INFLUENCE OF Cr CONTENT IN STEEL 12X1MF ON EXPLOITATION LIFE OF SUPERHEATER PIPES

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Abstract: The most widely-used material for tubes in ex soviet power plants is steel 12X1MF. Until today, 12H1MF has proven to be a reliable material for use in plants that operate in conditions of creep (temperature about 540-550 °C and pressure about 14-15 MPa). The microstructure of steel in the initial state depends on the heat treatment that it has undergone. Generally, low alloy CrMo(V) creep-resistant steels applied for construction of energy plants have initial ferritic-bainitic microstructure with fine dispersion of globular carbides precipitated in the ferritic matrix and at grain boundaries. Chromium has a positive effect on the heat resistance (resistance to oxidation) of the steel as well as hardenability and indirectly affects the creep resistance. Chromium should be in a solid solution. After complete heat treatment cycle, chromium carbides in 12X1MF should not exceed 10-20% of the total Cr+Mo+V carbide content. The effect of chromium in ferritic creep-resistant steels is complex. This paper deals with the case of a superheater pipe failure (fish-mouth rupture) which is partly caused by the fact that the pipe has a lower Cr content than that provided for 12X1MF steel.

1 INTRODUCTION

It is extraordinary that relatively simple materials can be designed and constructed to function so effectively as boiler tubes under high-temperature and high-pressure conditions, subject to potential degradation by a variety of mechanical and thermal stresses, and with the potential for environmental attack on both the fluid- and fire-side.

If there are no breakdowns from the original design conditions, water touched boiler tubes (waterwalls, economizers, etc.) are designed for, and should have, essentially infinite life. The case for steam-touched tubes, such as in the superheater (SH) and reheater (RH) sections of modern boilers, in somewhat different because of the inevitability of creep-limited liftime; although life-times well in excess of 200,000 operating hours are achievable.

Unfortunately, boiler tube failures (BTF) remain a significant and pervasive problem in the electric power industry. Historically, they have been a primary contributor to lost availability in fossil-fired power plants, ranking as the largest equipment problem based on the statistics [1].

Mo has been a standard alloying element used to produce creep-resistant steel capable of withstanding temperatures up to 500°C [2]. This is because Mo reduces the creep rate of steel successfully, as well as slows the coagulation and coarsening of carbides during high temperatures. Furthermore, this high-temperature suitability and creep-resistance mean the key application of Mo-based steel was in power generation.

However, continually increasing Mo content of steel in order to further improve its properties does not work since creep ductility actually decreases with increasing Mo [3]. Another limitation concerns the fact that graphitization (breaking down of iron carbides) takes place above 500 ° C. These drawbacks hinder the application of Mo-based steels.

A solution was discovered by chromium alloying with molybdenum. This gives steel a number of advantages not found in Mo-based alloys, and CrMo steels were the first to allow steam temperatures at power stations to exceed 500 °C [4].

The most widely used and confirmed steel for steam pipelines at power plants in eastern countries is steel of pearlitic class grade 12X1MF [5]. Fresh steam pipelines run at operating temperatures of 540 °C and 14 MPa pressure which represent the optimum operating conditions for this steel. Unlike steam lines, superheater tubes work at the upper temperature limit (tab.1) for this class of low alloyed creep resistant steels which is aprox.570 of the tube wall [6]. At these temperatures higher temperatures, all deficiencies of steel, primarily from a metallurgical point of view (heat treatment and alloying), quickly become apparent and reflect on life expectancy [7].

Table 1. Classification of creep resistant steels

Heat-resistant steels and special materials				
Bcc structure[A]				Fcc structure[B]
Up to 400 °C	Up to 500 °C	500 to 600°C	600 to 650°C	above 700 °C
unalloyed	alloyed		High-alloyed	
ferritic-pearlitic steels, fine-grain structural steels	Mo-legierte Stähle	bainitic (martensitic) ferritic steels	Martensitic 9 to 12% chromium steels	austenitic steels, Ni and Co-materials
P235GH	16Mo3	13CrMo4-5	X10CrMoVNb9-1	X8CrNiNb16-13
P355NH	18MnMo4-5	10CrMo9-10	X22CrMoV12-1	X8NiCr32-20
No extra proven methods; higher purity; fine grain	T_R-increase[C] through molybdenum alloying	Carbide/nitride formation + tempering	Precipitation hardening + spec. Heat-treatment	Fcc structure with high crystal recovery temperature
Guaranteed increase in temperature and creep rupture strength ⇨⇨⇨				

[A] bcc – body-centred cubic; [B] fcc – face-centred cubic; [C] T_R - recrystallisation temperature

In this paper, a practical example of superheater tube failure is presented which occurred in coal power plant in Bitola, Macedonia. This superheater tube section has evident lower metallurgical properties which inevitable led to significant shortening of service life and unexpected failure.

