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Influence of Post Weld Heat Treatment on Secondary Hardening of CrMoV Welded Joints

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Abstract:

The T23 and T24 steel were designed for welding membrane water walls without preheating and without PWHT. Our investigations concerning secondary hardening of steels containing vanadium show, that non-tempered welded joints undergo a significant increase in hardness during exposure at operating temperature. This process is accompanied by decreasing of impact toughness especially in heat affected zone (HAZ). It follows that Post Weld Heat Treatment (PWHT) of T23 and T24 welds is necessary.

1. Introduction

Construction of high efficiency power plants requires to obtain materials with improved high temperature strength, superior resistance to oxidation 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 water wall (MWW) tubes must provide improved high temperature strength [1]. Conventional world-wide used steel T22 (2,25Cr-1Mo) and 13CrMo4-4 don't have enough creep strength for the use as membrane water walls of ultra super critical boilers. This facts have led to development of new perspective low alloyed steels for membrane walls T23 (HCM2S) and T24 (7CrMoVTiB7-7). Both steels have excellent mechanical properties at high temperatures and improved weldability.

Development philosophy of T23 and T24 steels follows two main objectives. First, it is an increase of creep strength by optimization of the chemical composition. In comparison with conventional steel 10CrMo910 there is a small addition of V, Nb, B and especially W in T23 steel and V, Ti and B in T24 steel. Second, it is enhancement of weldability by reduction of C content below 0,10%.

Membrane water walls (MWW) are very large components, so there is an effort to produce MWW without post weld heat treatment (PWHT). On larger components only local PWHT is possible, which can cause additional stresses and strains in the component. Further more PWHT is expensive. If PWHT is mandatory, also the repair of MWW will be more difficult and costly.

In some research works [2, 3] authors conclude, that PWHT of T23/T24 welds is not necessary, nevertheless some recent works yield quite different conclusions. In the work [4] there was investigated creep behavior, hydrogen resistance and temper embrittlement behaviour of T23 and T24 steel welds. Within the experimental programme a wide variety of PWHT have been performed on many welded joints. Author concludes, that proper toughness

values of weld metal can not be achieved when a PWHT is omitted. P23 and T24 materials can not be used in "as welded condition" and repair without PWHT is not a realistic option [4]. Author asserts, that for obtaining a sufficient toughness is necessary a hardness criterion of max. 300 HV. This can be achieved only with PWHT.

The experimental part of the work [5] was focused on welding of piping made from steel P23 with several regimes of PWHT. Impact toughness and hardness testing of HAZ was performed. On the basis of achieved results authors recommend to apply PWHT in the range of 730 – 750 °C with holding time at least 60 minutes [5].

2. Hardening Mechanism of Modern Low-Alloy Steels

High creep resistance of steels alloyed with vanadium, or titanium and niobium is caused predominantly by dispersion of MX fine particles which have a significantly increased dimensional stability during extensive heat exposure in comparison to chromium carbide. On the other hand the major effect of dispersion of MX particles is a degradation of plastic properties due to secondary hardening.

Even after typical heat treatment of the steel, which comprises normalisation and subsequent tempering, the structure of these steels is not absolutely in equilibrium. During subsequent extensive exposure at operating temperature, which is lower than the tempering temperature, partial precipitation of MX particles occurs as a result of solid solution saturation.

This process is most significant in weld joints, where due to the welding process the degree of dissolution of dispersed particles varies. Subsequently, the correct tempering temperature may not be achieved, which causes imperfect precipitation of MX particles in weld metal and in the heat affected zone (HAZ). The microstructure of the weld without proper PWHT is not in equilibrium state which leads to the secondary hardening during subsequent exposure at high temperatures. Therefore, proper post weld heat treatment (PWHT) of CrMoV welds is quite necessary.

3. Experimental Material and Procedures

Mechanical properties and microstructure of 14MoV6-3, T23 and T24 steel welds depending on PWHT were investigated in the experimental program. Chemical composition of experimental parent material is given in table 1. Experimental welds were performed by manual metal arc welding (MMAW). Chemical composition of used welding materials is presented in table 2.

