

Andrzej Gruszczyk, Mirosława Pawlyta

Primary Reasons for the Brittleness of Welded Joints in Steel T/P24

Abstract: The article presents results of tests concerning the susceptibility of welds made of steel T/P24 (7CrMoVTiB10-10) to secondary hardness as well as the structure and the mechanical properties of the welds (KV, Rm, A₅, Z and HV₁) in the as-made state and after heat treatment performed at temperature restricted within the range of 100°C to 750°C. The tests revealed that the welding process triggered the decomposition of phases hardening steel 7CrMoVTiB10-10 and the transition of alloying components and impurities to the solution of body-centred cubic lattice A₂ (bcc). A thesis formulated by the Authors in relation to the test results stated that the primary reason for the deterioration of the plastic properties of the welds was the phenomenon of solid solution hardening. The Authors emphasized the necessity of performing the detailed analysis of interactions of substitution atoms and other defects of the Fe_a lattice with interstitial atoms. In addition, the Authors indicated the necessity of changing the criteria applied when assessing the weldability of technologically advanced steels as well as pointed mistakes made during the industrial implementation of steel 7CrMoVTiB10-10.

Keywords: steel T/P24, crystal lattice A₂, supersaturation, solid solution hardening, metastability, secondary hardness

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Introduction

Attempts at increasing the efficiency of power generation systems combined with the simultaneous reduction of their manufacturing costs resulted in the development of new low-alloy steel T/P24 (7CrMoVTiB10-10). Providing traditional steel grades T/P22 (type 2.25Cr-1Mo) with slight additions of vanadium, titanium and boron combined with appropriately adjusted heat treatment parameters increased the

precipitation hardening effect through stable MX type precipitates of appropriate dispersion. As a result, the creep resistance of the steel is similar to that of high-alloy martensitic steels. Another important feature of the steel is its low carbon content restricted within the range of 0.05% to 0.1%. Under the conditions of continuous cooling from the austenite range and depending on the rate of cooling, the steel structure becomes martensitic, martensitic-bainitic

dr hab. inż. Andrzej Gruszczyk (PhD (DSc) Habilitated Eng.), retired Professor of Silesian University of Technology; dr hab. inż. Mirosława Pawlyta (PhD (DSc) Habilitated Eng.), Professor at Silesian University of Technology

or bainitic. Because of the low content of carbon, the hardness of martensite is restricted within the range of 350 HV to 360 HV. The optimum heat treatment conditions involving hardening with cooling in water and tempering at a temperature of 750°C provide steel P24 with low nil ductility transition temperature (NDT) and high creep resistance [1–4].

A traditional approach to the assessment of weldability (based on such commonly used criteria as the carbon content and the maximum hardness of the welded joint) ranks steel T/P24 among materials characterised by high weldability. The fact that steel T/P24 is recognised as characterised by favourable weldability resulted in the development of related technological guidelines allowing the elimination of the preheating and the post-weld heat treatment (PWHT) of welded structures characterised by rather low wall thicknesses, e.g. membrane walls [1, 2]. However, industrial practice has not confirmed the above-named optimistic assumptions. Tests revealed that welded joints made in steel T/P24 contained cracks usually present in the welds and in the high-temperature area of the heat affected zone (HAZ). The presence and the development of the cracks were observed during welding, with the passage of time, in transit, during the storage and the assembly of structures as well as during the start-up and operation of boilers. In most cases, the above-named imperfections were observed in structures not subjected to post-weld heat treatment.

Views on reasons for the formation of cracks in welded joints made in the steel vary. Available test results imply that cracks present in welded joints are cold cracks (the development of which is triggered by the presence of hardened structures and hydrogen [5, 6, 18]), hot cracks or cracks initiated by hot cracks [6, 7], stress relief-induced cracks [6, 8] and stress corrosion-induced cracks [8, 9]. Other important causes could include secondary hardness [10] and the presence of notches in welded joints

of boiler waterwalls (with incomplete penetration of the flat bar) or gaps in welders' training [5, 11]. The above-presented problems were not observed in welded structure made steel T/P22 (2,25%Cr-1%Mo) not containing vanadium, titanium and boron additions.