2 IMPACT OF ALLOYING ELEMENTS ON STEEL 12X1MF WITH SPECIAL REFERENCE TO CHROMIUM

Chromium in small amounts (~0.5%) is a carbide former and stabilizer. In larger amounts (up to 9% or more), it increases the resistance of steels to corrosion. Chromium also influences hardenability.

The effect of chromium in ferritic creep-resistant steels is complex. By itself, chromium enhances creep strength, although increasing the chromium content in lower-carbon grades does not increase resistance to deformation at elevated temperatures [3]. When added to molybdenum steel, chromium generally leads to some reduction in creep strength, such as that shown in fig.1.

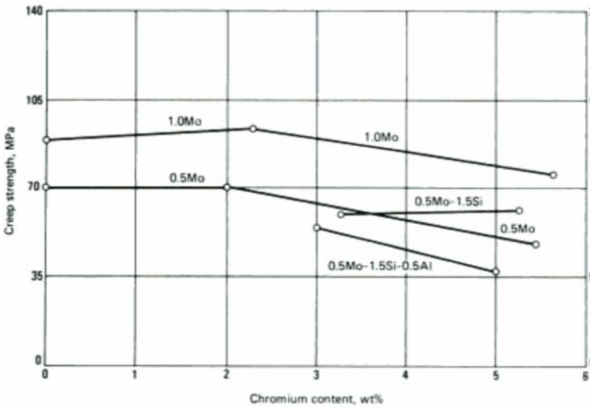


Figure 1. Effects of Cr on the creep strength (stress to produce a minimum creep rate of 0.0001% per hour) of several steels containg smallamounts of Mo, Si, Al at 540 °C

Chromium is most effective in strengthening molybdenium steels (0.5 to 1% Mo) when it is used in amounts of 1 to 2.5% [3].

Fig.2 summarizes the effects of chromium content on the tensile and yield strengts of Cr-Mo steels containg 0.5 to 1.0% Mo and various amounts of chromium. The effect of temperature is repored as the test temperature at which strength is reduced to 60% of its room temperature value. Chromium is most effective in strengthening these Cr-Mo steels when it is used in amounts of 1-2.5% [3].

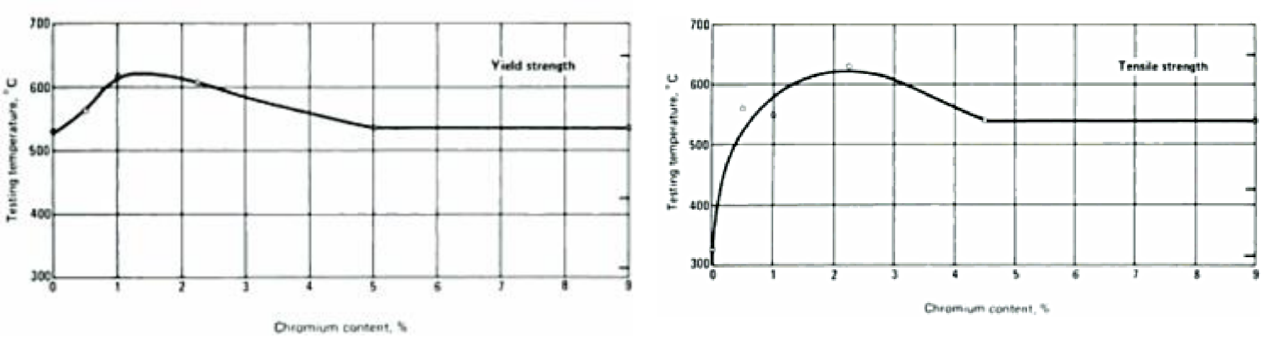


Figure 2. Effects of Cr content on strenght

Prolonged exploitation of elevated temperatures in creep conditions affects the character and morphology of carbide particle distribution. In the state after heat treatment, the basic carbide phases in the steel 12X1MF are M_3C and VC. During the exploitation, the phase composition of the steel changes: the amount of metastable M_3C carbides decreases and the amount of M_7C_3 (Cr_7C_3) and $M_{23}C_6$ carbides increases (fig.3), as well as Mo_2C. Vanadium carbide VC does not undergo changes during prolonged exploitation and has a minimal growth rate. The rate of coarsening of other carbides increases in the following order: Mo_2C, M_7C_3, $M_{23}C_6$, M_3C.

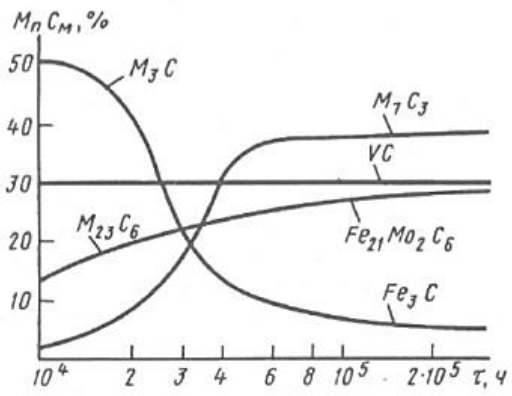


Figure 3. Kinetics of the change in the type and amount of carbide M_nC_m in the creep process in 12X1MF steel

The total solid solution of alloying elements (Cr+Mo+V) in Cr-Mo steels during creep can be recognize in the following pattern. In the initial state, after a full cycle of heat treatment (normalization and tempering), the content of carbides is approximately 25...30% as summary of Cr+Mo+V and increase to 45% in the process of prolonged exploitation of about 150,000.00h at temperature of 545°C. The permissible content of the carbide elements provided that the creep resistance is maintained is limited to 60%.

