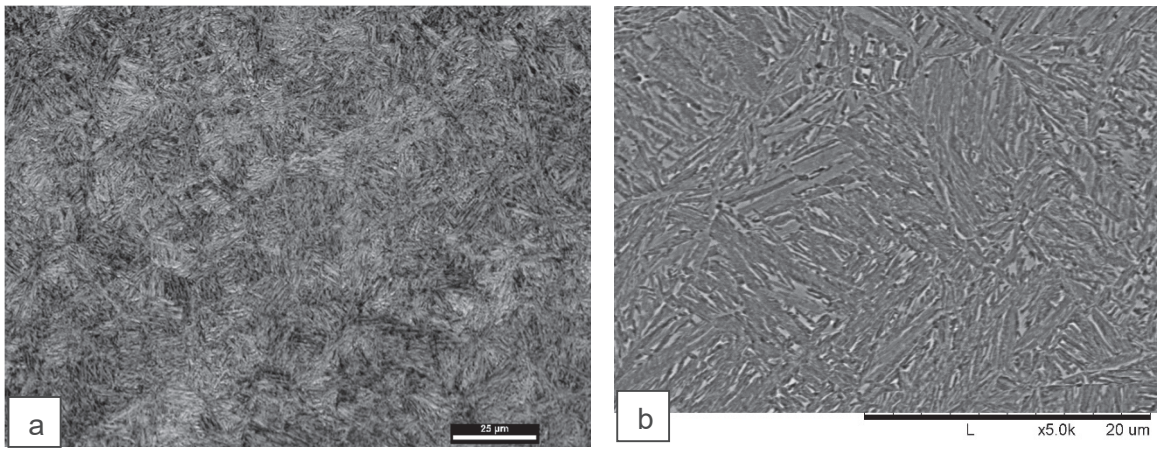

Fig. 1 Microstructure of 67SiMnCr6-6-4 baring steel after austempering treatment at 240°C for 61h observed using light microscope (a) and scaning electron microscope (b)

The acicular structure of the 67SiMnCr6-6-4 bearing steel was obtained by appropriate processing. The structure is composed of needles partially parallel and partially distributed at different angles, forming structural packets and clusters arranged in various directions (**Fig. 1**) Thorough phase identification was conducted using a transmission electron microscope and revealed the presence of a structure formed of bainitic ferrite plates with an average width of 49±3.7 nm. Residual austenite layers with an average width of 39±2.6 nm were deposited between the ferrite plates. So formed structure was considerably uniform within the observed area. On the basis of the microphotographs, the residual austenite fraction was estimated at ca. 38 % vol. of the evaluated material. The microstructures of the nano-structured bearing steel are shown in **Fig. 1-2**.