The unfavourable effect of alloying microagents on the plastic properties of welded joints was widely tested and discussed in the early 1970s as the then issue was the industrial implementation of high-strength micro-alloyed steels containing niobium, vanadium and titanium. The principal conclusion resulting from those tests was that the reason for the worsening of the plastic properties of welds containing significant contents of microagents was the precipitation of fine-dispersive carbides or carbonitrides of alloying microconstituents in welds. The plastic properties were improved by limiting contents of microagents in welds. The contents of niobium and vanadium were reduced in steels, the transfer of microagents from the welded material to the weld was limited by reducing welding linear energy. In addition, it was recommended that welding processes be performed using filler metals without microalloy agents [12, 13].

To provide welded joints of technologically advanced creep-resistant steels with appropriate operating parameters, such steels are welded using filler metals containing microagents. Usually, the number and amounts of the microagents correspond to the chemical composition of a given steel grade subjected to welding. Exceptions include filler metals used for the welding of steel T/P24, where titanium (because of its high susceptibility to oxidation) is replaced with niobium [14, 15]. Vanadium and niobium additives improve the high-temperature resistance primarily through MX type phase-based hardening, yet increased contents of vanadium and niobium in welds and steels reduce the plastic properties of the latter [15, 16]. Publication [17] states that static tensile tests revealed significant differences in the mechanical and

plastic properties of welds, pipes and flat bars of membrane walls made of steel T24. Mean Rm values of welds made using submerged arc were by approximately 47% higher than the strength of the pipe and the flat bar. In turn, the impact energy of weld deposits made using submerged arc and not subjected to heat treatment amounted to approximately 10 J.

Individual tests

The tests discussed in the article involved submerged arc butt welded joints (SAW) made in 6 mm thick plates made of steel 7CrMoVTiB10-10 as well as overlay welds made on the same steel using submerged arc and covered electrodes (MMAW process). The chemical composition of steel 7CrMoVTiB10-10 is presented in Table 1, whereas the chemical composition of a UNION S P24 filler metal wire (used in SAW processes) and of the weld deposit of THERMANIT P24 covered electrodes are presented in Table 2.

The susceptibility of welded joints made in steel 7CrMoVTiB10-10 to secondary hardness was assessed by performing surfacing tests. The tests involved overlay welds made on a 6 mm thick plate using the submerged arc welding

method (SAW) and covered electrodes (MMA process). The chemical composition of the plate material is presented in Table 1. The SAW process was performed using the UNION S P24 filler metal wire having a diameter of 2 mm (Table 2) and Böhler UV 305 flux. The manual surfacing process was performed using Thermanit P24 covered electrodes having a diameter of 3.2 mm. The surfacing process (not preceded by preheating) was performed using various values of linear energy. After surfacing the specimens were subjected for 45 minutes or 30 minutes to tempering performed at temperature restricted within the range of 100°C to 700°C (using an increment of 100°C) and at a temperature of 750°C. The mean values of five HV1 hardness measurements performed immediately after surfacing and heat treatment and concerning the cross-section of the overlay welds are presented in Figures 1–2.

Mechanical tests involved the welds of butt welded joints made in the 6 mm thick plate, the chemical composition of which is presented in Table 1. The joints were made in one run using the SAW method and a ceramic backing strip (without preheating). The welding process was performed using the UNION S P24 filler

Table 1. Chemical composition of steel 7CrMoVTiB10-10

Steel grade	Contents of alloying components [%]											
	C	Si	Mn	P	S	Cr	Mo	V	Ti	Al	N	B
7CrMoV	0.08	0.25	0.52	0.008	0.002	2.44	1.00	0.264	0.070	0.011	0.0085	0.0053
Composition in accordance with ASTM A 213	0.05	0.15	0.30	max.	max.	2.2	0.90	0.20	0.05	max.	max.	0.0015
	0.10	0.45	0.70	0.02	0.01	2.6	1.10	0.30	0.10	0.02	0.012	0.0070