Table 1: Chemical composition of experimental material in wt%

Steel	**C**	**Mn**	**Si**	**Cr**	**Mo**	**V**	**W**	**Nb**	**Ti**	**N**	**B**
14MoV6-3	0.16	0.61	0.29	0.52	0.37	0.24	-	-	0,019	0,005	-
T23	0.062	0.42	0.33	2.30	0.214	0.284	1.55	0.060	-	0.026	0.0042
T24	0.059	0.43	0.34	2.43	1.006	0.189	-	-	0.095	0.0094	0.0055

Table 2: Chemical composition of used welding materials in wt %

Consumables	**C**	**Mn**	**Si**	**Cr**	**Mo**	**V**	**W**	**Nb**
E-B321 (ESAB)	0.08	0.70	0.30	0.60	0.50	0.30	-	-
Thyssen Cr2WV (T23)	0.05	0.50	0.20	2.35	0.06	0.25	1.70	0.05
Thyssen Cromo3V (T24)	0.09	0.60	0.20	3.00	1.0	0.25	-	0.01

The Post weld heat treatment (PWHT) of 14MoV6-3 welds were performed at three temperatures: 650, 680 and 715 °C. In case of T23 and T24 one half of weld joints were tempered at 750 °C. The second half of welds were retained in “as welded” condition. Samples were aged without stress in temperature range 450-625 °C. Hardness and impact toughness have been subsequently measured on aged weld joints. Times of exposure were recalculated into working temperatures 450°C (14MoV6-3) and 550°C (T23, T24) using Arrhenius formula:

$$t = A_0 \cdot \exp\left[\frac{Q}{RT}\right] \qquad (1)$$

Final formula:

$$t_1 = t_2 \cdot \exp\left[\frac{Q(T_2 - T_1)}{R T_1 T_2}\right] \qquad (2)$$

Activation energy Q=292 kJ/mol [6, 7].

Measurement results of hardness and impact toughness were supported by a microstructral analysis of dispersed particles in heat affected zone (HAZ) of steels 14MoV6-3 and T24 using a transmission electron microscope (TEM). Image analysis was used to determine parameters of the dispersion phases in investigated samples.

14MoV6-3 steel

Three samples, marked 1.0, 1.1 and 1.20, were selected. Sample 1.0 represents the ”as welded” condition, sample 1.1 represents maximum of hardness after exposure, sample 1.20 represents a decrease of hardness. Real and extrapolated duration of TEM samples of 14MoV6-3 shows table 3.

T24 steel

Four samples, marked 1.1, 1.2, 1.2.5 and 1.2.8, were selected. Sample 1.2 represents the ”as welded” condition, sample 1.1 was post weld heat treated (2 hrs at 750 °C). Sample 1.2.5 represents condition without PWHT and after exposure of 127 hrs at 550°C. Sample 1.2.8 represents a condition without PWHT and after exposure of 359 hrs at 625 °C, see table 4.

Table 3: Heat treatment and heat exposure of samples of 14MoV6-3 welds for TEM

sample	PWHT	Simulated heat exposure at working temperature - ageing	
		Real experimental time and temperature (t2/T2)	Recalculation for 450 °C, using Arrhenius Formula, Q =292 kJ/mol (t1/T1)
1.0	2 h/750°C	-	-
1.1	-	50 h /550°C	18 400 h/450 °C
1.20	-	547 h/550 °C	200 000 h/450 °C

Table 4: Heat treatment and heat exposure of samples of T24 welds for TEM

sample	PWHT	Simulated heat exposure at working temperature - ageing	
		Real experimental time and temperature (t2/T2)	Recalculation for 550 °C, using Arrhenius Formula, Q =292 kJ/mol (t1/T1)
1.1	2 h/750°C	-	-
1.2	-	-	-
1.2.5	-	127 h /550 °C	127 h /550 °C
1.2.8	-	359 h/625 °C	12700 h /550 °C

4. Results

4.1. Hardness and impact toughness of 14MoV6-3

The affect of the PWHT temperature on weld metal hardness is illustrated in Fig. 1. Hardness of weld metal tempered at 650°C, lies during ageing approx. 60HV10 higher than weld metal tempered at 715°C, which means an increase in hardness by 25% average. Significant differences in weld metal hardness of weld joints can be seen in the initial condition, i.e. prior to extensive thermal exposure. Very similar curve profiles were obtained for the normalization zone and overheated zone of the HAZ [6].

Impact toughness values were determined for selected samples. A curve made from these values has its minimum in the maximum of hardness and in the area of minimum hardness impact toughness has an increasing trend, see Fig. 2.

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 715°C to 680°C, see Fig. 3.

