Recenzované vědecké články

Development of a New Type of Chromium Modified Steel

Vývoj nového typu chromové modifikované oceli

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The article outlines the development and verification of properties including the long-term creep strength of a new type of creep resistant chromium modified steel, which target material characteristic is 150 MPa of creep rupture strength at 650°C and that will find application in a pressure system of newly-built power plants (ultra-supercritical boilers). The development of this steel was initiated under the CRESTA project, where two modifications of chemical composition were set up in order to obtain either a steel without Z-phase or a steel with the modified Z-phase based on tantalum. Experimental melts were made and their properties and structure were analyzed in a comprehensive manner, including long-term creep tests. At the same time, filler metals and welding processes were developed, too.

The prospective results achieved under the project CRESTA are at present (2014-2018) followed-up by the project CRESTA 2, funded by the European Research Fund for Coal and Steel (RFCS).

***Key words**: Creep; chromium modified steels; pipe; material properties of steel and weldments*

V článku je nastíněn postup vývoje a ověřování vlastností včetně dlouhodobé creepové pevnosti nového typu žárupevné oceli patřící do skupiny modifikovaných chromových ocelí, jejíž cílovou materiálovou charakteristikou je hodnota meze pevnosti při tečení při teplotě 650 °C ve výši 150 MPa a která nalezne uplatnění v tlakovém systému nově budovaných energetických kotlů velkých výkonů, tzv. ultra-superkritických kotlů (USC). Vývoj této oceli byl zahájen v rámci projektu CRESTA, kde se na základě poznatků o nepříznivém vlivu přítomnosti Z- fáze na bázi Cr(Nb,V)N na dlouhodobou creepovou odolnost modifikovaných chromových ocelí, vyčlenily dva směry úpravy chemického složení s cílem získat buď ocel zcela bez Z-fáze, nebo ocel s modifikovaným složením Z-fáze na bázi tantalu, který nahradí niob. Byla vyrobena experimentální tavba oceli bez Z-fáze (Nb-free) a komplexně analyzovány její vlastnosti i struktura včetně dlouhodobých creepových zkoušek. Rovněž byl vyvinut přídavný svařovací materiál a postupy svařování. V článku jsou uvedeny výsledky creepových zkoušek základního materiálu trubky, prováděných při teplotě 600, 650 a 700 °C, a homogenního svarového spoje na tlustostěnné trubce při teplotě 600 a 650 °C, a to vše spolu s metalografickou analýzou creepového poškození v místě lomu, ke kterému došlo v jemnozrnné oblasti tepelně ovlivněné zóny (tzv. lom IV. typu). Dále článek uvádí výsledky proměření mikrotvrdosti přes svarový spoj v oblasti poškození. Na základě porovnání creepové pevnosti základního materiálu a svarového spoje byl stanoven redukční koeficient pevnosti svarového spoje (SRF faktor) ve výši 0,57, což je méně než pro oceli P 91 i P 92, u nichž tento parametr dosahuje hodnot nad 0,60.

Na nadějné výsledky, které byly v rámci projektu CRESTA získány, navazuje v současné době (2014-2018) pokračovací projekt New Creep Resistant Stable Steel for USC Power Plant (CRESTA 2) financovaný evropským fondem Research Fund for Coal and Steel (RFCS).

***Klíčová slova**: Creep; chrómové modifikované oceli; trubka; vlastnosti oceli a svarových spojů*

The degradation of long-term creep strength and oxidation resistance with increasing temperature limit the capability and lifetime of components fabricated from ferritic-martensitic steels. The strategy for improvement of temperature capability of these materials is to engineer microstructure for an optimum performance by knowledge-based modelling approaches, i.e. to optimize compositions and heat treatment in order to stabilize microstructures over an extended time period. This should be based on improved understanding of degradation processes including the detailed knowledge of Z-phase precipitation and coarsening. The development of these new steels started within the frame of CRESTA (New Creep Resistant Stable Steel for USC Power) project sponsored by EU Commission in 2008-2012) [1].