From the foregoing, it is clear that the creep resistance is primarily associated with the longer retention of the solid solution of molybdenum and chromium. It is not recommended that over 50% of molybdenum and chromium pass into carbides during exploitation.

Mo is well known to provide phase balance strengthening, through facilitating bainite transformation, and solid solution strengthening [8]. It can reduce the dynamic recrystallization rate of austenite, which may lead to grain refinement. Sometimes Mo can contribute to precipitation through the formation of Mo-rich carbides.

Similar to Mo, Cr facilitates the bainite transformation, may precipitate in complex Cr-rich carbides. In particular, Cr was observed delaying Fe_3C precipitation in low carbon steel. However, the solid solution strengthening effect of Cr is ~6 times weaker than this of Mo, and, therefore, Cr is less affective in retarding recrystallization.

3 MICROSTRUCTURE(-S) OF STEEL 12X1MF

The chemical composition of the steel 12X1MF is given in Tab.2.

Table 2. Chemical composition of 12X1MF [6]

Steel grade	Mass procent of elements, %													
	C	Si	Mn	Cr	Ni	Mo	W	V	Ti	B	Al	Cu	S	P
												Not more than		
12X1MF	0.10-0.15	0.17-0.37	0.40-0.70	0.9-1.2	Not more than 0.25	0.25-0.35	-	0.15-0.30	-	-	-	0.20	0.025	0.025

Based on technical instruction [6] “Classes of microstructures of tubes made of steel 12X1MF“, the microstructure are classified into acceptable classes of 1-5 and unacceptable of 6-9 (fig.4,5). Acceptable microstructures include those that contain sorbite of tempering not less than 15%. The group of unacceptable microstructures include those with a sorbite content of less than 15%, ferrite-carbide mixtures and structures containing secondary perlite grains along the ferrite and sorbite boundaries.

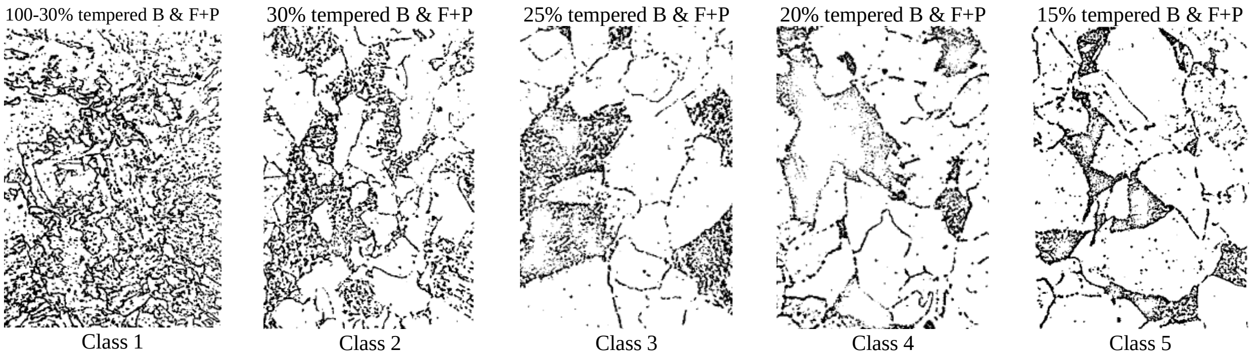


Figure 4. Acceptable classes (1-5) of microstructure of steel 12X1MF

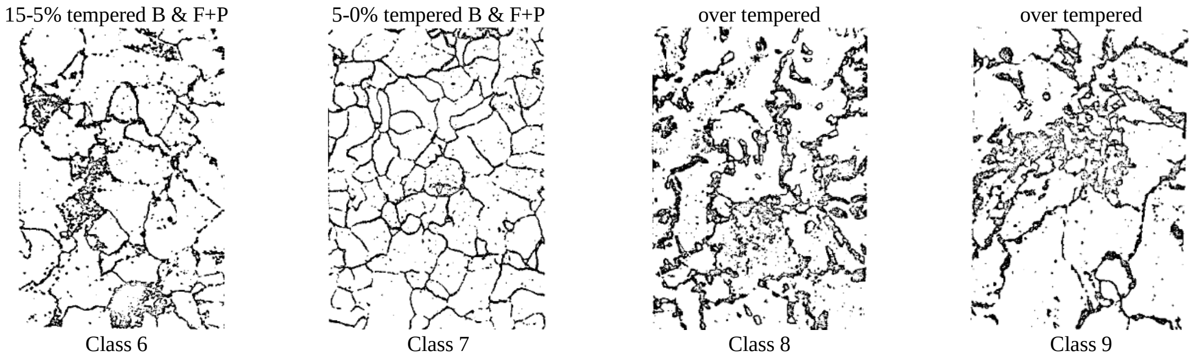


Figure 5. Un-acceptable classes (6-9) of microstructure of steel 12X1MF

Depending on the micro-structural state, the creep properties are characterized by a wide scattering field with respect to the creep strength reaching 35% of the nominal curves. In order to correctly select the creep properties of steel 12X1MF in relation to the microstructure state it is proposed to evaluate the creep strength of the metal by three structural groups (fig.6).