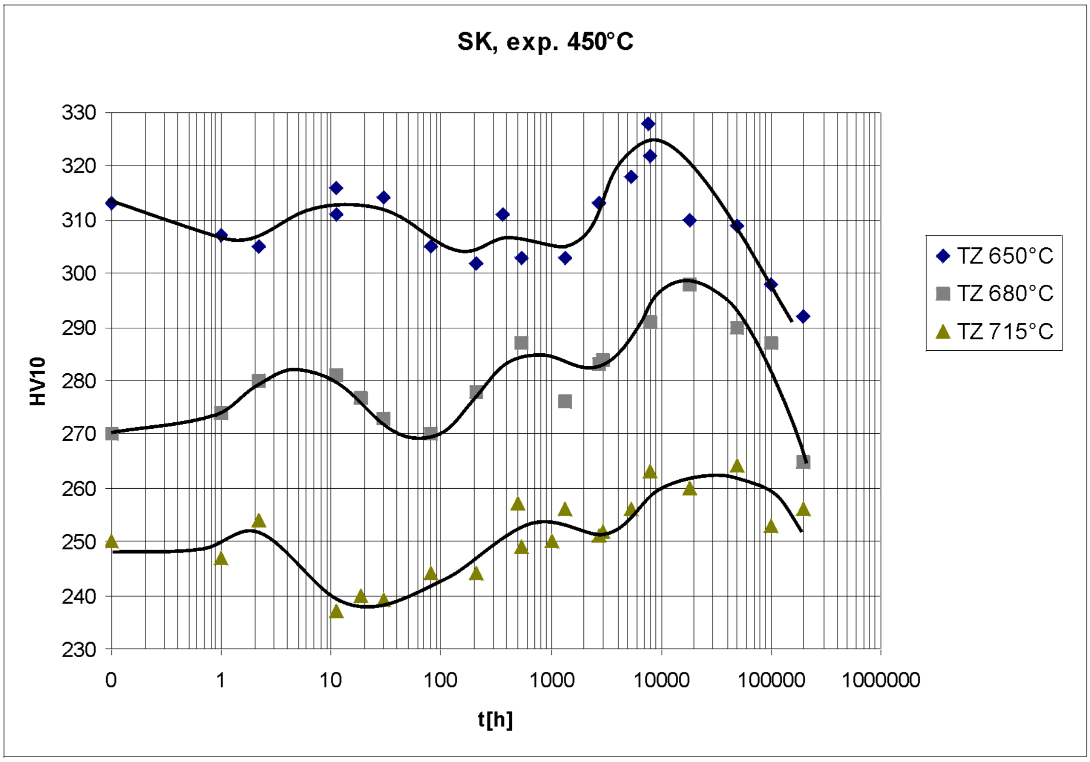

Fig. 1: Comparison of hardness profiles in the weld metal in dependence on tempering temperature, operating temperature 450°C

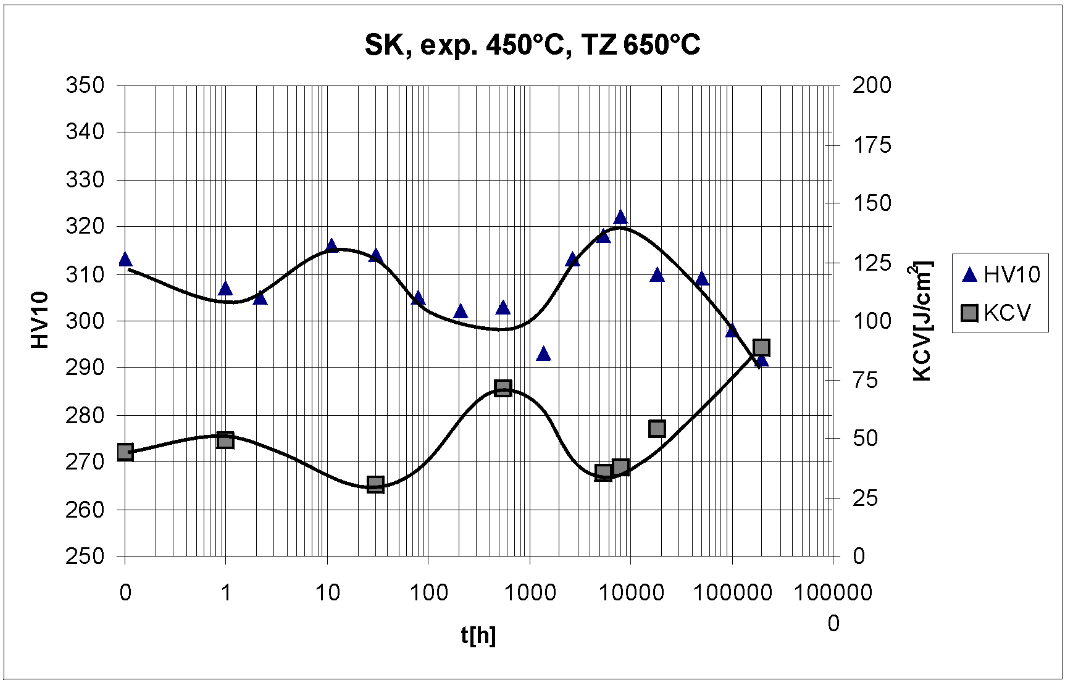

Fig. 2: Comparison of Hardness and impact toughness of the weld metal at operating temperature 450°C, PWHT 650°C/2h

