MONITORING THE CORROSION BEHAVIOR OF THE OPERATED AND NON-OPERATED MATERIAL OF THE MAIN CIRCULATION PIPE VVER 440 TYPE REACTOR

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Abstract

The material in nuclear reactors of the VVER 440 type and their main circulation pipes is exposed to temperatures in the range of 100-300 °C during the operating conditions, but in some nodes can be this range of temperatures exceeded. These temperature conditions are suitable for low-temperature sensitization and the microstructure sensitized in this way may be susceptible to inter-granular corrosion during long-term operation. The material 08CH18N10T that was subjected to observation was obtained from a real operation, where it was exposed to operating conditions for a long time. The microstructure of this material was compared with the microstructure of a new material of the same type that was exposed to operating temperatures in laboratory conditions. The new main circulation pipeline material is currently replacing the old one in real operation. The microstructure was evaluated based on the results from optical and transmission electron microscopy and for the identity of the secondary phases was used the selective electron diffraction. The specimens were subjected to a non-destructive corrosion test ASTM A262 method A, on the basis of which a statistical method was used to compare the percentage of attacked grain boundaries of the observed materials.

Keywords: Austenitic stainless steel, corrosion, precipitation, sensitization

INTRODUCTION

During the operation is the main circulation pipeline (MCP) exposed at the range of temperatures 100-300 °C, while in some nodes of the MCP can the temperature exceed this specified range of temperature. Long-term operation can result in sensitization of the MCP material. The sensitization mechanism, during the operating temperature, takes place in such a way that, precipitation of chromium-rich carbides or chromium-rich intermetallic phases occurs and that reduce the concentration of chromium in the matrix to such an extent that disturbed the passivation layer which ensure the corrosion resistance of the alloy [1]. This precipitation and subsequent chromium depletion is increased at the grain boundaries and this can lead to sensitization and subsequently to intergranular corrosion (IGC) of alloy [2].

Due to high affinity to carbon is the addition of stabilizing elements such as Ti, Nb, or Ta the most effective method to alleviate the problem. The carbides of these elements are formed preferentially over chromium carbides and thus prevent chromium depletion leading to corrosion attack at the grain boundaries [3]. The most important carbides are $M_{23}C_6$ and MC which are formed in these steels. MC is created precisely by adding stabilizing elements to the alloy. This results in the preferential formation of MC, and carbon removed in this way from the solid solution will prevent the formation of carbide $M_{23}C_6$, which results in a decreasing of the alloy corrosion resistance [4].

Sigma phase (σ) is a well-known intermetallic phase which is formed in the Fe-Cr system. Sigma phase precipitates first on triple points of GB and also forms on incoherent twin boundaries and intragranular inclusions, after long term ageing at high temperature. During the nucleation mechanism of sigma phase is the formation associated with the dissolution of $M_{23}C_6$, but also independently [5].

Another important intermetallic phase in austenitic steels is the chi phase (χ), whose composition is often compared to the sigma phase, but chi phase has a higher concentration of molybdenum and different solubility of carbon. It was observed that the chi phase nucleates and grows preferentially at the interfaces of δ-ferrite in austenite. However, the precipitation of the chi phase associated with $M_{23}C_6$ carbide precipitates was observed. The presence of precipitates in the chi phase generally reduces the fracture toughness at room temperature and reduces the corrosion resistance [6].

The experimental methods which were used in this study, to determine the corrosion resistance of the alloy are optical microscopy (OM), transmission electron microscopy (TEM), DL-EPR test and microhardness test. Based on these methods, it was determined the sensitization degree of the alloy occurs and how the corrosion resistance of the alloy is impaired.

1. MATERIALS AND METHODS

The chemical composition of the new material for main circulation pipelines (MCP-N) and of the used main circulation pipelines (MCP-V1) can be found in Tab. 1. In both cases it is an austenitic stainless steel with a low carbon content, which is stabilized by titanium.

Table 1 Chemical composition of MCP-N and MCP V1

specimen	Chemical composition (wt. %)										
	C	Si	Mn	P	S	Cr	Mo	Ni	Ti	Co	Fe
MCP-N	0.056	0.46	1.21	0.014	0.0024	17.89	0.038	12.50	0.57	0.033	balance
MCP-V1	0.047	0.59	1.05	0.013	0.0030	17.79	0.064	12.59	0.54	0.031	balance

1.1 Heat treatment and specimen preparation

Heat treatment of the experimental material consisted of isothermal aging at temperatures of 350 resp. 400 and 450 °C with a duration of 1000 hours. The types of precipitates and the preferential precipitation areas were identified for every single specimen. Selected area electron diffraction was applied to identify the precipitates.

