

## THE INFLUENCE OF THE STRUCTURE STAY OF HIGH ALLOYED CHROMIUM STEEL ON ITS BEHAVIOUR IN PASSIVE STATE

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### Abstract

High alloyed materials are required by certain industrial sectors as is power, chemical and nuclear industry, etc. These materials have superior mechanical properties and are resistant to chemically aggressive environment in which it must accommodate the long term mechanical stresses at high temperatures. However, in the course of operating loading reduces their service life. Steels are losing their specific characteristics and in particular the toughness and corrosion resistance.

This paper deals with the influence of the structure stay on electrochemical properties of steel, mainly the behaviour in the passivity area. The experiment was effected on the bearing body made from the high alloyed steel 440C. Specimens were treated to a different mode of heat treatment - quenching 930 °C to 1080 °C / 0.75 h / oil; following tempering 200 °C to 750 °C / 2 h / air; or freezing (-80 °C, 0.5 h). Microstructure was observed in two directions - on outside round surface and cross section. In addition to the optical microscopy have been used SEM and the EDX analysis. The volume of residual austenite was determined by XRD analysis. The changes of mechanical properties are verified by measurement of microhardness HV 0.01. Corrosion tests are proceeded out in hydrochloric and boric acid environment. Corrosion potential has been measured and corrosion loss (corrosion rate). The results showed that in the first environment corrosion occurs in the active area, in the second case in the passive. Also interesting connections were observed between corrosion rate and the development of hardness for each of the samples.

**Keywords:** High alloyed steel, passive state, corrosion rate, corrosion potential, heat treatment

### 1. INTRODUCTION

Martensitic high alloyed steels contain 11.5 to 18 % of chromium, from 0.15 to 1.2 % of carbon and other alloyed additions. Their advantage is that they can be heat-processed to various strength levels. Their use is partly limited by e.g. at welding hardening occurs in the heat-affected zone of the weld joint. These steels are susceptible to development of tempering brittleness and have lower corrosion resistance than the austenitic high alloy steel. They are susceptible also to hydrogen embrittlement and stress corrosion cracking in environments of chlorides and sulphides. In particular, if they are tempered in the interval 480 °C - 550 °C. Martensitic high alloy steels have a wide area of application, for example on the components of the turbines, valves, pipes, cutting tools and bolts. From the metallurgical viewpoint, are these steel polymorphic. And before the quenching must have the austenitic microstructure. The ingredient of niobium affects formation of carbide  $M_{23}C_6$  and limits its growth and consolidating at higher tempering temperatures. The following effect is to reduce the tendency to brittleness and the overall refinement of the microstructure. Nitrogen provides steel higher strength in the hardened state and increase heat resistance. [1-4]

Corrosion resistance of high alloy steels lies in their ability to pass into the passive state. Corrosion resistance of these materials in many environments is dependent on the stability of the passive layer, which guarantees their long-term stability with minimum corrosion (or weight) loss of the material. Ignoring the terms of the stability of passive layers can lead to damage to the materials, localized corrosion attacks, in less than unalloyed steels. [2, 5-7]

The aim of this paper is to verify the suitability of various heat treatment of martensitic stainless steels and its influence on the optimum mechanical or corrosion properties.