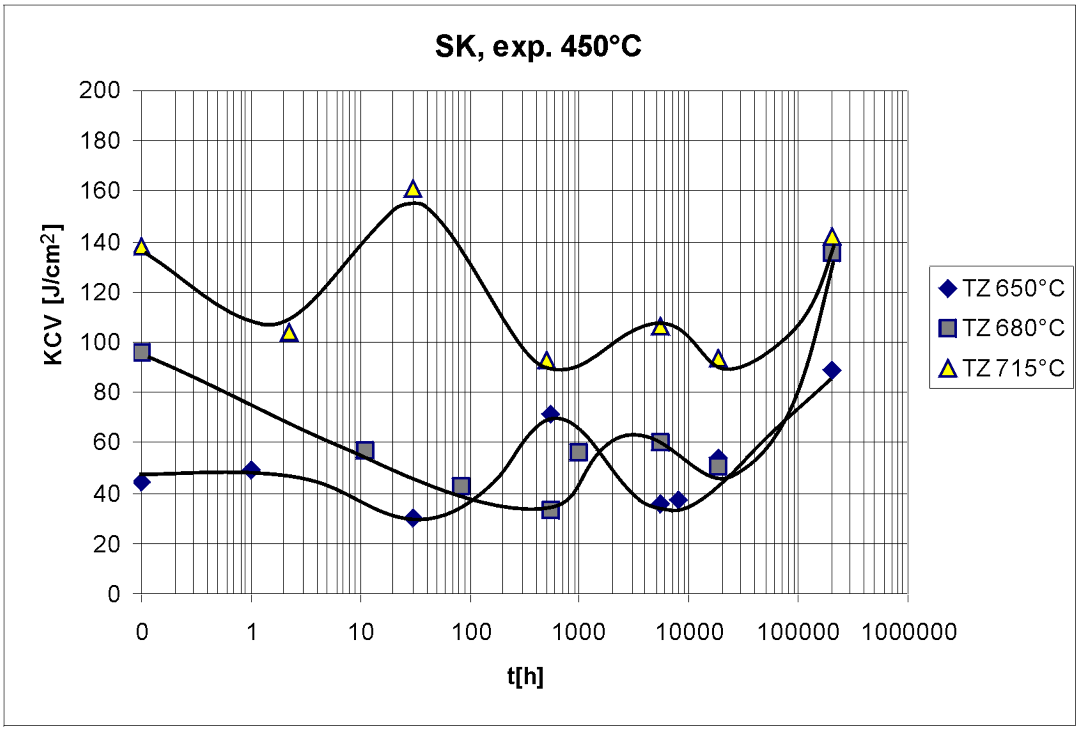

Fig. 3: Comparison of weld metal (EB 321) impact toughness profiles in dependence on tempering temperature, operating temperature 450°C

4.2. Microstructural analysis of dispersed particles of 14MoV6-3 weld

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

The mean inter-particle spacing was calculated according to Ashby [8]:

$$\lambda = 0{,}69 \cdot \left(n_v \cdot d_{ekv}\right)^{-1/2} - \sqrt{\frac{2}{3}} \cdot d_{ekv} \qquad (3)$$

where:

d_{ekv}…………………. equivalent particle diameter [nm]

λ …………………….mean inter-particle spacing [nm]

n_v ………………….. number of particles per unit volume

Table 5: Calculated results for d_{ekv} n_s, n_v , λ of 14MoV6-3 weld metal

Sample No.	A_X [nm^2]	d_{ekv} [nm]	n_s [m^{-2}]	n_v [m^{-3}]	λ [nm]
1.0.	168,24	13,65	$2{,}13037.10^{14}$	$1{,}79595.10^{22}$	32,92
1.1.	124,01	12,10	$7{,}96117.10^{14}$	$7{,}08676.10^{22}$	13,68
1.20.	246,10	16,91	$2{,}81644.10^{14}$	$1{,}82597.10^{22}$	25,46

4.3. Hardness and impact toughness of T23 and T24

Results of hardness and impact toughness of aged welds are presented in figures 4-7. Fig. 4 and 5 show hardness curves for the overheating zone of HAZ in T23 and T24 steel during simulated operation at 550 °C.