1.2 Optical microscopy

After heat treatment were the specimens metallographically prepared, which consisted of grinding on a set of sanding papers with graded grain size and mechanical polishing using diamond suspensions with a grain size of 9 and 3 μm. Specimens were after metallographic preparation subjected to the corrosion test ASTM A262 method A. The corrosion test is a rapid and non-destructive test used for the preliminary evaluation of material IGC and provide only a qualitative estimate of the degree of corrosion and the tendency of the material to IGC. In this test is the specimen electrolytically etched in 10% oxalic acid, with the etching time 90 seconds, at a current density of $1 A/cm^2$ and a temperature of 20°C. This microstructure was subsequently evaluated using OM [7]. The observation was carried out on a Neophot 32 optical microscope and the microstructure of individual specimen was documented using a digital camera.

1.3 Quantitative analyzes of the proportion of grains with precipitates

Micrographs according to which was analyzed the proportion of grains with precipitates were made in 5 side-by-side images in three rows below each other, which were connected to each other. The evaluation was processed as the ratio of attacked and unattacked GB. For the measurement was made used Image J software [8].

1.4 Transmission electron microscopy

For the TEM were prepared the thin foils by mechanically thinning a sheet of experimental steel to a thickness of 80-50 μm, followed by cutting out the circle with the diameter of 3 mm, which was finally electrolytically thinned in a solution of HNO_3 : CH_3OH in a ratio of 3 : 7 using the TENUPOL 5 device, at 15V/0.8A and a temperature of -35°C. The area observable by TEM is located around the perforation of the specimen [9]. Microstructure in TEM was documented in bright field (BF) and dark field (DF). The observation was made on a JEOL 200 CX transmission electron microscope with the point resolution of 0.23 nm

1.5 DL-EPR test

For the MCP-N specimens was used solution: 2 M H_2SO_4 + 0.05 M KSCN [10]. Scan speed: 100 mV/min, measurement range: -700 mV to 300 mV and back, measurement area approx. 30 mm^2, before the DL-EPR test itself was performed a 30-minute open circuit potential (OCP) measurement. The maxima of the current density during the activation i_A and reactivation i_R scan were monitored.

The degree of sensitization (DOS) was evaluated as the ratio i_R/i_A according to BS EN ISO 12732 (BS EN ISO 12732:2008 Corrosion of metals and alloys. Electrochemical potentiokinetic reactivation measurement using the double loop method (based on Cihal's method), BSI, 2008):

Below 1% - the sample is classified as non-sensitized
From 1% to 5% - slightly sensitive
Above 5% - strongly sensitized specimen [11]

1.6 Microhardness test

The microhardness test was performed on the Microhardness tester according Hanemann method, the value of the used test load was 100 g (HV 0.1). For each specimen, 10 impressions were made, from which the average and standard deviation were calculated.

2. RESULTS AND DISCUSSION

2.1 Optical microstructure

Figure1a shows the microstructure in the initial states of the MCP-N material. The microstructure has a polyhedral character, the matrix is formed by austenite and in all cases significant heterogeneity in grain size is observed. In addition to the austenitic matrix are observed the MC carbides and the presence of annealing twins was also observed in some austenitic grains [7]. The etching of the specimens is characterized as dual, which is caused by the precipitation of secondary phases at some grain boundaries and annealing twins which are preferential areas for the precipitation of secondary phases. **Figure1b** is the example of the specimen's microstructure after isothermal aging of 450°C/1000 hours. Etching is also characterized as dual but compared to the initial stage, a more significant etching of preferential precipitation areas is observed.

