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SECONDARY HARDENING OF LOW-ALLOYED CREEP-RESISTANT STEEL WELDS

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The T24 steel represents the new generation of low-alloyed creep resistant steels with higher creep resistance and lower carbon content. It was designed as prospective material for membrane waterwalls of ultra super critical (USC) power plants, enabling to avoid preheating and post weld heat treatment (PWHT) during welding. However, our investigations concerning secondary hardening of vanadium containing low-alloyed steels show that non-tempered welded joints undergo a significant increase in hardness during exposure to operating temperature. The results then imply that PWHT of T24 steel welds is necessary and this idea is at present supported by the occurrence of several troubles with new installations of USC blocks in Europe.

Key words: T24 steel, 14MoV6-3 steel, Welds, Mechanical Properties, Post Weld Heat Treatment

INTRODUCTION

Construction of high efficiency power plants requires materials with improved high temperature strength, superior oxidation resistance and resistance to high temperature corrosion. With the increase of pressure, not only the final superheater tubes, but all steel tubes including the economizer tubes and membrane waterwall (MWW) tubes, must provide increased high temperature strength and creep resistance [1]. Conventional and world-wide used steels T22 (10CrMo9-10) and T12 (13CrMo4-5) do not have as high creep strength as required for the membrane waterwall tubes of USC boilers. These facts have led to development of new perspective low-alloyed steels for membrane walls - T23 (7CrWVMoNb9-6) and T24 (7CrMoVTiB10-10).

Membrane waterwalls are very large components and the final welding is realized on site where the PWHT is difficult. Moreover, local PWHT made on site can cause additional stresses and deformation of the final component. Therefore, considerable effort is required to produce MWW without post weld heat treatment. Furthermore, PWHT is expensive as well as time consuming. If PWHT is mandatory, also the repair of MWW will be more difficult and costly.

In some research works authors conclude that PWHT of T24 welds is not necessary, nevertheless some recent works have yielded quite different conclusions [2, 3]. The work investigates creep behaviour, hydrogen resistance and temper embrittlement behaviour of T24 steel welds [4]. Within the experimental program, a wide variety of PWHT was performed on many welded joints. The author concluded that proper toughness values of weld metal could not be achieved when a PWHT was omitted. Besides, this T24 weld cannot be used in the "as welded" condition and repair without PWHT is not a realistic option [4].

High creep resistance of steels alloyed with vanadium and titanium is caused predominantly by dispersion of MX fine particles that have significantly higher dimensional stability during long-term heat exposure in comparison e.g. to chromium carbide. On the other hand, the negative effect of dispersion of MX particles is a degradation of plastic properties due to secondary hardening.

EXPERIMENTAL MATERIALS AND PROCEDURES

Mechanical properties and microstructure of 14MoV6-3 and T24 steel welds after different PWHT were investigated in the experimental program. Chemical composition of the parent material is given in Table 1. Experimental welds were performed by manual metal arc welding method (MMAW) and chemical composition of the used electrodes is presented in Table 2.

The PWHT of 14MoV6-3 welds were performed at three temperatures: 650, 680 and 715 °C. In case of steel T24 only a half of welded joints were tempered at 750 °C while the remaining welds were retained in the "as welded" condition. Samples prepared from the welded joints were then aged without stress within the temperature range 450 - 625 °C to simulate the long-term exposure at high temperature. Aging times were calculated by modified Arrhenius formula (1) in order to approximate long times of exposure at real working temperatures.

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Table 1 **Chemical composition of experimental material / *wt* %**

Steel 14MoV6-3 (15128)					
C	Mn	Si	Cr	Mo	V
0,16	0,61	0,29	0,52	0,37	0,24
W	Nb	Ti	N	B	
-	-	0,019	0,005	-	
Steel T24 (7CrMoVTiB10-10)					
C	Mn	Si	Cr	Mo	V
0,059	0,43	0,34	2,43	1,006	0,189
W	Nb	Ti	N	B	
-	-	0,095	0,0094	0,005	

Table 2 **Chemical composition of used welding consumables / wt %**

Electrodes E-B321 (for 14MoV6-3)			
C	Mn	Si	Cr
0,08	0,70	0,30	0,60
Mo	V	W	Nb
0,50	0,30	-	-
Electrodes Thyssen Cromo3V (for T24)			
C	Mn	Si	Cr
0,09	0,60	0,20	3,0
Mo	V	W	Nb
1,0	0,25	-	0,01

$$t_1 = t_2 \cdot \exp\left[\frac{Q}{R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)\right] \qquad (1)$$

where:

t time of exposure /h

T temperature /K

R universal gas constant /J/(mol·K)

t_1 calculated exposure time at working temperature /h

t_2 time of the experimental exposure /h

T_1 calculated working temperature /K

T_2 temperature of the experimental exposure /K

Q activation energy = 292 kJ/mol [5,6,7]

Hardness and impact toughness were subsequently measured on aged weld joints. The results of hardness and impact toughness testing were completed by microstructural analysis of dispersed particles in weld metal (14MoV6-3) and heat affected zone (T24) using a transmission electron microscope (TEM). Image analysis was used to determine parameters of the dispersion phases in the investigated samples.