Figures 6 and 7 give results of impact toughness measurements. The effect of tempering after welding on impact toughness of the HAZ in T24 steel is depicted in Fig. 6. This figure shows a significant difference between the impact toughness of tempered and non-tempered weld joints of T24 steel.

Figure 7 shows a comparison of hardness and impact toughness profiles in overheated zone of the steel T23 at operating temperature 550 °C. The toughness curve has its minimum where hardness has the maximum and a rising trend of toughness corresponds to area of hardness decreasing. This trend is similar to 14MoV6-3 steel, see fig. 2.

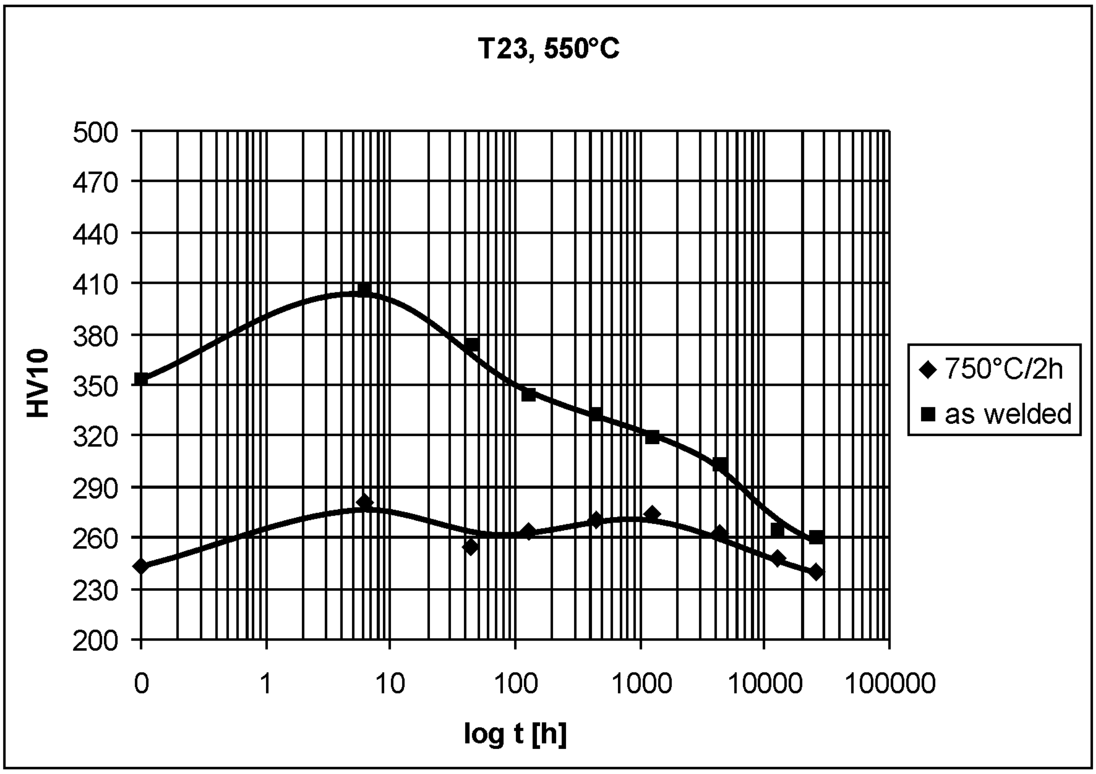

Figure 4: Hardness profiles in the HAZ - overheated zone of T23 steel, temperature of exposure 550 °C