Table 2. Chemical composition of the filler metals used for the welding and surfacing of steel 7CrMoVTiB10-10

Filler metal	Contents of chemical elements [%]											
	C	Si	Mn	P	S	Cr	Mo	V	Ti	Cu	Nb	B
Filler metal wire UNION S P24	0.10	0.19	0.57	0.005	0.003	2.52	0.93	0.219	0.002	0.01	0.053	0.0002
Weld deposit of electrode Thermanit P24	0.09	0.27	0.51	0.013	0.007	2.50	0.98	0.22	0.004	0.02	0.046	0.005

metal wire having a diameter of 2 mm (Table 2) and the Böhler UV 305 flux. The welding linear energy amounted to 12 kJ/cm. After welding, the joints (for 30 minutes) were subjected to heat treatment at a temperature of 300°C,

500°C, 600°C, 700°C and 750°C. Afterwards, the joints were subjected to static tensile tests (cylindrical specimen; Ø 5) as well as measurements of the toughness and the hardness of the welds in the as-made (as-welded) state and after heat treatment performed for a hold time of 30 minutes. The averaged results of the KV, HV₁, R_m, A₅ and Z tests are presented in Figures 3–6.

The structural tests of the welds, overlay welds and of the penetrated (melted) areas of steel 7CrMoVTiB10-10 (Table 1) involved the use light microscope, a scanning electron microscope and an S/TEM TITAN high-resolution transmission electron microscope (FEI). Typical structures and important observation results are presented in Figures 7–11.

The tests concerning the effect of tempering temperature on the hardness of overlay welds revealed their significant susceptibility to secondary hardness, regardless of the surfacing method and linear energy (Fig. 1 and 2). In the as-surfaced state, the overlay welds made using submerged arc were characterised by relatively low hardness (approximately 300 HV₁), to a little extent dependent on the surfacing linear energy applied in the process. The maximum hardness of the overlay welds was obtained after holding at a temperature of 600°C. In comparison with that of the as-surfaced state, the hardness of the overlay welds increased

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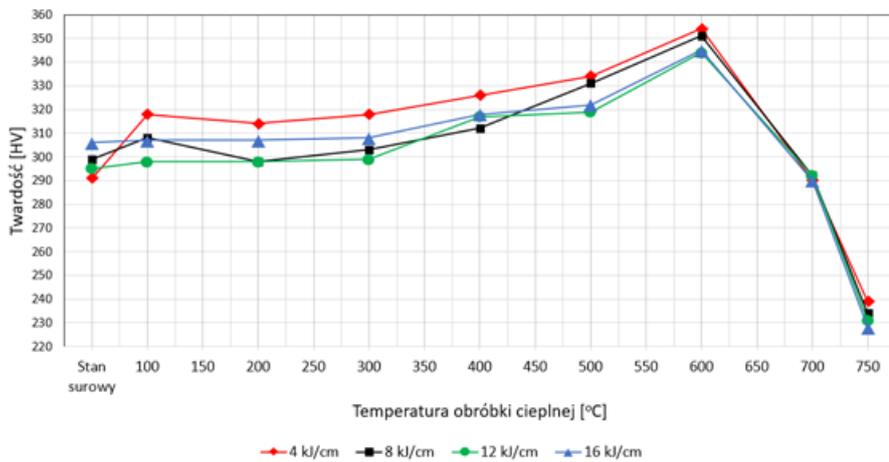


Fig. 1. Hardness of the overlay welds made using submerged arc (SAW); the as-surfaced state and the state after heat treatment, hold time at tempering temperature: 45 min