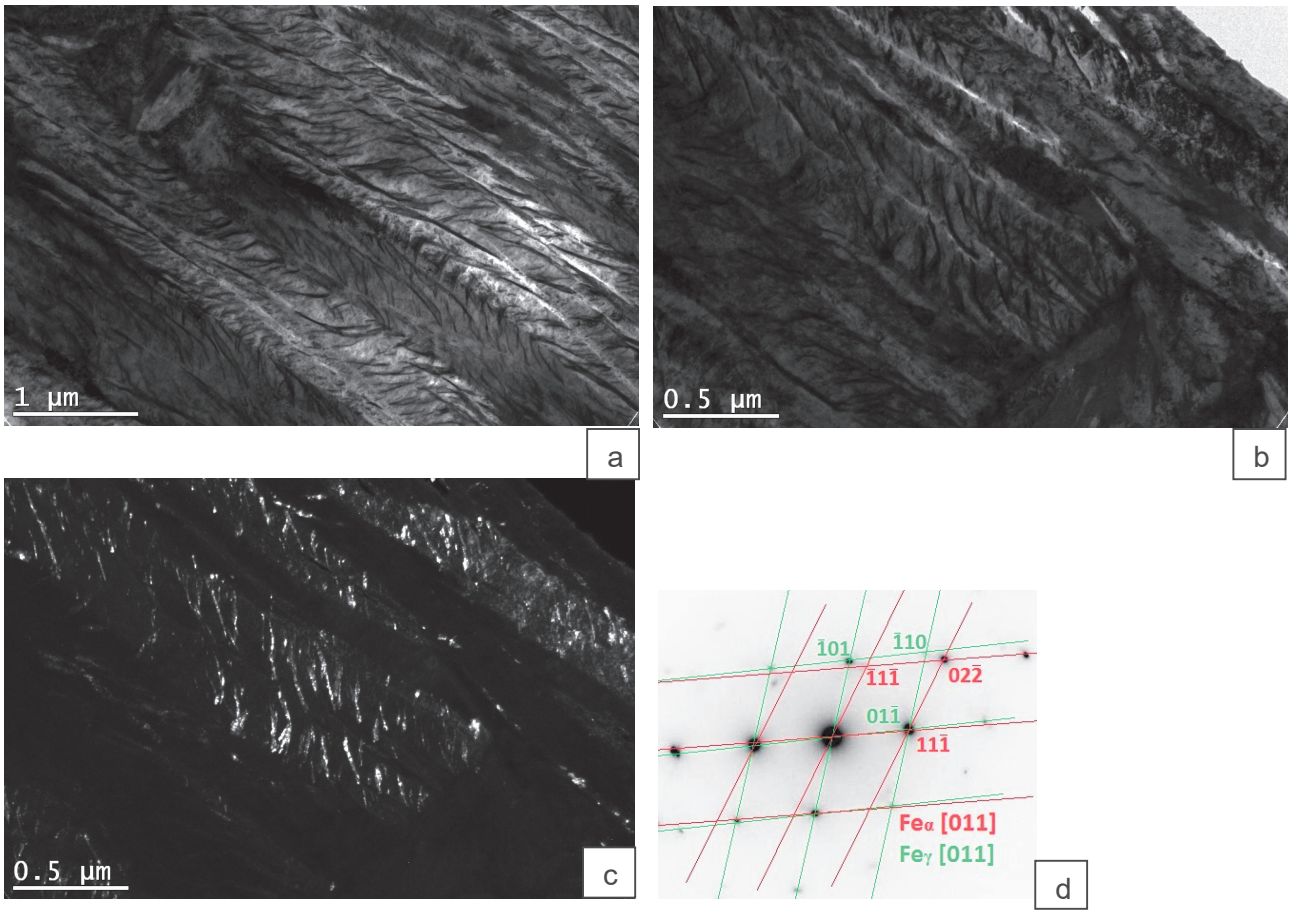

Fig. 2 Microstructure of 67SiMnCr6-6-4 bearing steel after austempering treatment at 240°C for 61h observed using transmission electron microsope: (a), (b) - bright field image, (c) - dark field image of (b) area for austenite reflection; d) diffraction pattern of (b) area

The study of corrosion resistance by electrochemical impedance spectroscopy indicates a similar electrochemical behaviour of the steel after nanostructuring treatment and after quenching and tempering treatment. In both, neutral and acidic environment for both type of treatments, double, overlapping capacitive peaks in the impedance spectra were observed, which indicates the presence of two phases with different corrosion resistance: there are two different electrochemical processes or a single process that occurs with a varying intensity. In acidic environment, irrespective of tested material, first of the processes (column 3 in **Table 2**) is characterized by a slightly less resistance and an order of magnitude greater capacity compared to the second occurring process (column 4 in **Table 2**). In neutral environment, irrespective of tested material, the resistance value for the first process is an order of magnitude lower and the capacity value order of magnitude higher compared to the same parameters for a second process. It can be assumed that the first capacitive loop is related to the electrochemical behaviour of the phase with weaker corrosion resistance - ferrite, and

the second capacitive loop characterized the phase with better corrosion resistance - austenite. In acidic environment the induction loop occurs at frequencies below 10^{-2}Hz, which may indicate the formation of corrosion products tightly adhered to the substrate - probably iron oxides Fe_3O_4. In neutral environment the induction loop is less separated, which suggest that formed in this environment corrosion products do not form an additional layer - layer of corrosion products consists mainly of iron oxide Fe_2O_3.

Table 2 Characteristic electrochemical parameters of 67SiMnCr6-6-4 bearing steel after austempering and quenching and tempering treatment in Na_2SO_4 acidic and neutral environment

Treatment	parameter	value	value
pH4			
austempering	R(Ωcm^2)	362.5	443
	Y_{CPE}(F/cm^2 *s^{n-1})	2.20E-03	4.40E-04
	n	0.92	0.83
quenching and tempering	R(Ωcm^2)	247.5	395.5
	C_{CPE}(F/ cm^2)/ Y_{CPE}(F/cm^2 *s^{n-1})	1.50E-03	3.00E-04
	n	1	0.8
pH7			
austempering	R(Ωcm^2)	156	1540
	Y_{CPE}(F/cm^2 *s^{n-1})	1.84E-03	6.00E-04
	n	0.63	0.92
quenching and tempering	R(Ωcm^2)	338	1139
	Y_{CPE}(F/cm^2 *s^{n-1})/ C_{CPE}(F/ cm^2)/	1,04E-03	3,80E-04
	n	0,69	0,99