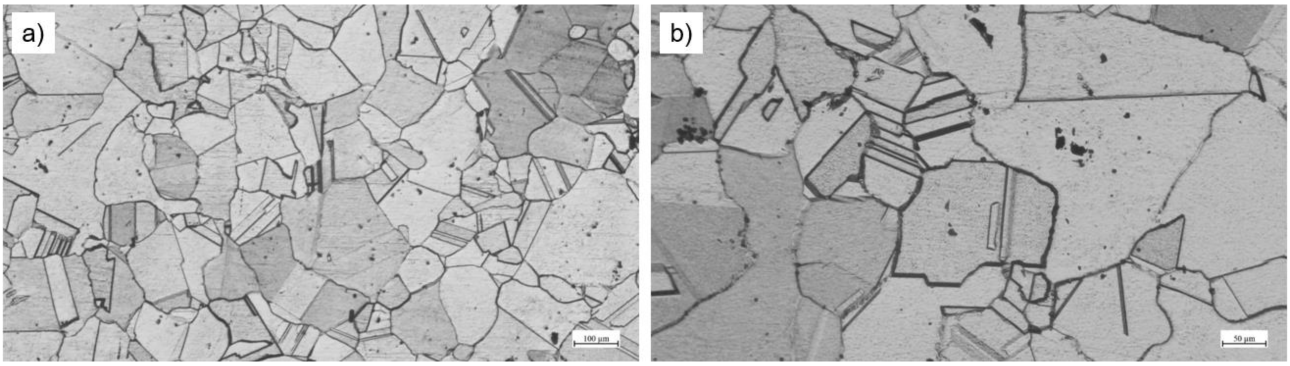

Figure 1 Optical micrographs of experimental steels, a) MCP-N initial state b) MCP-N after isothermal aging 450°C/1000h

However, more pronounced etching of grain boundaries and annealing twins is still not enough to be characterized as ditch. During annealing at the highest temperature, it is also possible to observe the precipitation of secondary phases at the interface of austenite and MC.

For the specimens which were isothermal aged of 350°C/1000h and 400°C/1000h was confirmed the gradual development of the precipitation preferential areas etching significancy logically following the tested parameters.

The initial state of the MCP-V1 microstructure of the steel was comparable to the state of the microstructure of the MCP-N 400°C/1000h and a slight increase in the density of the precipitates was observable at 450°C/1000h, but it was also comparable to the state of the MCP-N 450°C/1000h.

2.2 Quantitative analyzes of the proportion of grains with precipitates

Based on the results in the Table 2, is in the case of the MCP-N specimens, the largest proportion of attacked GBs can be observed only at the highest tested temperature of 450 °C.

Due to the long-term operation, a larger increase in attacked GB is understandable in the case of the MCP-V1 specimens already in the initial state, which increases only minimally with increasing temperature. A non-negligible increase is observable again at the highest tested temperature of 450 °C and the values are comparable to the same temperature for the MCP-N material.

Table 2 Results from statistical counting of un/attacked GB

-	MCP-N IS	MCP-N 350	MCP-N 400	MCP-N 450	MCP V1 IS	MCP V1 350	MCP V1 400	MCP V1 450
Attacked	1%	1%	2%	18%	7%	8%	11%	19%
Unattacked	99%	99%	98%	82%	93%	92%	89%	81%

2.3 TEM analysis

Based on TEM analysis, precipitation of secondary phases was confirmed in all cases, including specimens in the initial stage. Overview TEM images (**Figure 2**) of secondary phases which precipitates at grain boundaries (GB) and sub-grain boundaries (SGB) were found in all observed specimens.

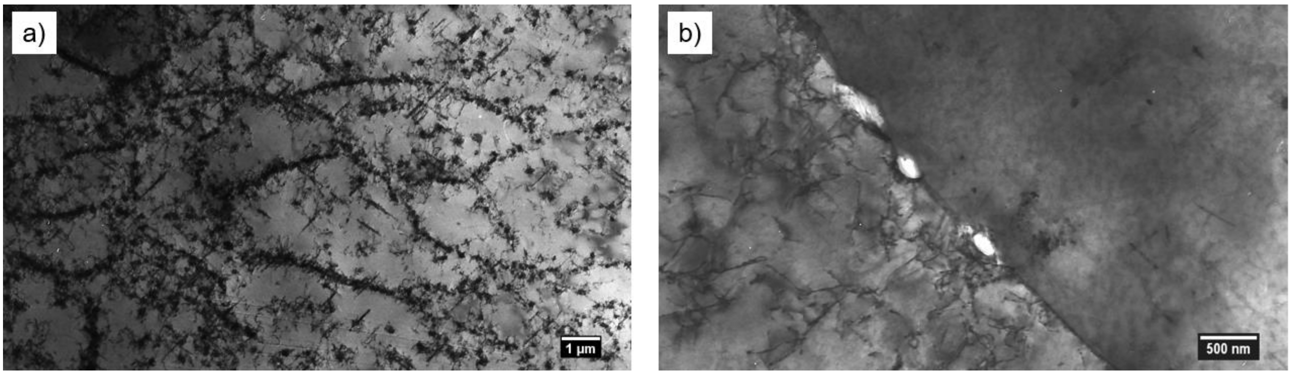

Figure 2 Overview of secondary phases precipitation in bright field, a) in initial stages at SGB MCP-V1 b) at GB of MCP-N specimen 450°C/1000h

By the method of phase identification using electron diffraction, $M_{23}C_6$ carbides were identified at GB and SGB. Precipitation of intermetallic phases sigma and chi were already identified in the initial stage of MCP-N material. Precipitation of these secondary phases was observed in all tested specimens.