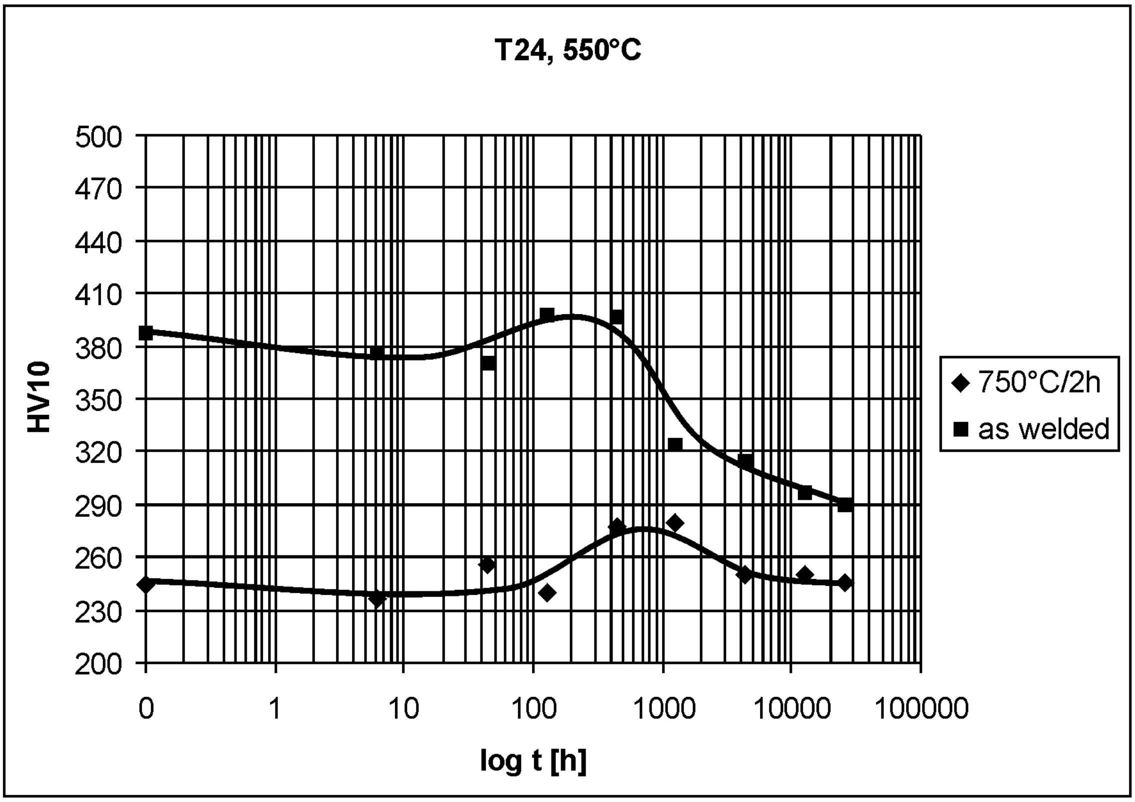

Figure 5: Hardness profiles of HAZ - overheated zone of T24 steel, temperature of exposure 550 °C

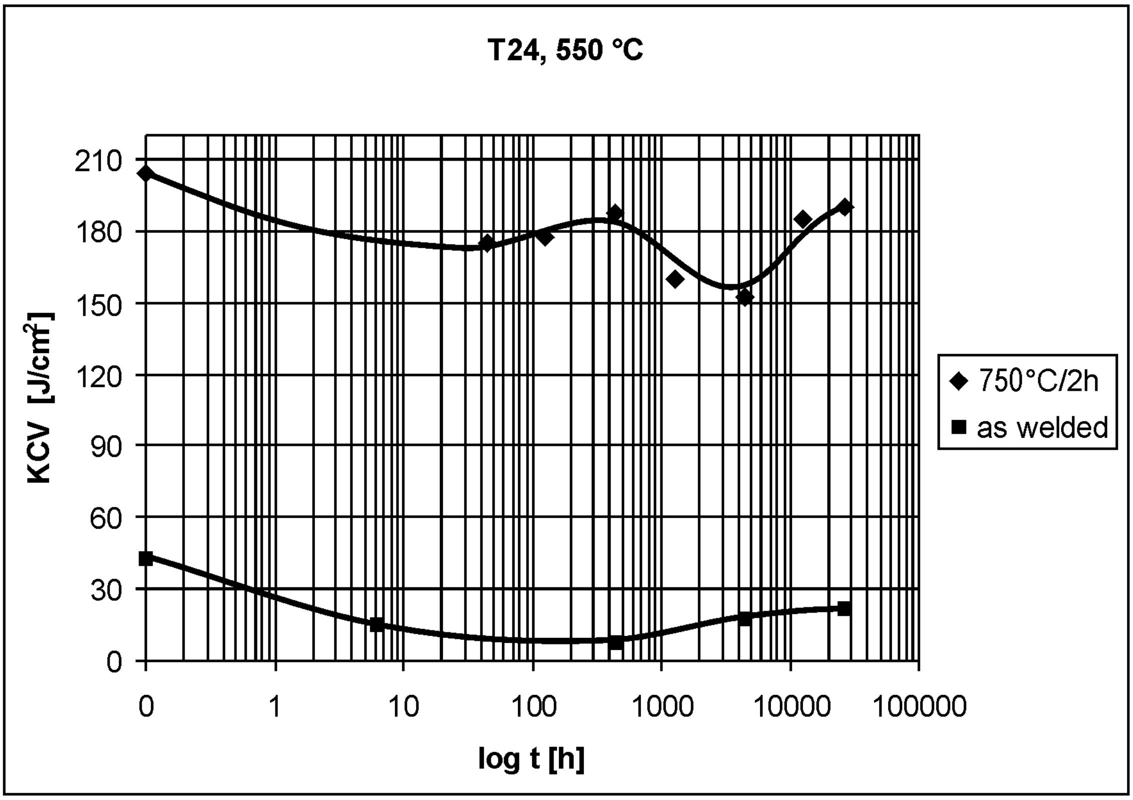

Figure 6: Impact toughness profiles of HAZ - overheated zone of T24 steel, temperature of exposure 550 °C