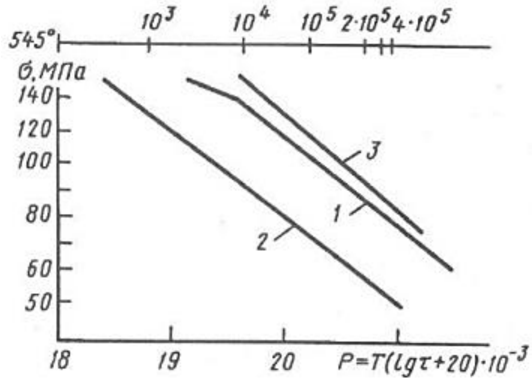


Figure 6. Diagram of creep rupture strenght for steel 12X1MF

Group I refers to tubes with an acceptable structure of ferrite and sorbit, class 2-5 (Fig.4). The line marked with -1- in Fig.6 is derived for guaranteed creep strength. The possible error in the assessment of creep rupture strenght is reduced by +25 .... 10%.

Group II (line 2) comprises tubes with an unacceptable microstructure (class 6-9, fig.5) in the form of sorbitol with less than 15% and a ferritic-carbide mixture. The possible error in the assessment of creep rupture strenght is in a scatter field that does not exceed 15%.

Group III (line 3) includes tubes with a structure of needle sorbite (class 1, fig.4) which is obtained by tempering of beinite.

According to the above, depending on the heat treatment and the chemical composition, the tube has a precisely defined structure leading to the determination of the service life.

3.1 Influence of heat treatment on 12X1MF steel tube microstructure

The heat treatment of such pipes in accordance with the requirements of TU 14-3-460-75 consists of normalization when heated to 950-980 ° C, tempering at a temperature of 725-750°C for 1-3 hours with cooling in air.

A detailed study of the relationship of the structure with the heat-resistant properties of 12X1MF steel was carried out by K. A. Lanskoy and E. N. Gorchakova, and later by T. G. Berezina [9]. To study the kinetics of austenite transformation during continuous cooling in 12X1MF steel, a thermokinetic diagram was constructed (fig.7).

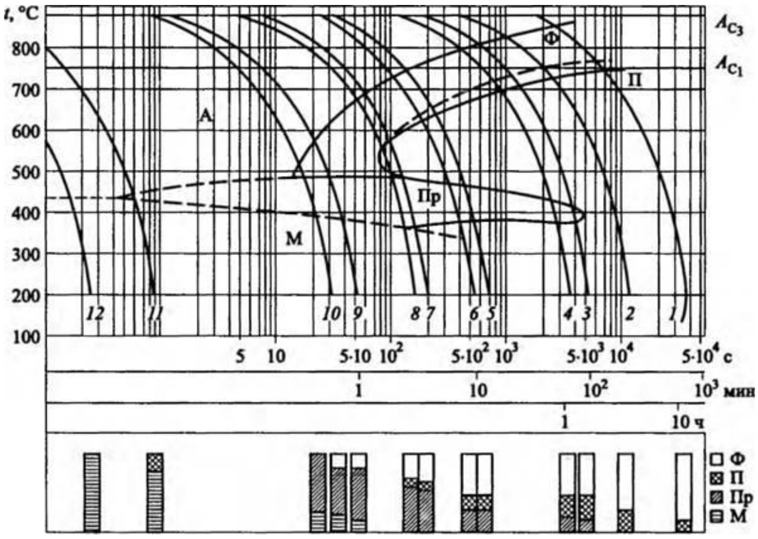


Figure 7. Thermokinetic diagram of 12X1MF steel at a cooling rate, °C/min: 1-1; 2-3; 3-6; 4-10; 5-55; 6-70; 7-185; 8-230; 9-800; 10-1660; 11-cooling in oil; 12-cooling in water; A-austenite; F- ferrite; P-perlite; Pr-an intermediate phase; M-martensite

As follows from this diagram, 12X1MF steel is characterized by three regions of austenite transformation: ferrite-pearlitic, ferrite-bainitic (intermediate) and ferrite-martensitic.

At low cooling rates (1, 3, 6 °C/min), the transformation of austenite occurs in the ferrite-pearlite region, which is limited by the temperatures of the critical points Ac3 and Ac1. The region of martensite formation corresponds to the highest cooling rates. The intermediate region is between these regions both in cooling rate and in temperature.