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ISSN 0018-8069

From this project, two types of 11 – 12 % Cr modified steels emerged, which showed very promising results:

- *Nb-free steel*; a steel with a long-term stable MX (VN) precipitates, which will provide good creep strength. The idea was to remove elements, which promote Z-phase precipitation, such as Nb, to reduce the Co content to save cost and to optimize the boron and nitrogen contents to improve the properties of welded joint and reduce the type IV cracking sensitivity;
- *Z-phase strengthened steel*; a steel that exploits tantalum addition and formation of fine and dispersed tantalum based Z-phase (CrTaN) that replace the strengthening effect of the unstable MX precipitates.

The paper describes the properties of the semi-industrial heat made of Nb-free steel.

1. Z-phase in chromium modified steels

Z-phase of Cr(V,Nb)N type is thermodynamically the most stable nitride in 9 – 12 % Cr steels alloyed with V, Nb and N but was never observed in these steels in the as-tempered state. In a 12 % Cr steel the Z-phase was found to replace nearly all MN nitrides after 12,000 hours at 660°C, but an accelerated heat treatment at temperature 725°C up to 1,000 hours on the same steel in the normalized and tempered condition could not provoke the Z-phase formation due to the solution temperature of the Z-phase being close to 800°C [2]. Modelling of the Z-phase transformation using MatCalc software showed that the VN dissolution accelerates after 3,000 hours at 650°C and confirmed an excellent correlation between VN removal from the steel and the loss of creep rupture strength [3]. The best known commercial example of such breakdown is the 12Cr-2W steel (T/P122) widely used for construction of power plants in Japan, but it is now being completely replaced by 9 wt.% Cr steels, such as grade P 91.

Z-phase was long known to precipitate in austenitic steels as CrNbN type. In contrast to the Z-phases in martensitic chromium modified steels, the Cr(Nb,V)N precipitates very rapidly in low carbon austenitic steels as small and finely distributed rod-like particles, and it has a pronounced strengthening effect, being thermally stable with a very low coarsening rate [4]. According to classical nucleation theory the Z-phase could be expected to nucleate already during tempering, since it is the most stable nitride. However, the MN nitrides are found to nucleate much faster, and once formed they lower solid solution concentrations of V, Nb and N, which are necessary for the Z-phase formation. The Z-phase does not nucleate according to the classical process, i.e. through the formation and growth of critical embryos, but it is created by Cr-diffusion from the ferrite matrix into the pre-existing MN nitrides having face cubic centered (FCC) unit cell, where CrMN FCC unit cell is formed. Later on, nitrogen and chromium atoms are ordered into the layered tetragonal unit cell structure of the Z-phase [5]. This complicated nucleation process is not yet completely understood and no good model of the nucleation process of the Z-phase exists. This complicates a prediction of maximum acceptable Cr content of the V and Nb containing martensitic steels, and evaluation of long-term stability of existing chromium modified steels.

2. Nb-free steel, production and properties

The long-term creep strength of the 9 – 12 wt.% Cr martensitic steels relies primarily on precipitation strengthening by small and finely distributed particles of (V,Nb)N. Even though these particles have a very low coarsening rate, they are not thermodynamically stable and will in time be replaced by a nitride known as the Z-phase, Cr(V,Nb)N, which is the cause of the microstructure instabilities [2, 3]. It was found that the Z-phase precipitated as large and coarsely distributed particles that did not contribute to strengthening and consumed the MX particles during their growth, causing a significant drop in creep strength. This replacement process is very slow and can even last decades at service temperatures. However, an increase in the overall Cr content from 9 wt.% to 12 wt.% causes a critical acceleration of this process from decades to years. This causes a breakdown in creep strength within the lifetime of the power plants.

