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## Material characterization of the main steam gate valve made of X20CrMoV 12.1 steel after long term service

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### Abstract

Martensitic steel X20CrMo12.1 has been extensively used within the last few decades as a material for tubing systems and pipelines in thermal power plants (TPP). Long term behavior of this steel is very well known and understood and because of that was found to be reliable material for prolonged service at elevated temperatures. It is well known that during operation TPP components are subject to microstructural changes that inevitably reflect decrease in their mechanical properties that lead to the loss of structural integrity and serviceability of component. This paper deals with the comprehensive investigation carried out on the main steam gate valve parent material of welded joint, as a part of main steam pipeline, after 170.000 h of service (545°C and 19MPa). The obtained results showed that the microstructural degradation caused by long term operation had little effects on the hardness and strength of material, while the changes in impact toughness were observed. Comprehensive microstructural analysis included the examination of the microstructure on the surface and through the wall thickness.

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## 1. Introduction

In the past decades, tempered martensite ferritic steels with 9-12% chromium and containing carbide stabilizing elements have been widely used for components which operate within the creep range, in power and process plant industry [Gandy, 2006; Van Zul et al, 2005; Eggeler, 1989]. One of the 12Cr1MoV steels, standardized for use for steam tubes and pipelines under the German standard DIN 17175 and later EN 10216-2 with lower sulphur and phosphorus content is steel X20CrMoV 12.1. Steel X20CrMoV 12.1, has been widely used for steam pipelines as well as for other thick section components at a temperatures up to 565°C. It has been used in power plants since the 1960s in Europe and other countries. The mechanical, creep, and fracture properties of X20CrMoV 12.1 steel depend strongly on the microstructure, which in turn depends on the chemical composition, casting, and cooling processes as well as on thermo-mechanical treatment [Gandy, 2006]. It is well known that many important components in power plants are exposed to mechanical and material property degradation under the real service conditions. Some of the steam pipelines made of X20CrMoV 12.1 steel have been in service more than 30 years, and as a result degradation of mechanical properties and microstructures has occurred. To evaluate the remaining service life of those pipelines, it is important to examine their mechanical behavior and microstructural stability.

The heat treatment of X20CrMoV 12.1 steel (W.Nr. 1.4922) consist of austenitizing (at 1020 to 1070°C) followed by air cooling and subsequent tempering (at 730 – 780°C) in order to achieve a long term stability as well as good combination of strength, toughness and high temperature creep strength. The microstructure of such steel is tempered martensite with fine dispersed carbides phase precipitating along the grain boundaries [Gandy, 2006].

A particularly important aspect of the microstructure is the distribution of carbide particles. Carbides undergo changes in their chemical and phase composition as well as their size with time during service. Some investigations on X20CrMoV 12.1 steels indicated that the carbides of  $M_{23}C_6$ ,  $M_7C_3$ ,  $M_2X$ , and  $MX$  are responsible for precipitation hardening and high creep strength [Straub, 1997; Zheng-Fei, 2003]. Basic strengthening mechanisms of X20CrMoV 12.1 are solid solution strengthening obtained by the high content of Cr and Mo, and strengthening by refined grains due to formation of tempered martensitic lath structure with high dislocation density, strengthening by precipitation of the uniform dispersion of  $M_{23}C_6$  carbides rich on Cr, Mo and  $MX$  particles mainly containing V. The inhibition of dislocation/grain boundary migration, recovery, and annihilation of dislocation by precipitates are considered to be the predominant mechanism of strengthening [Eggeler, 1989].

The changes of microstructure and morphology of the carbides occur after long-term exposure to elevated temperature and internal pressure, which is the final attribute to exhaustion of material. The carbides which can be expected in steel depend strongly on the service temperature and initial chemical composition. However, some of the investigations for X20CrMoV 12.1 steam pipelines indicated that severe softening did not occur after long-term service exposure at elevated temperature [Zheng-Fei, 2003]. Finally, creep rupture in tempered martensitic steels is usually controlled by cavity nucleation and growth [Eggeler, 1989] originating mainly on different inclusions particles [Van Zul et al, 2005; Sijacki et al., 2010]. This paper presents some results of comprehensive investigation carried out on the thick wall component (part of fresh steam pipeline) made of X20CrMoV 12.1 steel, after more than 170.000 h of service at operating temperature of 545°C and operating pressure of 19MPa.