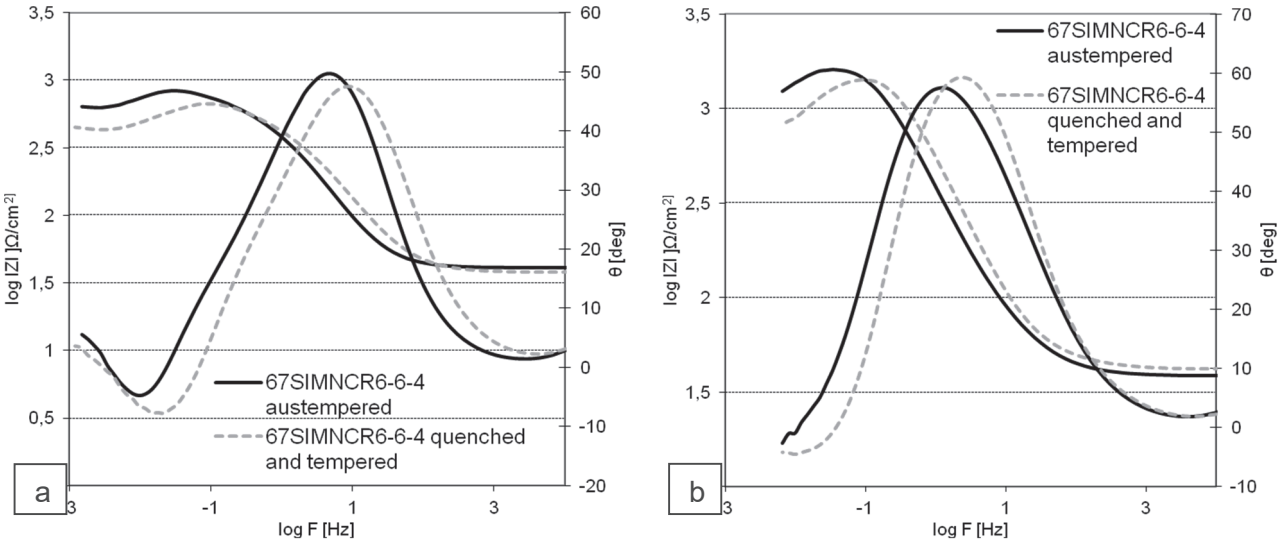

Fig. 3 Impedance spectra of 67SiMnCr6-6-4 bearing steel after austempering and quenching and tempering treatment in Na_2SO_4 acidic (a) and neutral (b) environment

The results obtained by the potentiodynamic method agree with the impedance results: nanostructure produced in 67SiMnCr6-6-4 bearing steel does not affect its corrosion resistance in comparison with steel after quenching and tempering to a similar hardness. At the same time the corrosion resistance in environment with varying degree of acidity changes very slightly for different heat treatments. No impact of different pH of a solution on the corrosion processes intensity may indicate that the layer of iron oxides Fe_3O_4 formed at the surface of the steel inhibit the electrochemical processes. The polarization curves obtained for all treatments

of 67SiMnCr6-6-4 bearing steel are characteristic of uniform/general corrosion. Representative images of corrosion damage on the surface of 67SiMnCr6-6-4 bearing steel are shown in **Fig. 5** and confirm the occurrence of general corrosion. In case of steel after quenching and tempering treatment, regardless of the corrosion environment, at the surface a number of pits were observed - probably caused by dissolution of secondary carbides or active nonmetallic inclusions.