The transformation of austenite in the ferrite-pearlite region upon cooling at a rate of 10 to 200 °C/min begins with the release of polygonal ferrite, after which the formation of perlite occurs. With an increase in the cooling rate, the amount of ferrite and perlite decreases and a new component, bainite, appears. A further increase in the cooling rate leads to a suppression of the transformation in the ferrite-pearlite region.

At cooling rates of 250-1660 °C/min, the transformation of austenite occurs in the intermediate region with the formation of a structure resembling granular perlite. In the structure of samples cooled in oil, needle-like bainite and martensite sites are observed.

One of the main goals of heat treatment of 12X1MF steel is to ensure high values of long-term strength due to phase hardening, dispersion hardening and thermal stability of a given structure. For this purpose, high tempering is used, in which the following processes occur in steel:

1. in ferrite, precipitation of dispersed carbides occurs along the boundaries and body of grains. This process increases the strength and creep resistance of ferrite grains;
2. in the pearlite component of the structure, there is a process of spheroidization of cementite plates and the pearlite structure in the metal of the steam pipes mainly has a granular structure;
3. in the bainitic component during tempering, the process of decomposition of the supersaturated solid solution occurs with the release of carbides and a decrease in the level of microstresses resulting from phase hardening. There is also the initial stage of the recovery and recrystallization processes. Thus, as a result of high tempering, a sorbite structure consisting of a fragmented ferrite matrix and carbides is formed at the site of bainitic grains. If bainite had a needle structure, then the same matrix structure is preserved in the sorbite grains of tempering.

Fig.8 presents the results obtained by T. G. Berezina [9] for determining the long-term strength of the metal of one pipe after different heat treatment modes, ie, from the microstructure score [6]. It can be seen that the value of the long-term strength of the metal with acceptance and rejection structures is noticeably different.

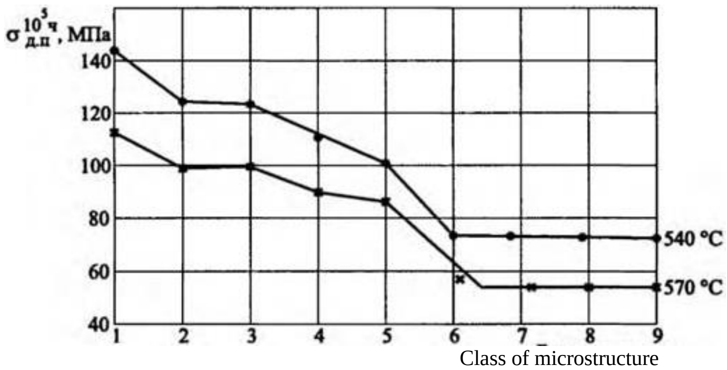
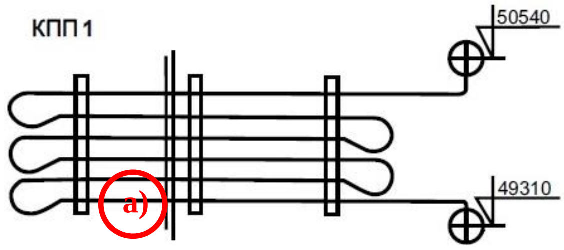


Figure 8. The long-term strength of the metal pipe made of steel 12X1MF, depending on the point of the structure on a scale TU 14-3-460-75 [6]

4 INVESTIGATION OF A SUPERHEATER TUBE WITH A SHORT-TIME EXPLOITATION LIFE

The short tube that is analyzed in this paper was built as a replacement segment in the super heater tubes unit (KPP) which is section of boiler type ZIO PP-700-13.8-545 located in Bitola, Macedonia. This replacement segment was built 8 years ago (2010), and has worked approximately 60,000.00 hours. In 2018, it suffered a failure, causing the block to stall. In Fig. 9 is shown the location and conditions under which the defect occurred.

a) Location of explosion
b) Failure segment (cc.300 mm)
c) Tolerance between holder and tubes
d) Unsupported (unrestrained) tube holders
e) Side damage from explosion (yellow)