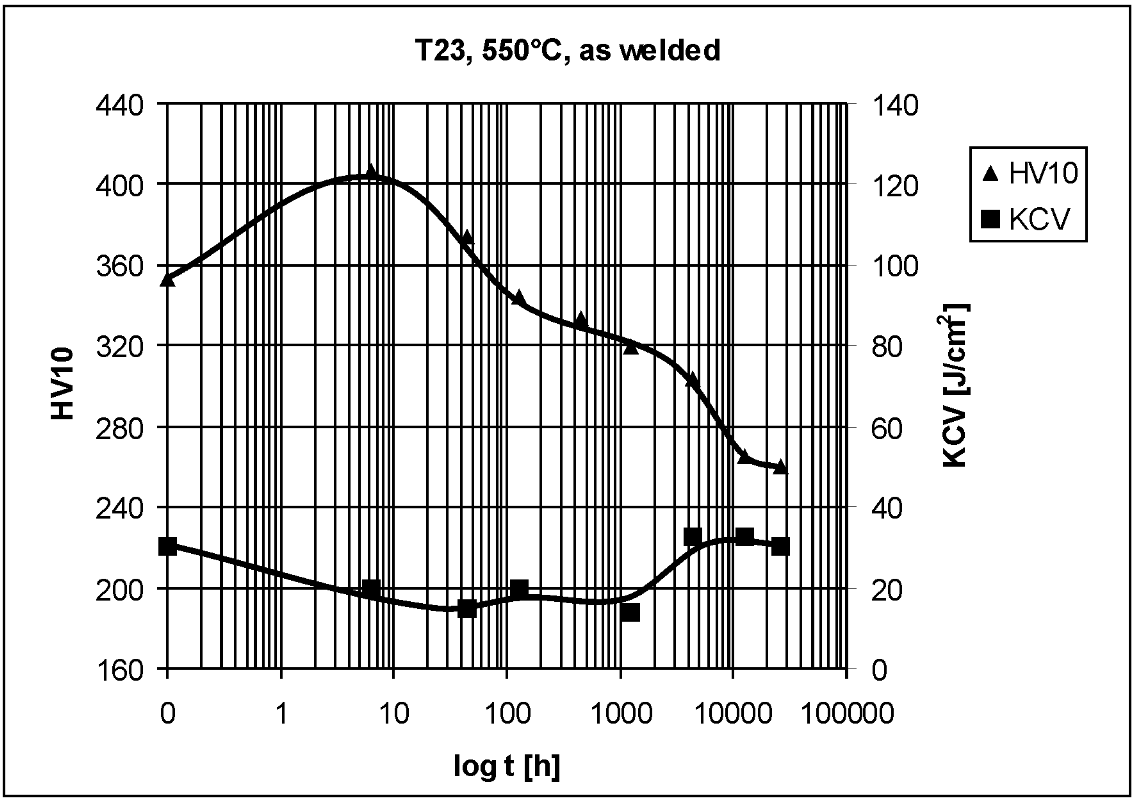

Figure 7: Comparison of hardness and impact toughness of HAZ - overheated zone of steel T23, temperature of exposure 550 °C, as welded condition

4.4. Microstructural analysis of dispersed particles of T24 weld

Microstuctural analysis was focused on fine particles MX in overheated zone of HAZ because the dispersion of these particles mainly influences both precipitation strengthening and mechanical properties.

Results for the equivalent particle diameter d_{ekv}, number of particles per unit area n_s, number of particles per unit volume n_v, and mean inter-particle spacing λ are presented in Table 6. The mean inter-particle spacing was calculated according to Ashby [8].