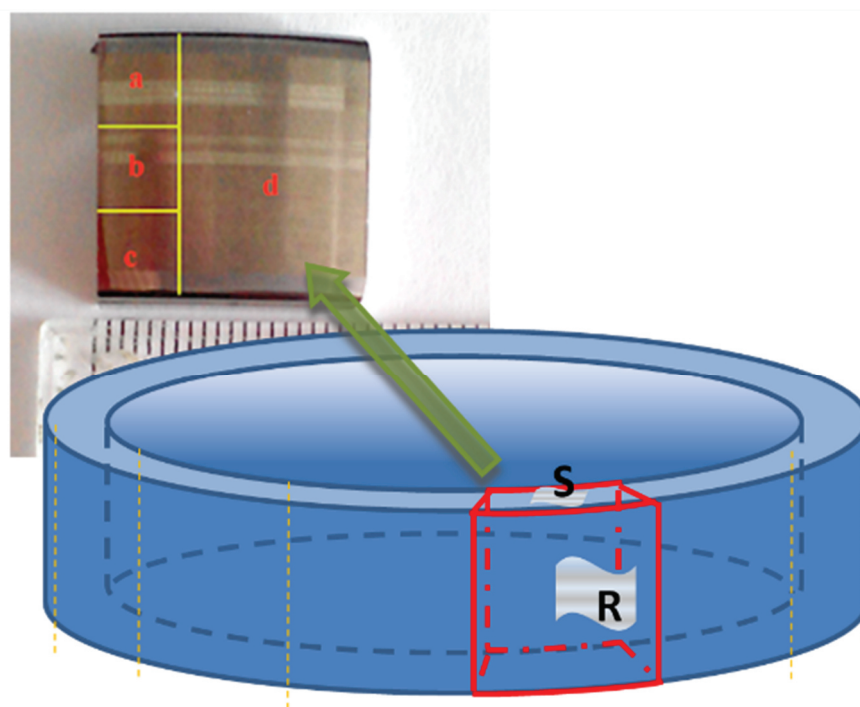
## 2. MATERIAL AND EXPERIMENTAL METHODS

For experiment two units of bearing body from the martensitic stainless steel 440C (EN grade 1.4125) were chosen. This material will achieve the highest hardness of the available hardenable stainless steels. It possesses good corrosion resistance, particularly in the hardened and tempered condition. The material is magnetic in all conditions. In order to achieve the optimum properties for this material, it is imperative that the correct heat treatment is carried out in accordance with the recommendations. Chemical composition of bearing body was verified by atomic emission spectrometry method (AES) by ARC-MET 8000 apparatus. It matches standard and is shown in the **Table 1**.

**Table 1** Measured chemical composition of a steel 440C of bearing body

element	C	Mn	Si	P	S	Cr	Ni	Mo	Cu
wt. %	0.895	0.393	0.508	<0.006	<0.006	15.9	0.251	0.449	0.062

Each bearing body unit was divided along the perimeter to twelve identically large parts (specimens) with dimensions of approximately 8 x 20 x 20 mm. Each of them was after heat processing, further divided into four parts for metallographic observation, corrosion tests and XRD analysis. The cutting scheme is on the **Figure 1**.



**Figure 1** The cutting scheme of bearing body

The individual samples were put to a heat treatment according to the schema in the **Table 2**. It proceeded in the laboratory resistance furnace in the standard atmosphere. Quenching around 950 °C and 1050 °C and consequently tempering 200 °C to 750 °C it was. Some of the samples prior to tempering were freezing by liquid nitrogen at a temperature of approximately -80 °C.

**Table 2** Modes of heat treatment and specimens marking

Heat treatment	Temperature (°C) / time (h) / cooling	Specimen marking	
		930-980 °C	1030 - 1080 °C
quenching	K or J / 0.75 h / oil	K	J
tempering	200 °C / 2 h / air	K20	J20
tempering	300 °C / 2 h / air	K30	J30
tempering	350 °C / 2 h / air	K35	J35
tempering	450 °C / 2 h / air	K45	J45
tempering	550 °C / 2 h / air	K55	J55
tempering	650 °C / 2 h / air	K65	J65
tempering	750 °C / 2h / air	K75	J75
quenching	K or J / 0.75 h / oil	KF	JF
and freezing	(- 80 °C) / 0.5 h		
tempering	300 °C / 2 h / air	K30F	J30F
tempering	350 °C / 2 h / air	K35F	J35F
tempering	450 °C / 2 h / air	K45F	J45F