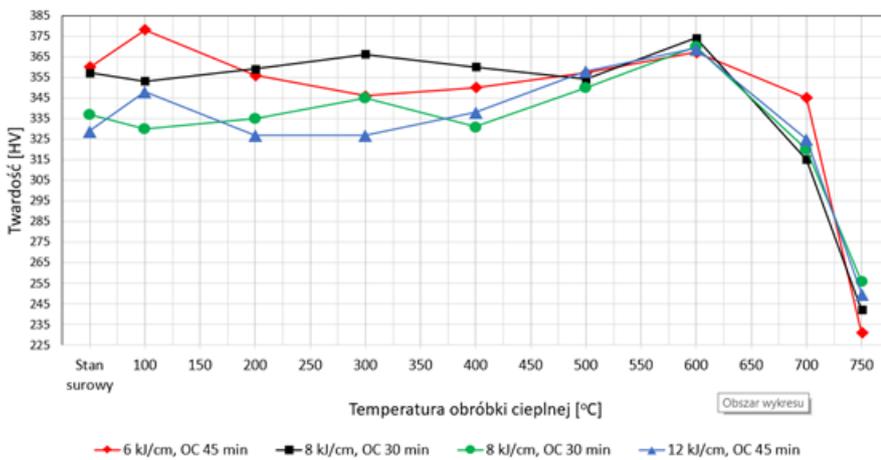


Fig. 2. Hardness of the overlay welds made using the covered electrodes (MMAW); the as-surfaced state and the state after heat treatment, hold time at tempering temperature: 45 min or 30 min

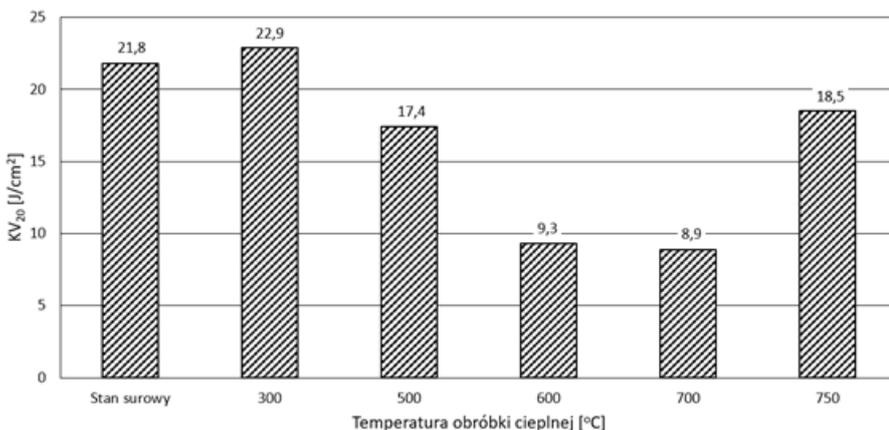


Fig. 3. Toughness (KV) of the welds made using submerged arc, the as-welded state and the state after heat treatment

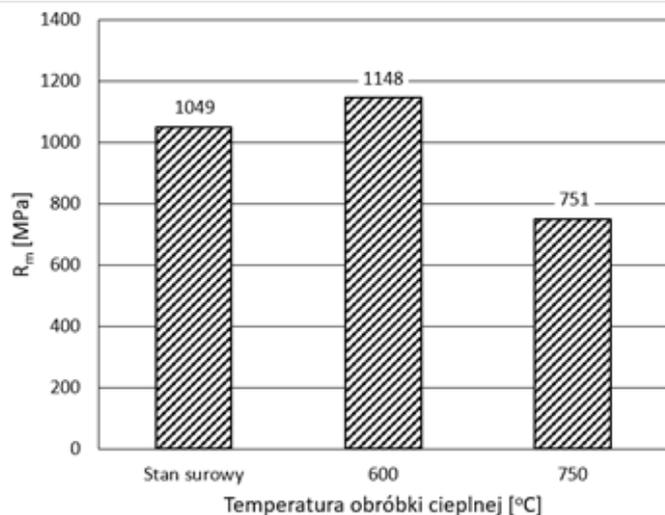


Fig. 4. Strength R_m of the welds made using submerged arc; the as-welded state and the state after heat treatment performed at a temperature of 600°C and 750°C