2.1 Production and properties of steel pipe

One way how to cope with this problem is to completely avoid niobium addition into Cr-modified steels. This so-called Nb-free steel was produced in the form of semi-industrial melt on vacuum–pressure induction melting (VPIM) device with the capacity of 1.7 ton in Materials and Metallurgical Research, Ltd., Ostrava. The heat was melted in argon atmosphere and refined in vacuum, then the ingot was refined by electroslag remelting process (ESR) and the final pipe of ø 219 × 25 mm was produced by piercing and pilgrim rolling, Fig. 1. Then the pipe was normalized at 1060°C, cooled in air and tempered at temperature 750°C for 6 hours.

Fig. 1 Sawing of ends of pipe after rolling on the pilgrim mill
Obr. 1 Řezání konců trubky po vyválcování na poutnické stolici

The target chemical composition of Nb-free steel is stated in Tab. 1 together with the composition of manufactured pipe. Yield stress (*YS*), ultimate strength (*UTS*), elongation (*A*) and reduction of area (*RA*) tested at room temperature (*RT*), as well as at 550, 600 and 650°C in transverse direction are summarized in Tab. 2 together with hardness HV.

Tab. 1 Chemical composition of Nb-free steel, target and that of pipe (wt.%)
Tab. 1 Chemické složení Nb-free oceli, cílové a trubky (hm. %)

	C	**Mn**	**Si**	**P**	**S**	**Cr**	**Mo**
target	0.10-0.12	0.47-0.53	0.35-0.40	≤0.02	≤0.01	10.80-11.20	0.12-0.16
pipe	0.12	0.46	0.35	0.010	0.004	10.60	0.16
	W	**Co**	**V**	**Ti**	**Al**	**B**	**N**
target	2.40-2.60	2.80-3.00	0.20-0.25	≤0.05	≤0.05	0.0050-0.0080	0.020-0.030
pipe	2.31	2.6	0.25	<0.10	0.025	0.0044	0.027

Tab. 2 Mechanical properties of manufactured pipe
Tab. 2 Mechanické vlastnosti vyrobené trubky

Temperature	**YS**	**UTS**	**A**	**RA**	**HV**
(°C)	**(MPa)**		**(%)**		
RT (+20)	615	785	25	66	258
550	387	448	29	80	-
600	307	365	31	85	-
650	210	271	34	91	-

The produced pipe exhibited a homogeneous microstructure through wall thickness consisting of tempered martensite with very few islands of delta ferrite phase, with size in the range 2 – 10 µm present at mid-wall and outer surface, see Fig. 2. Quite similar grain size distribution through the wall thickness was also observed with mean austenite grain size (*AGS*) in the range 32 – 35 µm (G = 6.5), Fig. 3.

Dilatometer test has been performed on the Nb-free steel pipe in order to determine the phase transformation temperatures. The change in length as a function of temperature is shown in Fig. 4. It was found that the Ac_1 and Ac_3 temperatures are 860 and 915°C, respectively, and M_s and M_f are 325 and 165°C, respectively.

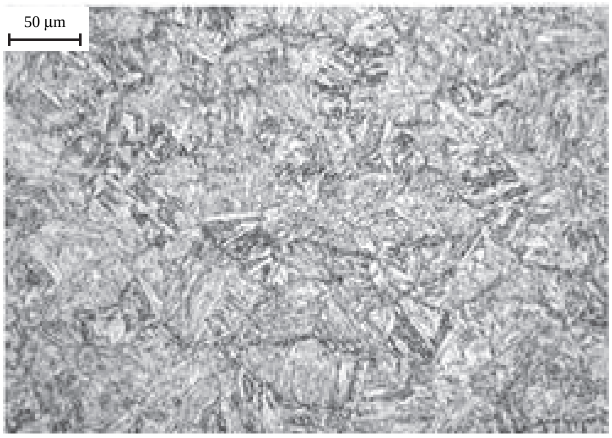

Fig. 2 Microstructure at the outer surface of the pipe
Obr. 2 Mikrostruktura na vnějším povrchu trubky