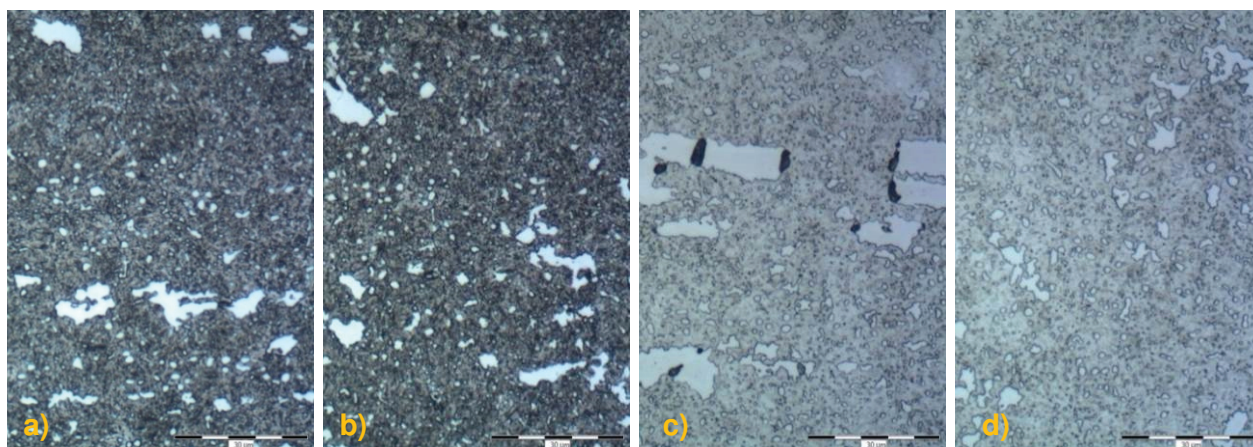
After heat treatment scales were removed from specimen surfaces by grinding. For metallographic investigations have been used segments “b” for round surface (direction R - see **Figure 1**) and “a” for side surface (direction S). Microstructure was developed by solution “COR” (10 ml hydrochloric acid+ 6 ml acetic acid+ 1-2 g picric acid + 100 ml ethanol). EDS analysis of substructural particles proceeded by SEM microscope JEOL JSM-6490LV. And for all samples was performed by XRD analysis (diffractometer Bruker AXS D8 used) to determine the amount of residual austenite.

Microhardness measurement by Vickers method HV 0.01 was applicate for each heat treatment mode. Matrix hardness and hardness of carbides formations were determined.

Corrosion tests were carried in containers with a volume of 50 ml. First twice times in the 0.2% hydrochloric acid solution with time exposure 4 hours. In these tests was determined corrosion rate “ $V_{cor}$ ” (weight loss) and corrosion potential “ $E_{cor / ACLE}$ ”. This was followed by the exposure in a solution of 12.2 g / l boric acid. With the control time (measuring of corrosion potential) at 1, 27, 48, 72 and 96 hours. Weight loss was determined after 96 hours. Corrosion potential was measured by argent chloride reference electrode type RE 404. The weight loss of specimens on digital analytical scale was measured.