Table 6: Results of d_{ekv} n_s, n_v and λ calculations, MX particles

sample	A_x [nm2]	d_{ekv} [nm]	n_s [nm-2]	n_v [nm-3]	λ [nm]
1.1	743	30	1.72 . 10-5	5.93 . 10-7	138
1.2	-	-	-	-	-
1.2.5	326	20	4.59.10-5	2.46.10-6	83
1.2.8	560	26	7.94.10-6	3.12.10-7	219

5. Discussion

14MoV6-3 welds

Electron microstructural analysis together with image analysis confirmed that during extensive thermal exposure in the sub-creep range, changes in dispersion phase of the 14MoV6-3 welds occur. The maximum hardness during thermal exposure corresponds to the area of supplementary precipitation of MX particles (sample 1.1). This is indicated by the highest amount of particles per unit volume, smallest particle size and smallest mean inter-particle spacing. On the other side, decreasing of hardness is related to growing of secondary phase (sample 1.20). Proof of this is the largest mean particle area, decrease of number of particles per unit volume and almost a double increase in the mean inter-particle spacing with respect to the supplementary precipitation area. The significant influence of the dispersion phase on mechanical properties of 14MoV6-3 grade steel is confirmed by the fact that dislocation density was practically constant during ageing [6].

T24 welds

Comparison of post weld heat treated (1.1) and „as welded“ (1.2) samples show that MX particles were identified only in heat treated condition (sample 1.1). In „as welded“ condition MX particles were not identified (sample 1.2). It implies that fine particles MX were dissolved during welding (1.2) and post weld heat treatment at 750 °C/2 h induced precipitation of MX particles (1.1).

The precipitation of MX particles was observed after heat exposure 127 hours at 550°C (sample 1.2.5). In comparison with regularly heat treated sample (1.1) particles MX have lower inter-particle spacing, lower equivalent particle diameter and the number of particles per unit volume is higher. It corresponds with higher hardness of sample 1.2.5. In this sample took place secondary hardening.

Dispersion of MX particles in sample 1.2.8 represents growing of these secondary phase. In comparison with sample 1.2.5 inter-particle spacing and equivalent particle diameter increases and the number of particles per unit volume decreases. It corresponds with lower hardness of sample 1.2.8.

6. Conclusions

Results presented in this article demonstrate that weld joints of low-alloy creep-resistant steels hardened by dispersed MX particles are subject to a process of secondary hardening during extensive thermal exposure at elevated temperatures. It was proved by microstructural analysis of MX particles. This secondary hardening is common for all steels containing vanadium including T23 and T24 steel. Results of harness and impact toughness during high temperature exposure of T23 and T24 show, that secondary hardening is present here and omission of PWHT is non realistic, which is corresponding with [4].

The extent of this hardening depends on the temperature and duration of tempering after welding. Weld joint brittleness also depends on the operating temperature of the welded unit. In 14MoV6-3 grade steel brittleness is seen at temperatures under 500 °C, for T23 and T24 grade steels we can expect brittleness at even lower temperatures.

From the achieved results we can conclude that PWHT of weld joints of 14MoV6-3, T23 and T24 grade steels is necessary especially in terms of obtaining sufficient plastic properties. For 14MoV6-3 welds the optimal tempering temperature is between 715 and 730 °C. For T23 and T24 welds can be recommended tempering temperature 750 °C in order to achieve permissible hardness and sufficient durability.

References

[1] TOHYAMA, A., MINAMI, Y. Development of 2Cr-Mo-W-Ti-V-B Ferritic Steel for Ultra Duper Critical Boilers, In: *Proceedings of COST Programe part I: Materials for Advanced Power Engineering 1998,* Vol. 5, ISBN: 3-89336-228-2

[2] KARLSSON, A., RASMUSSEN, F., MONTGOMERY, M. On-Plant Test of TÜV HCM12 and ASME T23 Alloys for Use as Water Wall Materials.Key Engineering Materials Vols. 171 – 174 (2000), 2000 Trans Tech Publications, Switzerland, p. 169 – 178

[3] The T23/T24 Book. New Grades for Waterwals and Superheaters. Vallourec & Manesmann, 2001

[4] WORTEL, H. P23 and P24 Power Generation and Hydrogen Service – Challenges and Limitations. In. 27. Vortragsveranstaltung, 26.11. 2004, Düsseldorf, Stahlinstitut VDEh, 2004, p. 21 - 31

[5] PECHA, J. MEŠKO, J. Weldability of New Creep Resistant Cr-Mo Steel with Tungsten Content. Materials Engineering, Vol. 13, 2006, No. 2, p. 9-14

[6] MOHYLA, P. Changes of mechanical properties of CrMoV steel welds during long term heat exposure in sub-creep range, Ph.D. thesis, VŠB – TU Ostrava, 2001

[7] SELLARS, C.M. Proceedings *Creep strength in Steel and High Temperature Alloys*, ISI Meeting 20-22, September 1972, Sheffield

[8] ASHBY, M.F. Physics of Strength and Plasticity, *A.S. Argon*, MIT Press, 1969, p. 113