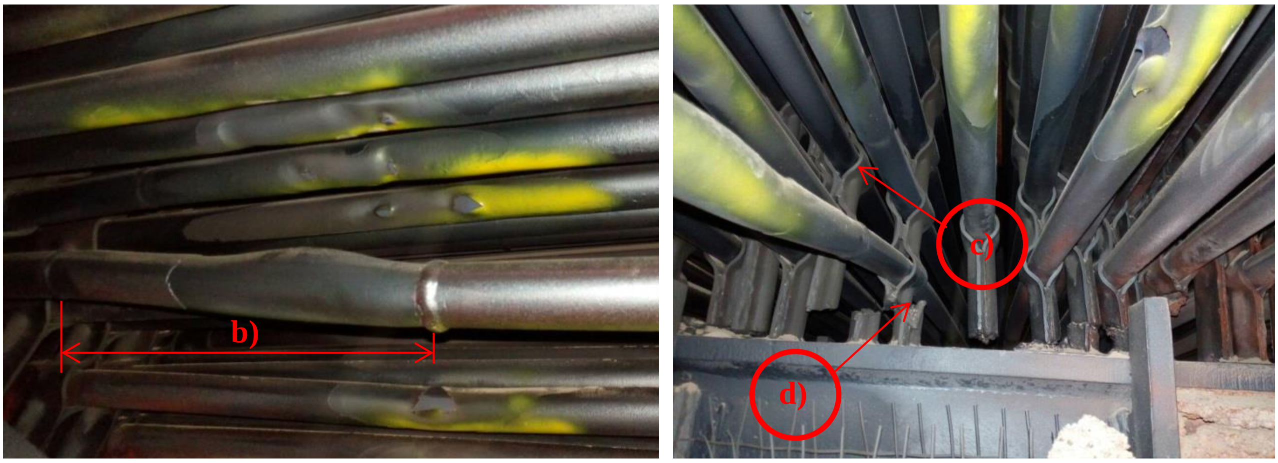


Figure 9. Location and restrains of failure tube segment

Fig.9 clearly shows that it is newer segment that was installed later as replacement because of abrasion. From the surrounding area of exploded tube it is seen that there are no conditions for restricting the dilatation of tubes which can be considered as one possible reason that leads to increased stress and premature creep aging rupture.