## 2. Background

Main steam gate valve (MSGV) is the part of fresh steam pipeline of one 620MW unit, and as the rest of the line is made from German grade X20CrMoV 12.1 steel (W.Nr. 1.4922). MSGV is steering valve with electric actuator having basic dimension of pipeline on the connection with MSGV of  $\varnothing 602 \times 61$  mm (for MSGV - NO450/NP640). Assemble length of MSGV is 1950 mm and weight 6348kg. Design working parameters of MSGV are temperature of 545°C, working pressure 20,5 MPa and proof pressure test at 41.2 MPa.

During operation, MSGV is exposed to highest parameters of steam as a connection to high pressure turbine inlet, and after overhaul, MSGV functions as a divider valve between high pressure turbine. After 175.586 h MSGV was replaced with a new valve [Sijacki et al., 2010]. During service valve had been exposed to temperature within in range of 530–545°C and pressure up to 19 MPa.

After 175.586 h of service there is no evidence of localized damage on surface in the form of surface cracks or cavitation obtained by regular non-destructive testing and with replica testing. The goal of this investigation was to

estimate the level of component exhaustion due to prolonged service at high temperature and static loading and low cyclic loading. These results should be added to regular non-destructive testing results of fresh steam pipeline components in order to clearly understand the exhaustion of fresh steam pipeline and its remaining life assessment [Sijacki et al., 2010]. The results of base material testing of MSVG connection pipe are presented in this paper.

### 3. Materials and methods

The investigated samples were taken from the connected pipe of main steam gate valve (MSGV) in the vicinity of main steam pipeline welded joint. Valve and connected pipe are made of X20CrMoV 12.1 steel welded with matching filler material [Sijacki et al., 2010]. In the aim of testing one ring app. 150mm width was cut from the connection pipe-welded joint zone. Specimens were prepared from the connection pipe wall with width of cut part large enough to test base material of welded joint without significant influence of heat affected zone (HAZ). The MSGV with connected pipe and connected welded joint are shown on Fig.1(a), while scheme of base material sampling is shown on Fig. 1(b).

Following tests were performed on specimens of base material: tensile tests at room temperature (TR), tensile test at elevated temperature (TE) at 550°C, Vickers hardness measurements (HV), full size Charpy V notch impact specimens tested at -20°C, 0°C, 20°C, 40°C, 60°C, 80°C and 100°C (KV). The chemical composition of base metal (CH) was performed using optical emission spectroscopy. Microstructural study (M) of the test specimens included optical microscope (OM), scanning electron microscope (SEM; type JEOL JSM-6460LV) with energy dispersive spectrometer (EDS; Inca, Oxford, UK), as well as surface microstructure analysis by acetate replica. SEM and EDS analyses were carried out on fracture surfaces on specimens from temperature set with the lowest impact toughness value. For OM and SEM observation, specimens were polished and etched with 4% picric acid in ethanol.

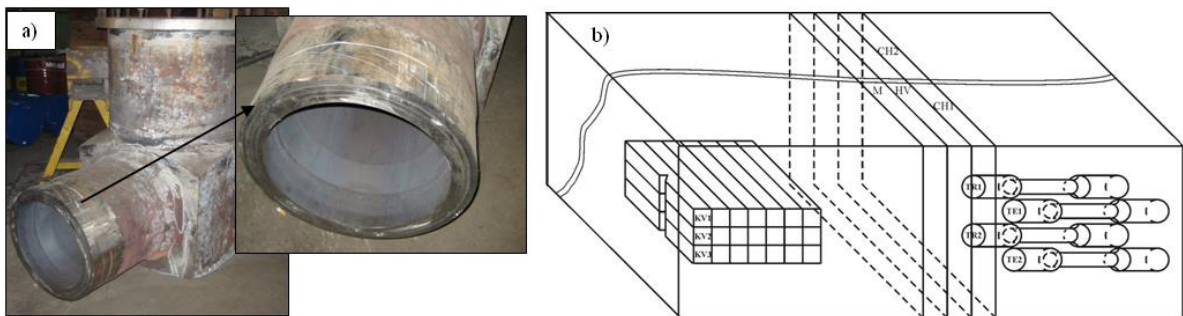


Fig. 1. (a) Main steam gate valve and sampling zone on connected pipe in vicinity of welded joint; (b) Scheme of sampling.