2.4 DL-EPR test

Figure 5 and **Table 3** represents the results from DL-EPR for specimens MCP-N. Due to the similarity of the chemical composition and the agreement of the results obtained by other scientific methods, DL-EPR was performed only for the MCP-N specimens.

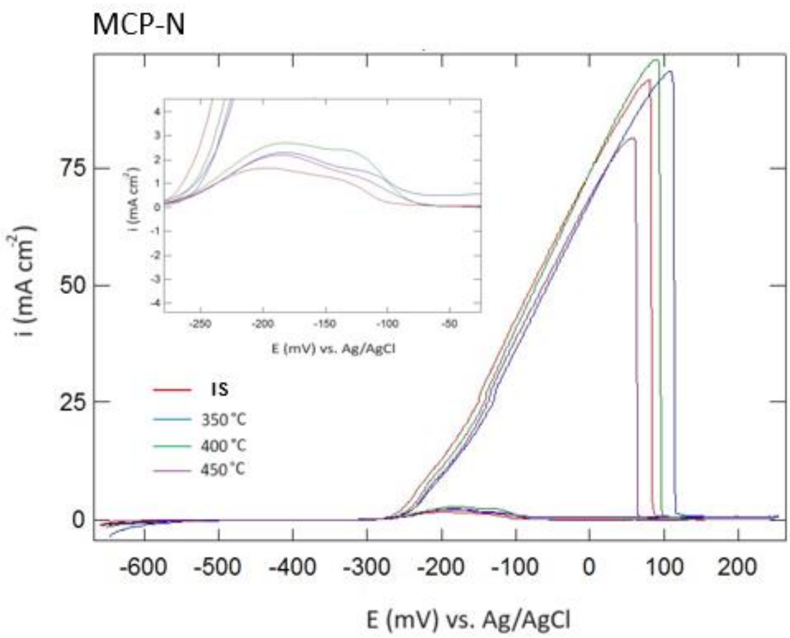

Figure 3 DL-EPR measurement of MCP-N specimens

Table 3 represents the measured values of potentials and current densities from the DL-EPR test and calculated degree of sensitization for individual specimen of MCP-N (DOS = i_R/i_A)

Table 3 DL-EPR results for MCP-N

Specimen	i_A [mA cm^{-2}]	i_R [mA cm^{-2}]	DOS [%]
IS	93.78	1.25	**1.75**
350 °C	95.60	2.38	**2.40**
400 °C	98.10	2.00	**2.72**
450 °C	80.09	2.19	**2.73**

All specimens are rated as slightly sensitized based on the scale published above, despite the slight difference in sensitization between IS and others. The results correspond to the observed character of the microstructure.

2.5 Microhardness test

Table 4 shows the calculated microhardness values based on the microhardness test for individual specimen.

Table 4 Average microhardness value and standard deviation for MCP-N and MCP-V1 specimens

MCP-N IS	MCP-N 350	MCP-N 400	MCP-N 450	MCP-V1 IS	MCP-V1 350	MCP-V1 400	MCP-V1 450
167 ± 12	160 ± 7	160 ± 8	164 ± 7	152 ± 15	156 ± 11	153 ± 9	152 ± 9

Significant deviations in the values on the basis of which the evaluation would be possible are not possible based on the results. The results for both series of specimens are similar, which means that there are no significant changes in the microstructure based on the microhardness.

3. CONCLUSION

Based on the material analysis of the MCP-N and MCP-V1 specimens, which included monitoring the effect of long-term operation in a nuclear power plant and the effect of isothermal annealing at temperatures of 350, 400 and 450°C with a duration of 1000 hours, it was found:

1. The corrosion test and the resulting etching of the specimens was not characterized as ditch in any case. This means that the specimens, despite the exposure at the highest temperature, cannot be evaluated as sensitized.
2. Based on TEM analysis, secondary phases are already found in the initial matrix, but long-term operation (V1) and even higher temperatures in some nodes (MCP-N 450°C/1000h and MCP V1 450°C/1000h) did not sensitize the steel to such rate to cause a higher susceptibility to IGC, which was confirmed on the basis of the quantitative analyze of the proportion of grains with precipitates**,** microhardness test and the DL-EPR test.

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