Figure 10. Measurment inspection of exploded segment

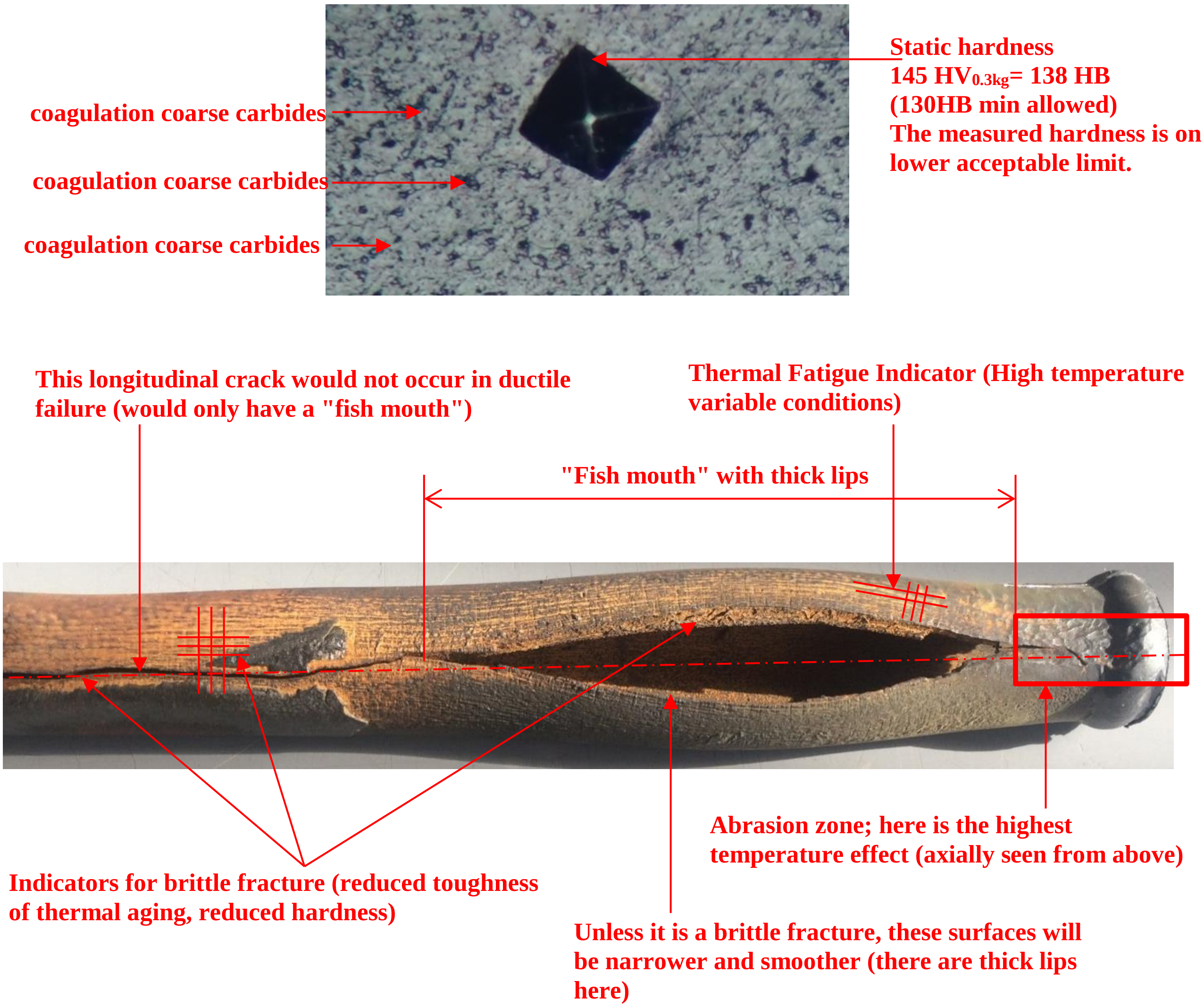


Figure 11. Micro-hardness and visual inspection for creep indicators

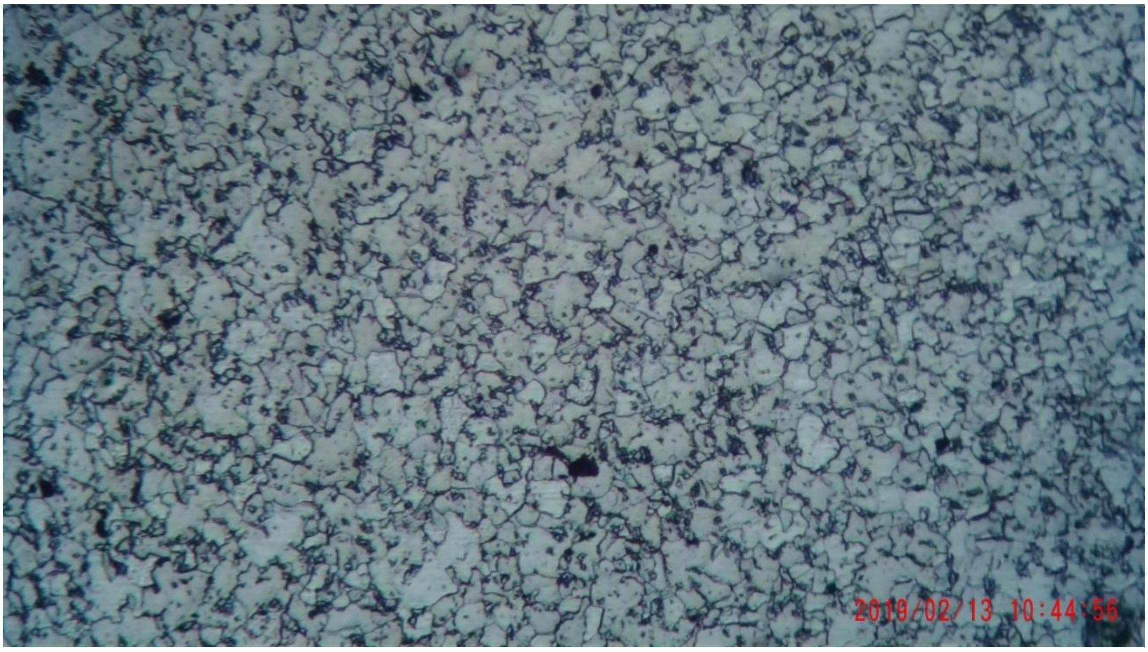
Figure 12. Oxide scale (non critical thickness)

Table 3. Chemical composition of investigated tube with fish mouth

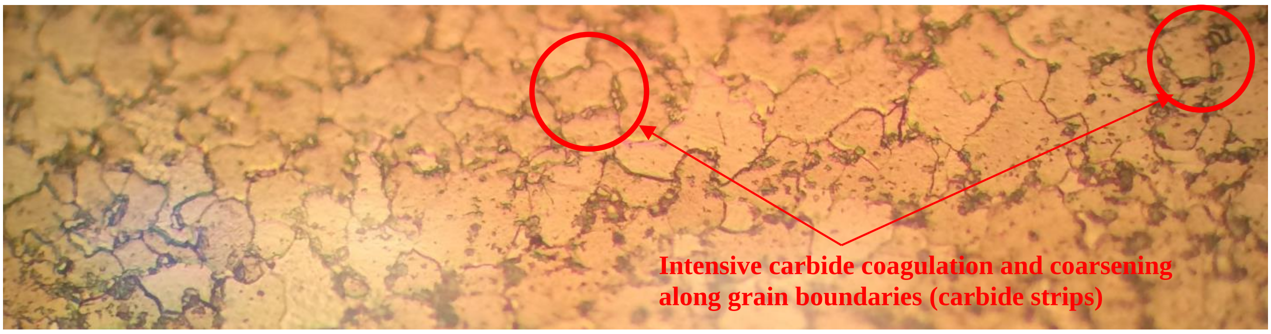
Steel grade	Mass procent of elements, %													
	C	Si	Mn	Cr	Ni	Mo	W	V	Ti	B	Al	Cu	S	P
													-	
12X1MF ?	**0.156**↑	0.31	0.54	**0.85**↓	0.17	0.272	-	0.221	-	-	-	0.19	0.019	0.010

Table 4. Chemical composition of un-damaged adjoining tube with 250,000.00h

Steel grade	Mass procent of elements, %													
	C	Si	Mn	Cr	Ni	Mo	W	V	Ti	B	Al	Cu	S	P
													-	
12X1MF	0.116	0.21	0.53	1.03	0.16	0.284	-	0.154	-	-	-	0.16	0.022	0.008



x200



x500

Figure 13. Ferritic-carbide mixture, 80% degraded microstructure of investigated tube

Visual inspection and measurement of the dimensions of the damaged segment clearly shows that it was exposed to abrasion, but the rupture didn't happened where the wall thickness is thinnest (1.3-1.5mm, fig.10). The minimum thickness provided in the boiler passport for this segment is 4.7mm.