RESULTS

1 Hardness and impact toughness of 14MoV6-3 weld

The effect of the simulated ageing parameters (temperature and time) on weld metal hardness is illustrated in Figure 1. Significant difference in weld metal hardness can be seen already after PWHT, i.e. prior to the thermal exposure. As can be expected, the higher the temperature of PWHT the lower the resulting hardness.

Hardness of weld metal tempered at 650 °C was approx. 60 HV10 higher than hardness of weld metal tempered at 720 °C, which means an increase by 25 %, and this tendency is kept during almost the whole experiment. Very similar hardness profiles were observed also in the normalization zone and coarse-grained zone of the HAZ [5], see Figure 2.

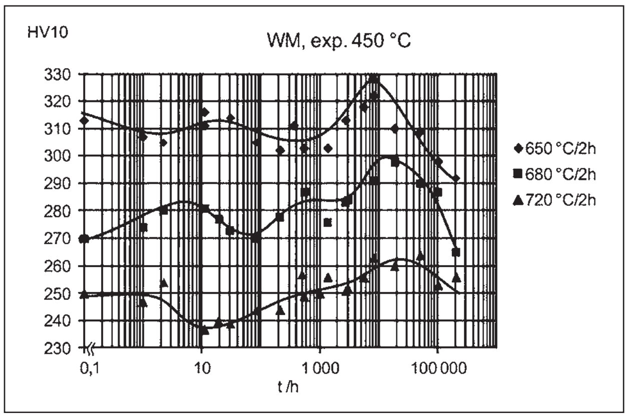

Figure 1 Dependence of weld metal hardness on time and tempering temperature, operating temperature 450 °C

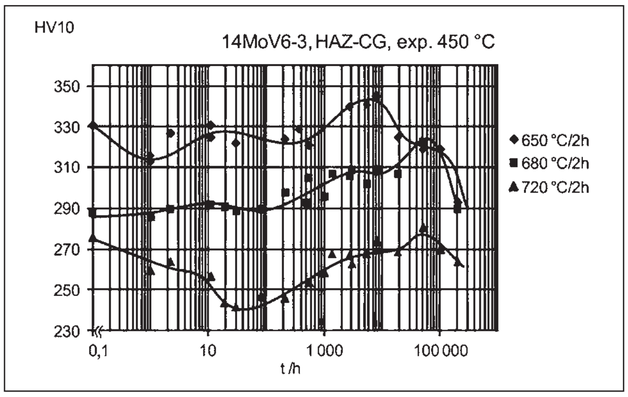

Figure 2 Dependence of CG HAZ hardness on time and tempering temperature, operating temperature 450 °C

In order to complement the results, impact toughness values were determined for the selected samples.

Experimental results show that the impact toughness of weld joints is significantly dependent on the tempering temperature. The greatest difference was seen when the tempering temperature was lowered from 720 °C to 680 °C, see Figure 3.

2 Hardness and impact toughness of T24 weld

The results of hardness and impact toughness of aged welds are presented in Figures 4 - 6. Figure 4 and 5 show hardness curves for the weld metal and coarse-grained part of HAZ in T24 steel during simulated operation at 500 °C.

Figure 6 shows the results of impact toughness measurements. The tempering after welding significantly increases impact toughness in coarse-grained part of the HAZ.

3 Microstructural analysis of dispersed particles

TEM analysis focused especially on the dispersion parameters of secondary particles was performed on the selected samples of both steels. The identification of samples, their aging parameters and the adequate recal-

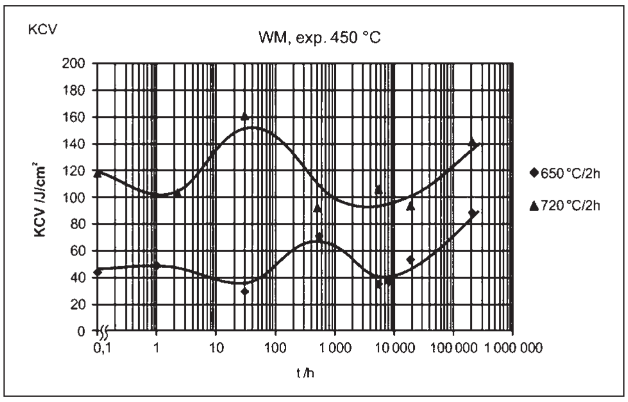

Figure 3 The effect of various temperature of PWHT on impact toughness of weld metal EB 321, operating temp. 450 °C