### 4. Results and discussion

The sample of X20CrMoV 12.1 in chemical composition contain: 0.18 wt.% C, 9.87 wt.% Cr, 0.88 wt.% Mo, 0.30 wt.% V, with 0.20 wt.% Si, 0.48 wt.% Mn, 0.026 wt.% P and 0.022 wt.% S. Chemical composition of the samples investigated in the present study are in the required limits for all alloying elements for declared materials X20CrMoV 12.1 according to DIN17175. The tensile properties of the examined materials tested at room temperature and at 550°C are given in Table 1. The yield strength ( $R_{0.2}$ ) and ultimate tensile strength ( $R_m$ ) of samples are considerably above standard limits. The values of the mechanical properties at elevated temperature (at 550°C) are in allowable limits stipulated for declared X20CrMoV 12.1 material.

Commonly, the hardness of high Cr ferritic steels decreases during operation due to recovery of the lath structure and coarsening of precipitates and based on the fact that one of the methods for life assessment for X20CrMoV 12.1 steel is based on drop of hardness value [Gandy, 2006]. In this case, hardness measurement values for base material were in the range 233 - 243HV, for HAZ in the range 221 - 232HV and for welded filler metal 243 - 270HV, are in required range according to VGB 508 L norms (215-261HV) for declared material X20CrMoV 12.1. These results were expected because of great wall thickness of component that indicate lower level of working stresses. Besides,

for thick wall components some investigations of X20CrMoV 12.1 steam pipes that were in service up to 200.000 h at about 550°C indicated that severe softening did not occur and only very weak effects of the service exposure could be recognized in the microstructure due to relatively low service temperature [Zheng-Fei et al., 2004]. The explanation for not significant hardness changes in this case could be associated with the fact that carbides transformation during prolonged service of ferrite heat resistant steels includes changes of existing carbide phase, their size and composition, and the fact that some carbide phases were formed during service from the solid solution [Bakic et al., 2013], especially V-rich carbides [Zheng-Fei et al., 2004]. The next stage of the microstructural changes is the significant disintegration of the tempered martensite with the decay of the martensite laths, numerous chains of precipitations on the former austenite grain boundaries, significant amount of carbides precipitations in the former martensite laths boundaries, growth of subgrains and size of the  $M_{23}C_6$  type carbides [Dobrzanski, 2005]. The results of full size Charpy notch impact testing for temperature range from -20°C to 100°C (step  $\Delta T=20^\circ\text{C}$ ) are given in Table 2. It was found that ductile to brittle transition temperature is +30°C [Sijacki et al., 2010]. Relatively low values of impact toughness and increase of brittle fracture temperature clearly show most significant change in material after long-term service exposure. The same result for X20CrMoV 12.1 steel has been reported by Dobrzanski (2005).

Table 1. Results of tensile tests.

Tensile test at 20°C			Tensile test at 550°C		
R <sub>0,2</sub>	R <sub>m</sub>	A	R <sub>0,2</sub>	R <sub>m</sub>	A
MPa	MPa	%	MPa	MPa	%
556	703	20,4	434	532	14,4
552	717	21,4	473	554	14,8
min. 490	690 - 840	min. 17	min. 250	-	-

Table 2. Results of mean impact energy value at different temperatures.

Temperature	-20°C	0°C	20°C	40°C	60°C	80°C	100°C
Impact toughness	7,3 J	13,3 J	27 J	36,6 J	52 J	56 J	60,6 J