Fig. 3 Austenite grain structure at the outer surface of the pipe
Obr. 3 Zrna austenitu u vnějšího povrchu trubky

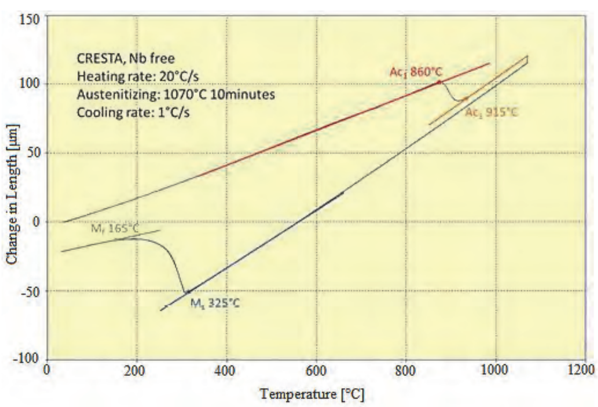

Fig. 4 Results of dilatometry test on pipe material
Obr. 4 Výsledek dilatometrické analýzy materiálu trubky

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2.2 Welding and welded joints

Various multi-pass fusion arc welding methods are employed in USC plants for headers and pipework fabrication. Welding of 11 % Cr-class steels can be accomplished with GTAW, SAW, SMAW and FCAW methods. SAW process offers significant productivity potential where it can be used (i.e. PA position), with FCAW following next. GTA welding is most often successfully employed for performing root pass in joining pipes, while SMAW is often the preferred method for repair or for welding in-field in locations with difficult access. Similar to the base materials, the weld metal microstructure consists after PWHT of a tempered martensite. This has to be obtained also in multilayer weldments. For design purposes, weld metal has to have comparable tensile (short-term) and creep rupture strength as the parent steel, sufficient ductility, and impact toughness, ferritic matrix that promotes similar thermal expansion behaviour, which limits thermal fatigue damage of thick-walled welded components during high temperature service.

As the principal application of Nb-free steel is intended for headers and piping, the welding programme was performed according to WPQR requirements of EN ISO 15 614 [6] for thick walled components. The circumferential butt weld was manufactured by using GTAW method (141) of welding in position PA with limited grinding between the layers. Wires with diameter 2.4 and 3.2 mm with matching chemical composition were used as a filler metal. Preheating at the temperature range 200 – 250°C and maximum interpass temperature 250°C were applied. Necessary post weld heat treatment was subsequently performed in accordance with requirements for grade P 92.

Material analyses according to EN ISO 15614-1 were performed on weld joint including NDT, tensile testing at ambient and elevated temperature, side bend tests, impact tests of weld metal and heat affected zone, hardness testing at cover and root pass cross to the weld, analyses of macrostructure and microstructure across to the weld (HAZ, weld and base metals). All the performed tests have confirmed good material properties of welded joints.

2.3 Creep testing of pipe and welded joints

As the developed material is intended for high temperature use in USC blocks, one of the principal characteristics is the creep resistance of base material, as well as weld joints. Therefore, creep testing program of the base metal has been launched at temperatures of 600, 650 and 700°C and at temperatures 600 and 700°C in the case of welded joint. All stress rupture tests were performed in accordance with the standard ISO 204 [7]. The results of the base metal and weld joint are illustrated in Fig. 5 recalculated as the stress dependence of Larson-Miller parameter P_{LM} according to the Eq. (1) [8]:

$$P_{LM} = T \cdot \left[log(t) + C \right] \tag{1}$$

with the usual meanings of the variables. Constant C equals to 26.8, which is the value calculated by the method of least squares from data stated in [9] and valid for P 92 steel.