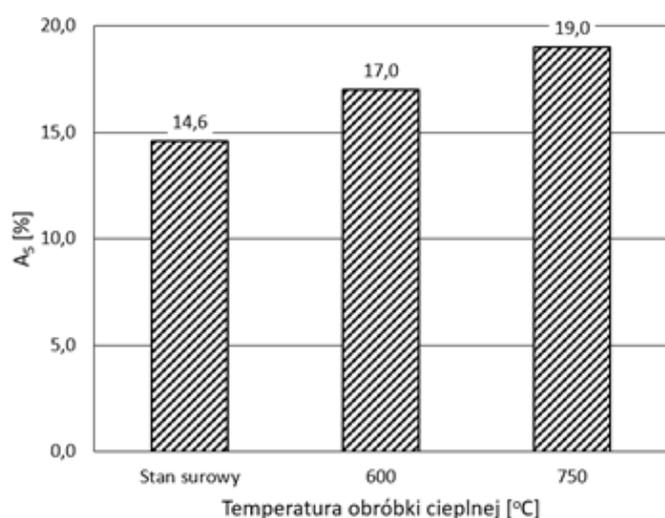


Fig. 5. Elongation A₅ of the welds made using submerged arc; the as-welded state and the state after heat treatment performed at a temperature of 600°C and 750°C

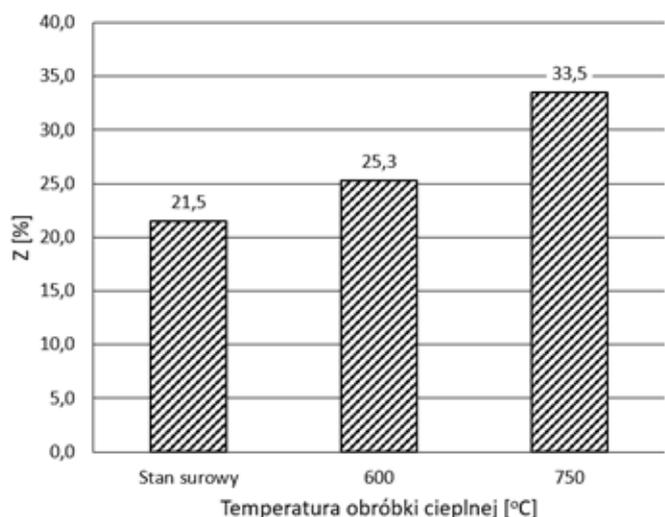


Fig. 6. Area reduction Z of the welds made using submerged arc; the as-welded state and the state after heat treatment performed at a temperature of 600°C and 750°C

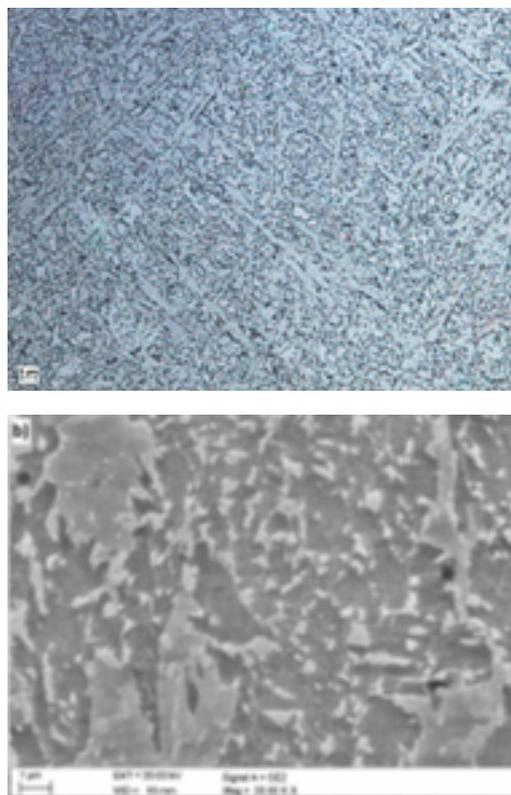


Fig. 7. Structure of the weld made using submerged arc; E=12 kJ/cm, a) optical microscope and b) scanning microscope