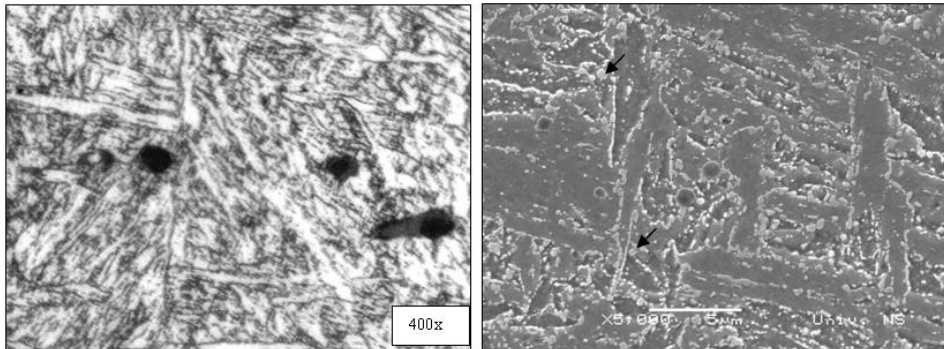


Fig. 2. Microstructure of base material: a) acetate replica optical microscopy; (b) SEM of the middle cross section.

Results of the microstructure examinations carried out on the SEM revealed that material microstructure is composed of the lath martensite and carbide precipitated on the former austenite grain boundaries and on the boundaries of the tempered martensite laths, Fig. 2(b). Partial decay of martensite laths was observed, as well as chain like precipitations on former austenite grain boundaries and numerous coarse carbides most probably the  $M_{23}C_6$  type. It was shown that the creep strength of the material strongly relies on  $M_{23}C_6$  carbides which stabilize the subgrain structure [Aghajani et al., 2009]. In addition, optical microscopy investigation showed that there were no essential differences in microstructure degradation at surface and in the cross-section, Fig. 2(a,b). Coarse carbide network on the former austenite grain boundaries is not characteristic of the material in regular virgin state [Dobrzanski, 2005].

Two other precipitate families, VC and Laves phase, were also detected. Laves phase particles were formed during creep and EDS analyses of Laves phase particles confirmed high molybdenum content, as well as chromium and iron suggesting that basic composition are  $(Fe, Cr)_2Mo$ . EDS of some of analyzed particles revealed low content of Si and P in their composition. According to Aghajani et al., (2009) the chemical composition of the Laves phase particles is not affected by stress and does not change during long-term creep, but the size of particles change. In this case, relatively large particle of Laves phase, 0.5-0.8 $\mu$ m is the effect of prolonged service. Furthermore, a lot of large, different, non-metallic inclusions observed in the microstructure were to be expected due to lower purity and higher limitation in S and P content in older manufactured steels. EDS analyses show that inclusions are mostly MnS type, but some of them are complex like  $TiOx-Al_2O_3$  complex oxides on which MnS inclusion was formed during fabrication as a surface layer, Fig. 3(a). Also, inclusions are initial places of void coalescence during fracture, Fig. 3(b).

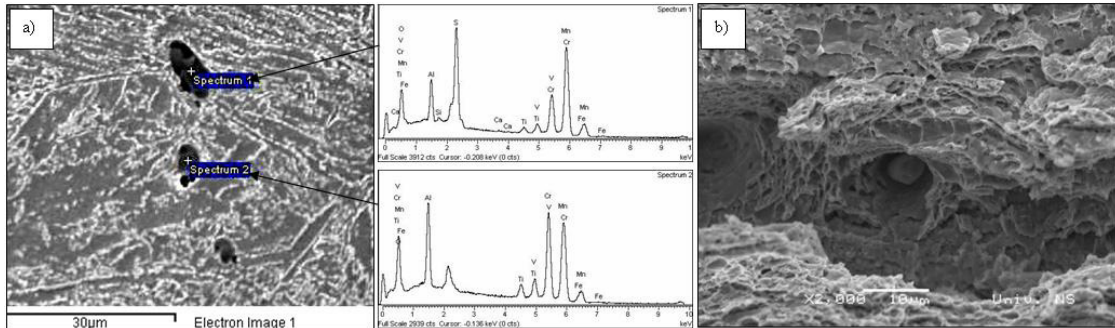


Fig. 3. Inclusions in the matrix: a) complex oxides  $TiOx-Al_2O_3 + MnS$ ; b) fracture surface at 80°C; MnS inclusion in the cavity.