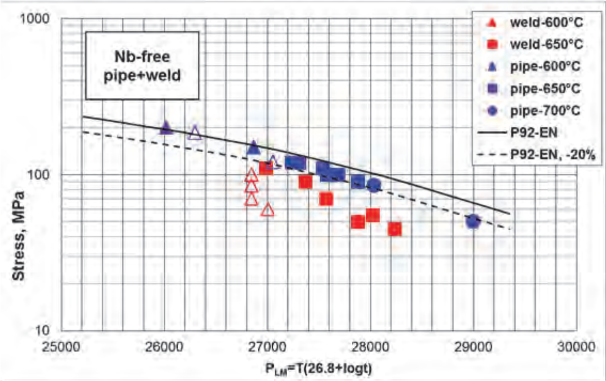

Fig. 5 Stress dependence of Larson-Miller parameter of base material and weld joint of the steel Nb-free

Obr. 5 Závislost napětí na Larson-Millerově parametru pro základní materiál a svarový spoj oceli Nb-free

Full points in Fig. 5 represent the ruptured specimens, while empty points are still running creep tests. The solid line labelled P92-EN represents the standardized mean creep strength of the steel P 92 according to [9] and the dashed line the lower -20% tolerance limit. All the results confirmed slightly worse creep resistance compared to the P 92 steel and very pronounced drop of creep strength of welded joint at least at 650°C.

2.4 Rupture location analysis of creep specimens of Nb-free steel weldment

Macrostructure and microstructure of the ruptured creep specimens of Nb free-steel weldment was analysed using optical microscopy with the special attention to identification of the failure location, the extent of creep cavitation damage and hardness profile measurement through the weldment. The failure locations in all analysed creep tests were practically identical, the rupture occurred in the fine-grained heat affected zone (FG-HAZ), as it can be seen in Fig. 6, when the macro-etch of the stress rupture specimen exposed at temperature 650°C and stress 70 MPa for 1,186 hours is shown.

Microstructure analysis then revealed that all the fine-grained parts of HAZ were heavily cavitated, while neither in the coarse-grained HAZ (CG-HAZ) nor in the weld metal and/or base material revealed any signs of cavitation damage, compare Figs. 7 to 10.

Fig. 6 Macrostructure of the stress rupture specimen exposed at 650°C/70 MPa/1,186 h

Obr. 6 Makrostruktura creepové zkoušky po expozici 650°C/70 MPa/1186 h

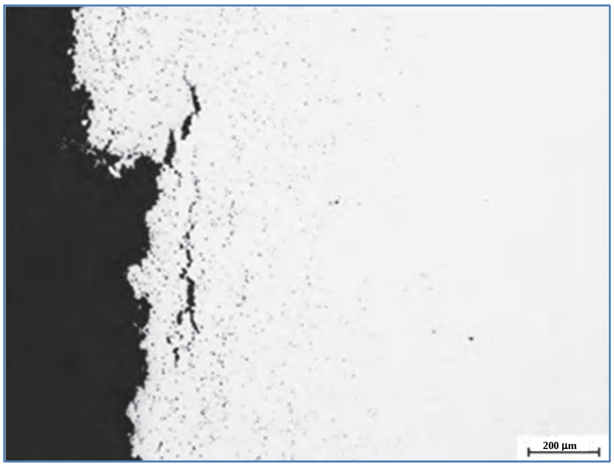

Fig. 7 Heavy cavitation in the fine-grained HAZ of the specimen creep exposed at 650°C/70 MPa/1,186 h

Obr. 7 Rozsáhlá kavitace jemnozrnné oblasti TOO po creepové zkoušce po expozici 650 °C/70 MPa/1186 h