Table 3 Characteristic electrochemical parameters of 67SiMnCr6-6-4 bearing steel after austempering and quenching and tempering treatment in Na_2SO_4 acidic and neutral environment

treatment	I_{kor} [µA/cm^2]	E_{kor} [mV]
pH4		
austempering	10	-710
quenching and tempering	11	-710
pH7		
austempering	9	-635
quenching and tempering	10	-635

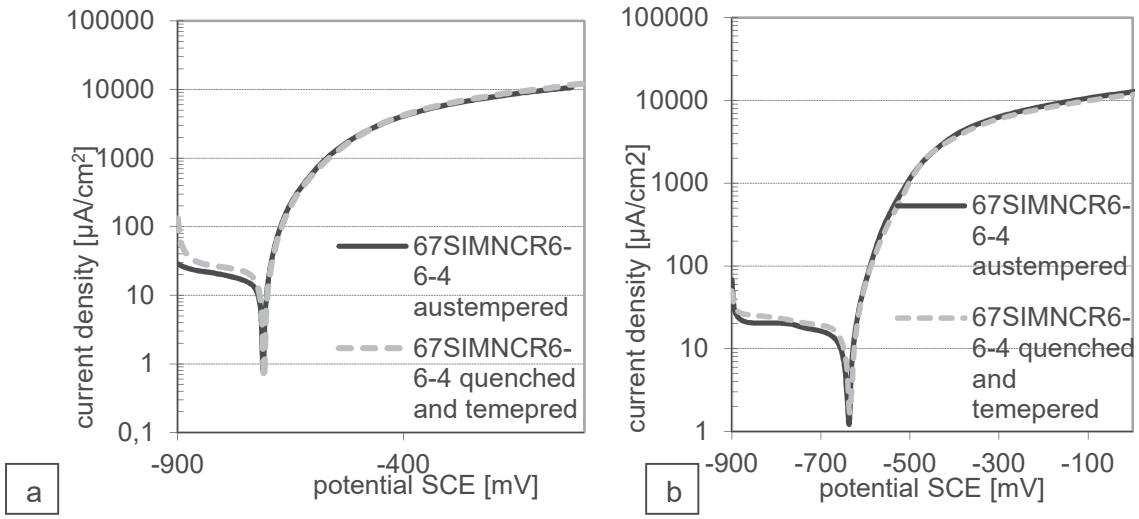

Fig. 4 Polarization curves obtained for 67SiMnCr6-6-4 bearing steel after austempering and quenching and tempering treatment in Na_2SO_4 acidic (a) and neutral (b) environment

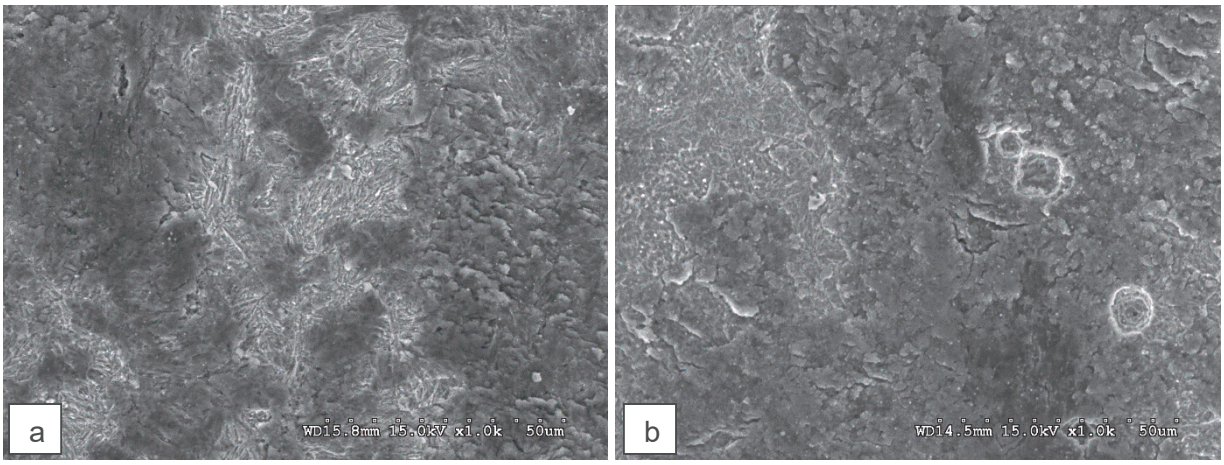

Fig. 5 Surface appearance of 67SiMnCr6-6-4 bearing steel after austempering (a) and quenching and tempering (b) after corrosion tests in Na_2SO_4 neutral environment

SUMMARY

So called nano-bainite, the nanocrystalline structure of the 67SiMnCr6-6-4 bearing steel, composed of lamellae of bainitic ferrite separated by residual austenite layers, was obtained. Electrochemical studies have shown that the corrosive resistance of the bearing steel with nano-bainitic structure is not worsened when compared to the tempered martensitic bearing steel with a similar hardness. The corrosion environment has no impact on the results. The EIS method revealed the presence of two phases of different corrosion rates.

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