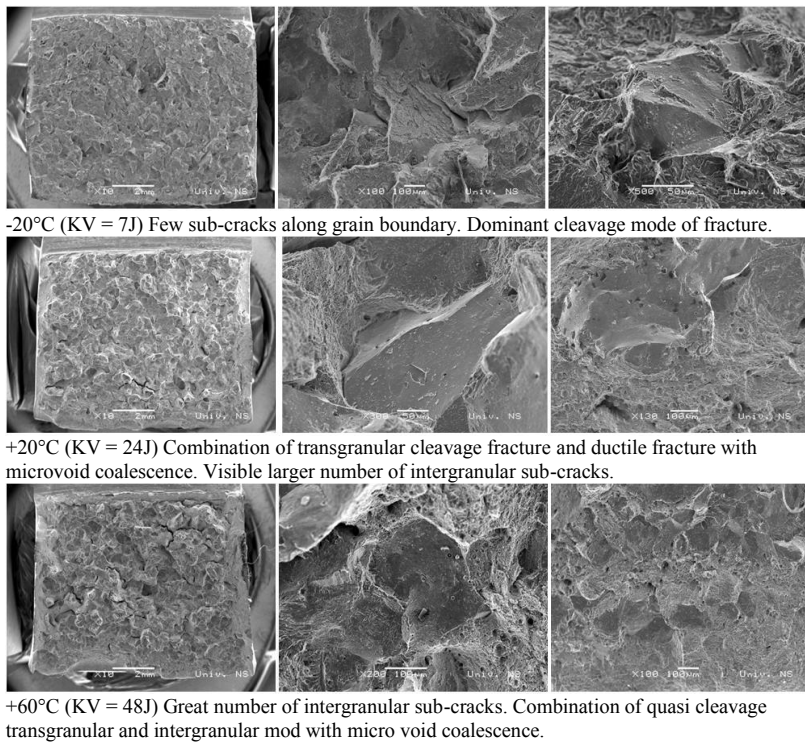


Fig. 4. Fracture surfaces of Charpy V notch specimens at different temperatures.

SEM characterization of Charpy V notch specimens fracture features indicate on fracture mode transition with temperature increase, from completely brittle mod at  $-20^{\circ}\text{C}$  to mix mode at higher temperatures, with micro void coalescence mod contribution increase beside cleavage, and increase number of intergranular sub-cracks on former austenite grain boundaries, Fig. 4. Microvoids during fracture are initiated on different particles, mainly non-metallic inclusions according to EDS analyses. Also, it was reported [Dobrzanski, 2005; Van Zul et al, 2005; Eggeler, 1989] that nucleation of voids during creep of the steel with the tempered martensite structure in the initial state may be connected with the material decohesion on the interstitial phase boundary between matrix and particles of the carbide precipitates for fine voids or non-metallic inclusions for larger one. It was observed that the voids nucleate most often on grain boundaries of the former austenite and the martensite lathes with beneficial orientation for crack propagation. At a given carbon content, toughness of martensitic steel depend on the level of chemical impurities such as phosphorous, sulphur and nitrogen as well as the presence of coarsened carbides in the grain boundaries during long-term exposed service at high temperature [Hu et al., 2004], due to weaken cohesion strength of grain boundaries. All observed fracture details indicate the extensive level of material exhaustion due to long term high temperature service, thus providing explanation for lower values of toughness, as well as relatively high values of hardness.

## 5. Conclusions

Characterization of metal degradation after prolonged service is necessary for evaluating component exhaustion and its remaining service capability. Microstructural changes of material result in the changes of its functional properties caused by long-term service. In this case, sample taken from the MSGV connection pipe made of the X20CrMoV 12.1 steel after more than 170.000 h in service within the temperature range of  $530\text{--}545^{\circ}\text{C}$  and pressures up to 19MPa, have satisfactory mechanical properties (hardness and tensile properties), and also do not have significant microstructural changes after prolonged service (still tempered martensite). However, the impact toughness and shifting of ductile to brittle transition temperature ( $+30^{\circ}\text{C}$ ) indicate significant level of material exhaustion. Low values of impact toughness are the consequence of carbide coarsening and formation of carbides network, as well as impurities segregation, on former austenite grain boundaries and martensitic laths. The role of different kind of inclusions in initiation and propagation of cracks is very highlighted. A very good indication of level of material exhaustion is the precipitation and coarsening of Laves phase, revealed in the microstructure.

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