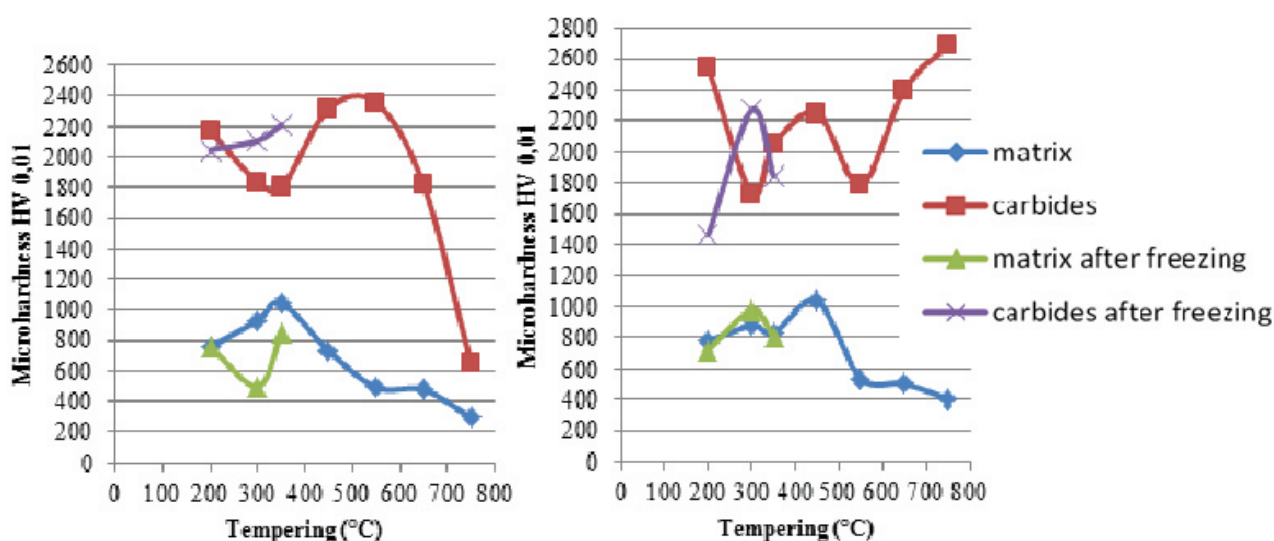
### 3. RESULTS AND DISCUSSION

Microstructure analysis did not demonstrate significant differences in quality. The specimens largely have Martensitic matrix with segregation of carbides particles (precipitates). The differences are mostly only in size and the form of distribution (exclusion) of the particles. For the idea are in **Figure 2a** or **2b** (structure in the direction R or S, see **Figure 1**) - stay after quenching only compared with the microstructure of the specimen K20 (see **Table 2**). **Figure 2c** is R-direction and **2d** is S-direction. On the **Figure 2c** are good visible light carbides formations. EDS analysis of these formations showed their composition on the chromium, respectively iron carbides. XRD analysis of residual austenite did not show markedly differences between the samples. Perhaps only for a couple of samples of the K20 and J20 (tempering at 200 °C) due to the higher austenitization temperature to increase the amount of residual austenite. Greater impact (influence) - reducing the amount - had freezing.



**Figure 2** Microstructure material after quenching at 950 °C: a) - R-direction; b) - S-direction; and after consequent tempering 200 °C: c) - R-direction; d) - S-direction

Both programs of heat treatment (quenching of 950 °C and 1050 °C) reported a similar course of microhardness HV 0.01 progress (see **Figure 3**). Hardness of matrix moves in the level of 400 HV to 1100 HV. The hardness of the carbide particles is significantly higher, in the range 1700 HV to 2400 HV. Hardness of these particles is significantly different, however, in the mode of tempering at 750 °C. After quenching at 950 °C it is 680 HV opposite 2680 HV after quenching at 1050 °C. On average, they are all slightly higher hardness values after hardening of the higher temperature. The effect of freezing is more manifested after quenching at 950 °C.

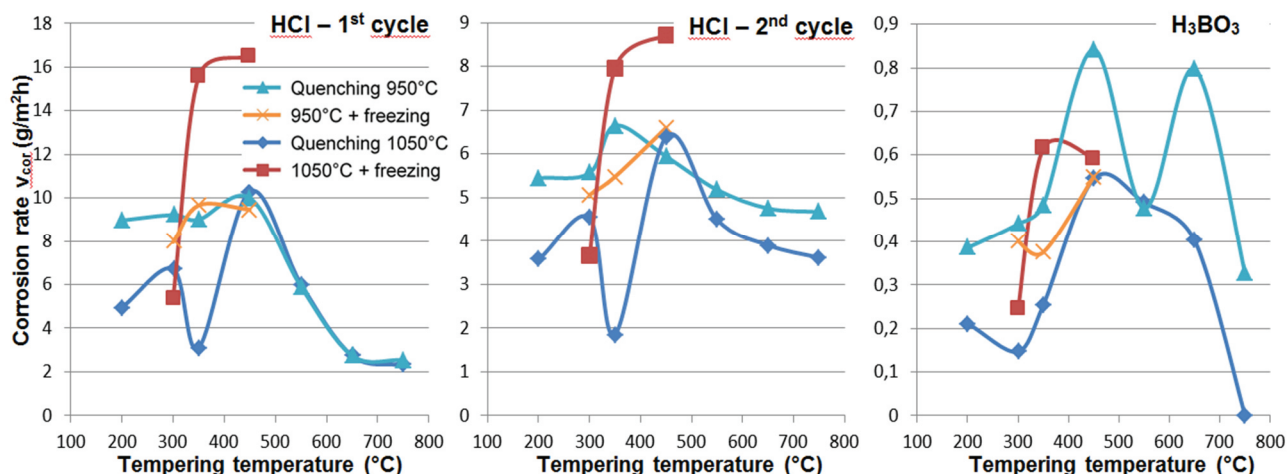


**Figure 3** Progress of microhardness HV 0.01 after different mode of heat treatment (tempering): after 950 °C quenching - left; and after 1050 °C quenching - right