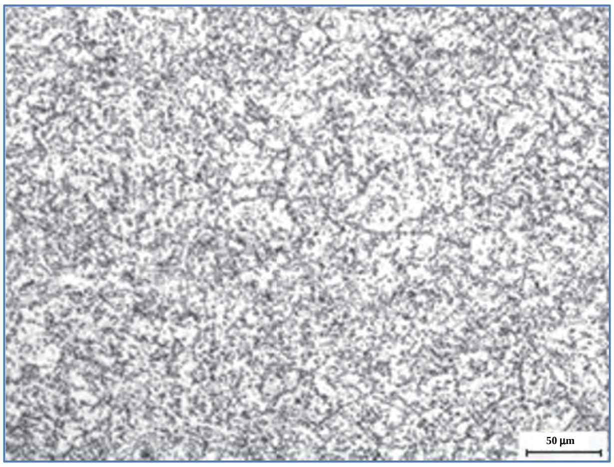

Fig. 8 Cavity free microstructure of the coarse-grained HAZ of the specimen creep exposed at 650°C/70 MPa/1,186 h

Obr. 8 Mikrostruktura hrubozrnné oblasti TOO bez kavit po creepové zkoušce po expozici při 650 °C/70 MPa/1186 h

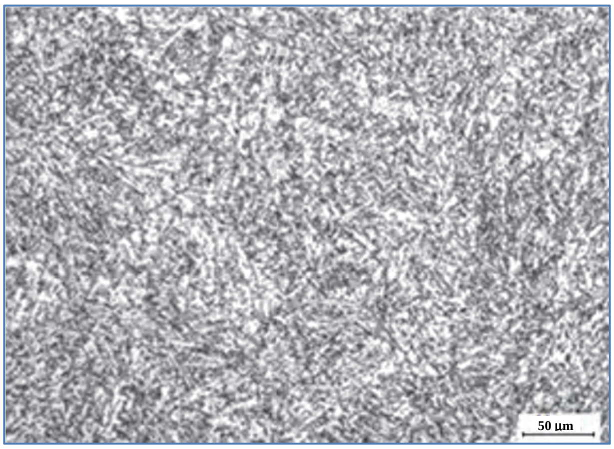

Fig. 9 Cavity free microstructure of the weld metal of the specimen creep exposed at 650°C/70 MPa/1,186 h

Obr. 9 Mikrostruktura svarového kovu bez kavit po creepové zkoušce po expozici při 650 °C/70 MPa/1186 h

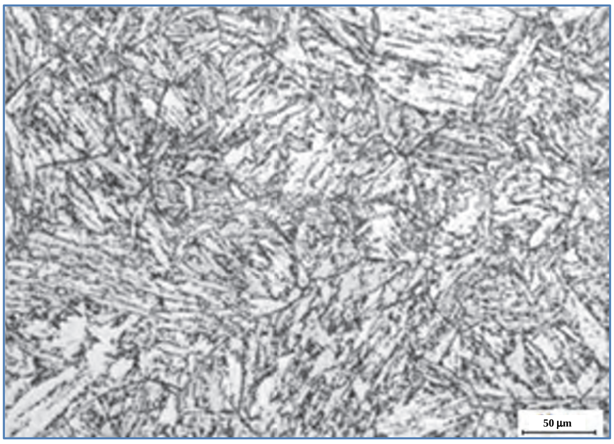

Fig. 10 Cavity free microstructure of the base metal of the specimen creep exposed at 650°C/70 MPa/1,186 h

Obr. 10 Mikrostruktura základního materiálu bez kavit po creepové zkoušce po expozici při 650 °C/70 MPa/1186 h

Microstructural analysis was complemented by microhardness measurements HV 1 across the whole weldment. The hardness profile is shown in Fig. 11 through the individual parts of weldment, as well as with marked location of the failure. It is clear that failure did not occur in the place with the minimum hardness, that is in the base metal, but in HAZ when the hardness fluently dropped down from the fusion line towards the base metal.