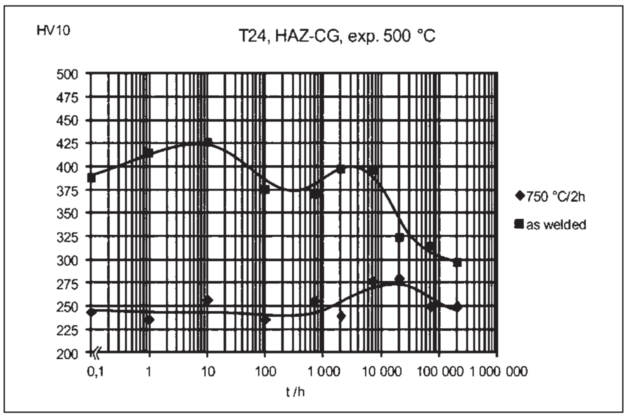

Figure 4 Hardness profile of weld metal in as welded and tempered condition of T24 steel at 500 °C

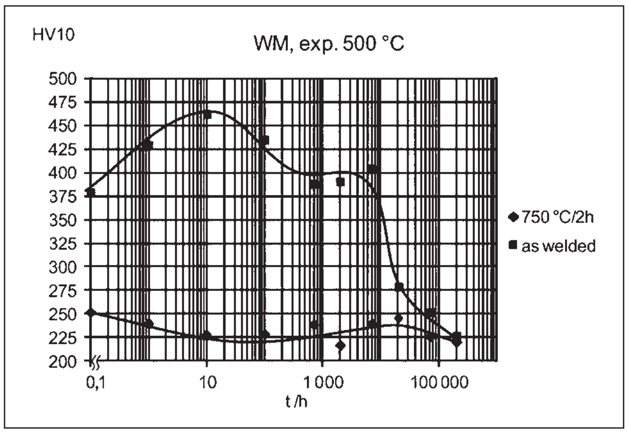

Figure 5 Hardness profile of CG-HAZ of T24 steel in as welded and tempered condition at 500 °C

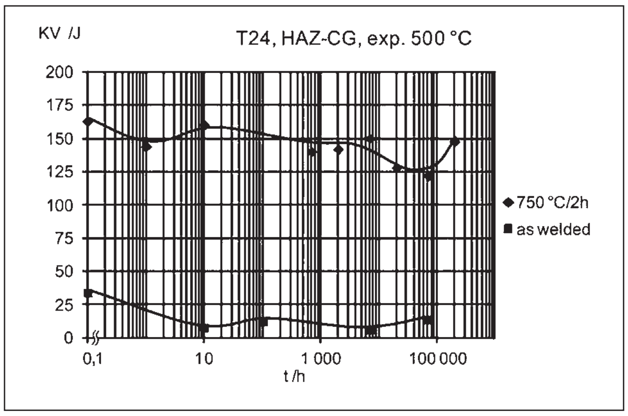

Figure 6 Impact toughness of coarse-grained HAZ of steel T24 in as welded and tempered condition, exposure temp. 500 °C

culated exposure times are summarized in Tables 3 and 4. Sample 1.0 in this table represents the ”as welded” condition, sample 1.1 had maximum hardness after aging, sample 1.20 then showed the “overaged” state, i.e. decrease of hardness.

3.1 14MoV6-3 weld

Calculated results for the equivalent particle diameter d_{ekv}, number of particles per unit volume n_v, and mean interparticle spacing λ are presented in Table 5.

3.2 T24 weld

The microstructural analysis was focused on fine particles MX in coarse-grained zone of HAZ because the dispersion of these particles principally influences both precipitation strengthening and mechanical properties.

The results for the equivalent particle diameter d_{ekv}, number of particles per unit volume n_v, and mean interparticle spacing λ are presented in Table 6.