Corrosion tests in hydrochloric acid had a similar course in the both four - hour cycles. The corrosion potential before and after each test was moved in the interval -400 mV to -470 mV, without evident depending on the heat treatment parameters of various specimens. Weight losses, resp. resulting corrosion rate, moves in the first test cycle in the range 2.3 till 16.5 g / m<sup>2</sup> h with the highest values after tempering at 450 °C (see **Figure 4**). When the second cycle of measurements were temperature dependences similar with the smaller dispersion of values, which were approximately in the range of 50 to 70 % of the values measured in the first testing cycle (**Figure 4**). This disproportion may be the cause of it, that the original surface before testing has been modified



(stripped of scales) by grinding. It partly led to the enlargement of the actual surface and, where appropriate, to its mechanical activation.



**Figure 4** Corrosion rate in various solutions: from left - hydrochloric acid - first cycle; second cycle; boric acid

Results of measurement of corrosion potential in boric acid are summarized in **Table 3** for quenching at 950 °C (at 1050 °C are similar) and indicate the corrosion processes in passive area. The values for individual samples all show a declining trend in the first half of the total exposure time (48 hours) and then renewed growth. The tendency of depending: corrosion rate - tempering temperature (**Figure 4**) are similar as in the previous two cases. However, the absolute values of the corrosion rate are about the tenth of the values measured in the hydrochloric acid and they range in tenths of a g / m<sup>2</sup>h. Interesting are the higher values throughout the temperature range for samples after quenching at 950 °C opposite 1050 °C and fact, that freezing not so significant an impact as in previous cases.

**Table 3** Corrosion potential after exposition in boric acid for specimens after quenching at 950 °C

specimen	exposition time (h); E <sub>cor</sub> / ACLE (mV)				
	1	24	48	72	96
K20	-33	-23	-33	84	117
K30	42	-41	-42	93	118
K35	23	14	-3	-12	121
K45	-33	-55	-120	-94	-82
K55	21	42	-61	-75	-29
K65	-7	-104	-127	-94	-64
K75	12	-60	-73	-60	-5
K30F	25	-8	-7	-13	15
K35F	-14	-43	-20	20	118
K45F	-62	-121	-112	-78	-78

#### 4. CONCLUSIONS

Tempering temperature had a significant influence on hardness of quenched steel 440C. Maximum hardness for specimens quenched by temperature 950 °C was at a tempering temperature 350 °C and for specimens

quenched by temperature 950 °C was at a temperature 450 °C. The austenitization temperature did not significantly affect the resulting hardness. Freezing of steel is reflected by decreasing the content of residual austenite. Metallographic responses were not significant.

From the results of corrosion tests in hydrochloric acid shows that the corrosion occurred in the activity area. Between the various modes of tempering there were not great differences. It is noticeable that at lower temperatures is the maximum corrosion rate caused by local matrix depletion of chrome near carbides, which arise when temperatures lower mobility of chromium. At higher temperatures the precipitation of carbides there was the influence of the speed of diffusion Cr / C to offset the concentration differences. In case of specimens hardened from temperature 950 °C and tempering at the temperature 350 °C in hydrochloric acid solution is corrosion rate higher. In case of samples hardened from temperature 1050 °C are visible two increases that match the maximums in the microhardness progress. It is possible, therefore, to consider, that when you achieve a higher hardness and corrosion rate increases.

During the test, the specimens, quenched at 950 °C, are in the boric acid solution behaving differently than in hydrochloric acid. Although there was an increase in the corrosion speed, but it did not answer the hardness progress of these specimens. Significant corrosion rate was achieved when tempering temperatures of 450 °C and 650 °C. For specimens quenched at 1050 °C was the maximal corrosion rate at tempering temperature 450 °C and this maximum coincides with the maximum micro hardness value for these specimens. Again, this implies, that occurs when a higher hardness increase in the corrosion speed.

The corrosion potentials of steel corroding in hydrochloric acid and boric acid suggests different corrosion area: in hydrochloric acid corrosion occurred in the activity (active state), while in boric acid in passivity (passive state). In hydrochloric acid was corrosion process controlled by the reduction of hydrogen cation, in boric acid by reduction of the oxygen dissolved in the solution.

Experiment confirmed the need for a careful choice of heat treatment of martensitic stainless steels for various corrosion environments in combination with their required mechanical properties.

## ACKNOWLEDGEMENTS

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