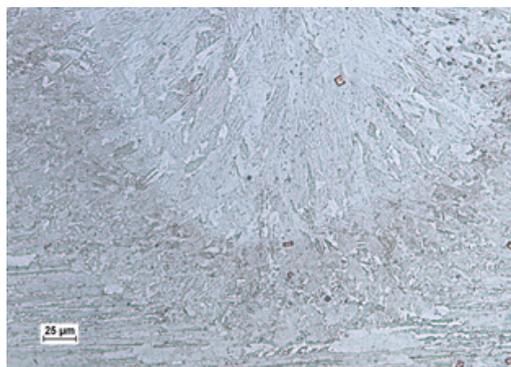


Fig. 8. Primary TiN precipitates in the base material, HAZ and laser-melted area, E= 0.4 kJ/cm

by approximately 50 HV₁. A significant decrease in hardness was observed after tempering at a temperature of 750°C. The overlay welds made using the covered electrodes (Fig. 2) were characterised by higher hardness directly after surfacing (330–360 HV₁) and by significant differences in hardness in the as-surfaced state and after tempering at a temperature of 100°C, 200°C, 300°C and 400°C. After tempering at a temperature of 600°C, all of the specimens were characterised by a hardness of approximately 370 HV₁. It was also possible to observe an increase in the hardness of the overlay welds after

holding at low temperatures. The specimens subjected to heat treatment for 45 minutes were characterised by a significant increase in hardness after holding at a temperature of 100°C. In terms of the remaining specimens, subjected to heat treatment for 30 minutes, an increase in hardness was related to holding within the

temperature range of 200°C to 300°C. In the overlay welds made using submerged arc, an increase in hardness after holding at low temperature as well as differences in hardness measurement results in relation to various values of surfacing linear energy were less evident. The foregoing could result from the lower stability

of the MMAW process and the less efficient shielding of the liquid metal pool from oxygen and atmospheric nitrogen. Therefore, it can be assumed that the above-presented situation could lead to fluctuations and an increase in the content of nitrogen in welds [19], significantly above that of 120 ppm, permissible for steel 7CrMoVTiB10-10 in the ASTM A 213 standard.

The toughness of the SAW welds in the as-welded state amounted to 21.8 J/cm². The minimum toughness amounting to approximately 9 J/cm² was obtained after holding for 30 minutes at a temperature 600°C and 700°C. An increase in the toughness of the welds was observed after holding the latter at a temperature of 750°C (Fig. 3).

The static tensile test results revealed the high strength R_m of the welds in as-welded state (approximately 1050 MPa) and a further increase of 100 MPa after tempering at a temperature of 600°C.

The tempering of the welds at a temperature of 750°C reduced the strength R_m of the welds to approximately 750 MPa (Fig. 4). The parameters characterising the plastic properties of the welds in the static tensile test reached the minimum values,

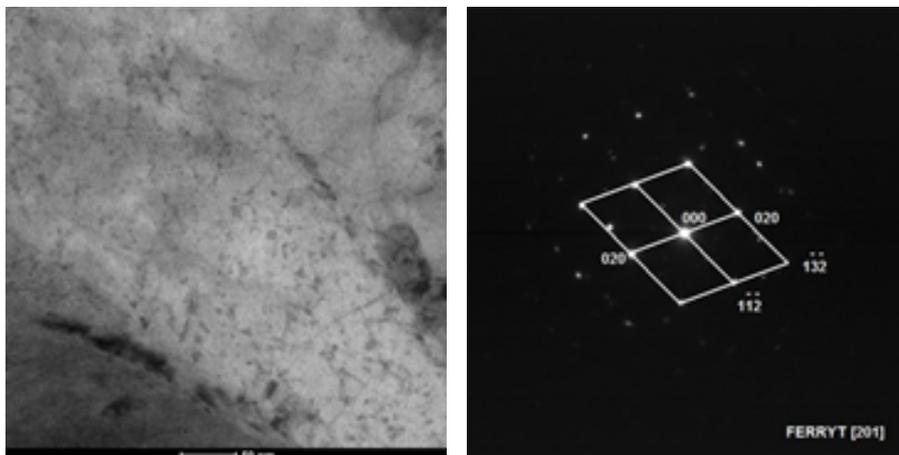


Fig. 9. Transmission electron microscope a) structure of the weld made using submerged arc; E = 12 kJ/cm, in the as-welded state, b) solution the diffraction pattern