DISCUSSION

Substructural analysis together with image analysis confirmed that substantial changes in dispersion of the secondary MX phase occurred in the 14MoV6-3 welds during extensive thermal exposure within the sub-creep

Table 3 **Real and recalculated aging parameters of 14MoV6-3 steel weld samples**

Real parameters of experiment			
Sample	PWHT	Temperature (T_2)	Time (t_2)
1.0	2 h / 750 °C	-	-
1.1		550 °C	50 h
1.20		550 °C	547 h
Recalculated parameters			
Sample	PWHT	Temperature (T_1)	Time (t_1)
1.0	2 h / 750 °C	-	-
1.1		450 °C	18 400 h
1.20		450 °C	200 000 h

Table 4 **Real and recalculated aging parameters of T24 steel weld samples**

Real parameters of experiment			
Sample	PWHT	Temperature (T_2)	Time (t_2)
1.1	2 h / 750 °C	-	-
1.2		-	-
1.2.5		550 °C	127 h
1.2.8		625 °C	359 h
Recalculated parameters			
Sample	PWHT	Temperature (T_1)	Time (t_1)
1.1	2 h / 750 °C	-	-
1.2		-	-
1.2.5		500 °C	2 000 h
1.2.8		500 °C	200 000 h

Table 5 **Results of d_{ekv}, n_v and λ calculations, MX particles, 14MoV6-3 weld metal**

Sample No.	Recalculated time at 450 °C / h	d_{ekv} /nm
1.0	-	13,65
1.1	18 400	12,10
1.20	200 000	16,91
Sample No.	n_v /m^{-3}	λ /nm
1.0	$1{,}79595 \cdot 10^{22}$	32,92
1.1	$7{,}08676 \cdot 10^{22}$	13,68
1.20	$1{,}82597 \cdot 10^{22}$	25,46

Table 6 **Results of d_{ekv}, n_v and λ calculations, MX particles, coarse-grained zone of T24 steel**

Sample No.	Recalculated time at 500 °C / h	d_{ekv} /nm
1.1	-	30
1.2	-	-
1.2.5	2 000	20
1.2.8	200 000	26
Sample No.	n_v /nm^{-3}	λ /nm
1.1	$5{,}93 \cdot 10^{-7}$	138
1.2	-	-
1.2.5	$2{,}46 \cdot 10^{-6}$	83
1.2.8	$3{,}12 \cdot 10^{-7}$	219

temperature range. The maximum hardness that evolved during thermal exposure corresponded to the conditions when supplementary precipitation of MX particles occurred. This was indicated by the highest amount of particles per unit volume, the smallest particle size and the smallest mean interparticle spacing. On the other hand, decreasing of hardness is related to the coarsening of secondary phase particles taking place at longer time of exposure (sample 1.20). This is proven by the largest mean particle area, decreasing of number of particles per unit volume and almost doubled mean interparticle spacing. The significant influence of the dispersion phase on mechanical properties of 14MoV6-3 grade steel is confirmed by the fact that dislocation density was constant during ageing [5].

Practically the same was true in case of T24 weldment. The substructural analysis of post weld heat treated and the "as welded" samples showed that MX particles precipitated only in the heat treated condition (sample 1.1) while no MX particles were identified in the „as welded" state (sample 1.2). It implies that fine particles MX were dissolved during welding and not re-precipitated during cooling down cycle after welding. Then, these particles again appeared after post weld heat treatment at 750 °C / 2 h. After exposure to the temperature of 550 °C for 127 hours (sample 1.2.5) precipitation of MX particles was observed again. In comparison to the post-weld heat treated condition, (sample 1.1) particles of MX in this case had lower interparticle spacing, smaller equivalent particle diameter and the number of particles per unit volume was higher, too. It corresponded well to the higher hardness of this sample as a result of secondary hardening.

In general, precipitation of fine MX particles at relatively low temperatures brings about a severe danger of very low plasticity and impact toughness.

CONCLUSIONS

The results presented in this article demonstrated that weld joints of both investigated steels 14MoV6-3 and T24 are subjected to secondary hardening during extensive thermal exposure at elevated temperatures. It was proven by microstructural analysis of MX particles.

This secondary hardening is a common feature of all low-alloyed heat resistant steels containing vanadium including 14MoV6-3 and T24 steels. Results of hardness and impact toughness change during high temperature exposure of T24 welds showed that secondary hardening was present there and therefore it is necessary to apply PWHT, which is in correspondence to [4, 8]. It must be pointed out that such heat treatment must be made regardless to the thickness of the welded material. From the achieved results we can conclude that PWHT of weld joints of 14MoV6-3, and T24 grade steels is necessary especially in terms of obtaining sufficient plasticity and impact properties. For 14MoV6-3 welds the optimum tempering temperature ranges between 715 and 730 °C. For T24 welds tempering temperature of 750 °C can be recommended in order to achieve permissible hardness and safe long-term exposure.

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