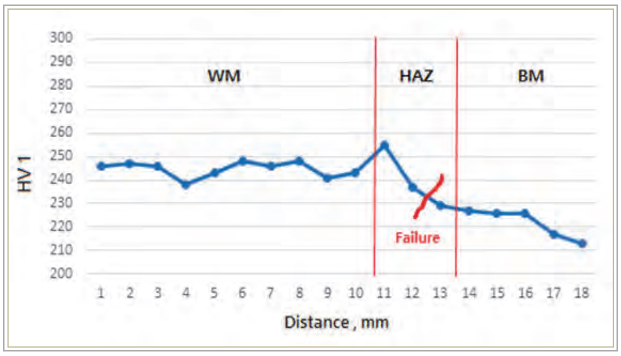

Fig. 11 Hardness profile of creep exposed specimen at 650°C/70 MPa/1,186 h

Obr. 11 Profil mikrotvrdosti HV 1 přes svarový spoj creepové zkoušky po expozici 650 °C/70 MPa/1186 h

Heat affected zone or, more precisely its fine-grained part thus again proved as the weakest part of the welded joints of chromium modified steels.

3. Discussion of results

Although significant improvements in high temperature properties of ferritic steels have been achieved by alloy modification, creep properties of the weld joints have been found to be inferior to those of the base material and the weld metal. This is due to the problem of Type IV cracking, a fracture in the HAZ close to the base metal during high service temperature or during a creep test. The inter-critical HAZ (IC-HAZ) is heated to a maximum temperature between A_{c1} and A_{c3} and the

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ISSN 0018-8069

FG-HAZ is heated to just above A_{c3} [10, 11]. Both these zones have therefore essentially a very fine structure. In both FG-HAZ and IC-HAZ the previous fine austenite grains formed during welding thermal cycle transform, depending on the chemical composition, to martensite/bainite during cooling. In IC-HAZ, not all the ferrite transforms to austenite during heating and hence some ferrite remains untransformed throughout the welding thermal cycle. As the peak temperatures, to which these zones are heated, are not very high and duration of heating is short, many of the precipitates do not dissolve in the austenite matrix, but they rather coarsen. In contrast to this, in the CG-HAZ, the transformations of the matrix and the dissolution of precipitates is almost complete and hence the structure is similar to that of the normalized steel at the end of the welding thermal cycle.

Although Type IV cracking is a well-known problem in ferritic steels, its significance is greater in the newly developed grades, because the difference in the rupture strength of the base metal and the weld joint is higher for these steels than for conventional CrMo steels [12]. Further it is reported that there is a significant evidence to indicate that Type IV cracking in advanced fossil power plants may become a problem of concern at temperatures above the temperature of 565°C [13]. It has been found that in some of the new generation steels, the rupture life for the weld joint can be as low as 20 % of that of the base metal at high temperatures and long rupture times [14].

The best way how to compare the creep rupture strength of the base material and welded joints is to analyse the results of parallel long-term creep tests of both weld joints and base material, i.e. the pipe used for preparation of the welded joint. In this case, the strength reduction factor (SRF) can be expressed in the form:

$$SRF = \frac{R_{mT}(weld)}{R_{mT}(pipe)} = f(t_r, T) \leq 1 \qquad (2)$$

where R_{mT}(weld) and R_{mT}(pipe) are the creep rupture strengths of weldment and of the base material (pipe).

As the stress rupture tests of both welded joint, as well as of the base material were performed simultaneously, it was possible to calculate the SRF factor at least for the temperature of 650°C and 10,000 hours. The calculated SRF is 0.57, which is even less than in the case of the formerly tested and calculated SRF on P 91 (0.70) and P 92 (0.68) steels for 650°C/10^5 h [15, 16].

Conclusions

The results and know-how acquired at the testing of material Nb-free in the frame of CRESTA project are at present exploited for development of a new generation of microstructurally stable very high chromium martensitic steels for components in advanced ultra-super-critical (A-USC) power plants with steam operating temperature in the range of 650 – 700°C that are under development in the follow-up project "New Creep Resistant Stable Steel for USC Power Plant" (CRESTA 2).

Acknowledgement

Authors of the paper thank to for the received funding from the Research Fund for Coal and Steel in the frame of the project RFS-CT-2014-00032 "New Creep Resistant Stable Steel for USC Power Plant" (CRESTA 2).

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