Most likely, the rupture line appearance is related to the local tube damage which has a sharp edge on the generating line and causes a local increase in stress (explosion line, fig.10). It is worth noting that adjacent pipes with similar wall thickness (cc.1.7-2.2mm), and significantly longer working hours (over 200,000.00h), with chemical composition (tab.4) and microstructural changes within normal limits, have not yet experienced such a failure. Fig.12 shows that there are no conditioning problems with the steam that can lead to additional thermal overload of the tubes.

It is evident from the analysis given in fig.11 of the visual inspection, that the segment suffered a brittle fracture as a result of thermal aging. Micro-hardness is measured to see the effect of thermal aging. Obtained value with static method is 138 HB and it is low. The low limit according to the technical instructions for 12X1MF is 130HB, measured with a dynamic method.

According to the chemical composition (tab.3), there is a deviation from the permissible limits corresponding to 12X1MF steel. The wt.% of chromium is below the lower limit. Adjacent tubes who didn't suffered failure, but still have bellow acceptable wall thickness, have normal chemical composition which can be seen in tab.4. For this type of Cr-Mo low alloyed steel optimal wt.% for Cr [3] is clearly above 1.0%. Under this quantity, steel does not have the optimum creep resistance properties.

The microstructure presented in fig.13 confirms the above explained. Namely, it is a steel that had original un-acceptable microstructure class 6, below 15% sorbite [6]. There are no traces of tempered bainite microstructure (sorbite), which is not the case with surrounding pipes with similar wall thicknesses and much longer exploatation life.

The shape of the accumulated boundary carbides in fig.13 and having in mind fig.5 and fig.8, it can be concluded that the solid chromium solution is significantly depleted leading to a major reduction of creep strength and brittle fracture.

5 CONCLUSION

The quality of the 12X1MF steel in terms of long service life under creep conditions is the result of precisely determined chemical composition, heat treatment cycle, and thus the required microstructure.

The presence of chromium in its solid solution for min. 1% wt. gives it high temperature features, that its competitors such as 14MoV6-3 do not have.

Investigated tube segment has been operated as part of superheater that goes well above optimum settings (540°C) at about 570°C. Additionally, for superheater it is not so rare, short-term overheating that goes above 570°C as major cause for short term overheating of tubes as damage mechanism [10].

The superheater is a vital part of the boiler and this paper proves that during overhaul, material control, chemical and metallographic, is vital in order to ensure uninterrupted operation of the power plant throughout the year.

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6 REFERENCES

[1] B. Dooley, W. McNaughton, 1995, *Boiler Tube Failures: Theory and Practice-Volume 1: Boiler Tube Fundamentals*, Electric Power Research Institute (EPRI)

[2] A. Nagode et al., 2011, Review of creep resistant alloys for power plant application, *Metalurgija*, 50 (1), pp.45-48

[3] Joseph R. Davis, 1997, *ASM Specialty Handbook: Heat-Resistant Materials*, ASM International, pp. 90

[4] F.A. Hromcenko, 2002, *Residual life of steam tube weldments*, Masinostroenie, Moscow, pp.14 (in Russian)

[5] S.A. Loskutov et al., 2014, Optimization of the structure and properties of 12X1MF steel pipelines by the use of regenerative heat treatment after long service life, *Bulletin of the South Ural State University Series "Metallurgy"*, vol.14(4), pp.45-51 (in Russian)

[6] TU 14-3-460-75: 2009, Seamless Steel Pipe for Steam Boiler Pipeline (in Russian)

[7] V.I. Gladshtein, 2013, *Damage assessment of power plant components operating under high-temperature creep conditions*, Energetik, Moscow, pp.36 (in Russian)

[8] Kostryzhev, A.; Singh, N.; Chen, L.; Killmore, C.; Pereloma, E., 2018, Comparative Effect of Mo and Cr on Microstructure and Mechanical Properties in NbV-Microalloyed Bainitic Steels. *Metals*, vol.8 (2), pp.134

[9] Yu.L. Izrailev et al., 2002, *Vitality of steam pipelines of aging thermal power plants*, TORUS PRESS, 3rd ed., p.616 (in Russian)

[10] J.D. Angelo et al., 2016, Modelling of thermal behavior of iron oxide layers on boiler tubes, *Journal of Physics: Conf. Ser.* 721(1):012002