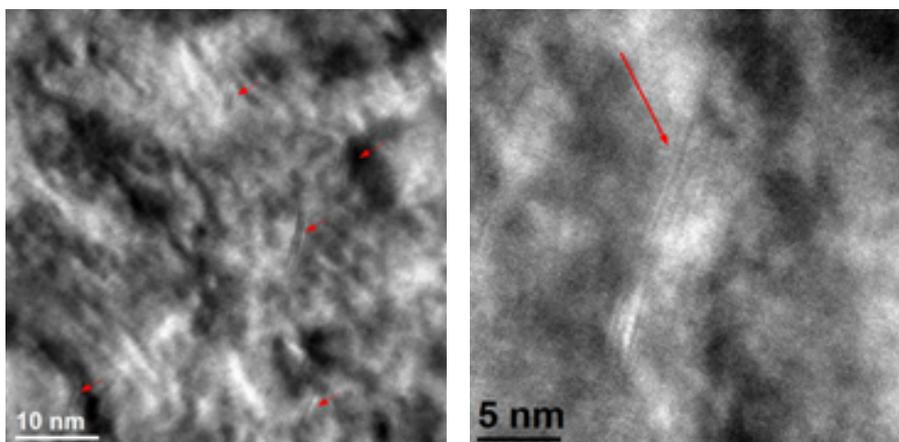


Fig. 10. Transmission electron microscope a) structure of the weld made using submerged arc; E = 12 kJ/cm; tempering temperature: 600°C; hold time: 30 min

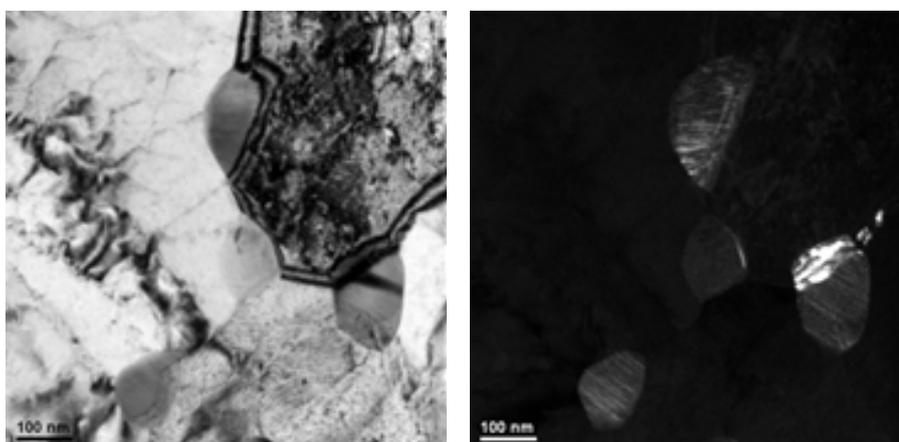


Fig. 11. Transmission electron microscope a) structure of the weld made using submerged arc; E = 12 kJ/cm; tempering temperature: 750°C; hold time: 30 min

i.e. A5 amounting to 14.6% and Z amounting to 21.5%, in relation to the welds in the as-welded state (Fig. 5 and 6).

The metallographic tests performed using an optical microscope revealed that the test welds and the overlay welds in the as-made state only contained oxide precipitates and, sporadically, the primary precipitates of titanium nitride (TiN). The tests involving the laser melting of steel 7CrMoVTiB10-10 revealed that in relation to very low laser melting linear energy the TiN precipitates in the partially melted zone (near-weld zone) were similar to those present in the base material and the HAZ of steel 7CrMoVTiB10-10 (Fig. 8). The higher values of welding linear energy and surfacing linear energy led to the dissolution of the stable TiN phase in the matrix or the total decay of the former (Fig. 7). The foregoing indicated that during the metallurgical process there were conditions enabling the stable bonding of nitrogen in massive TiN precipitates and that the aforesaid phase underwent either partial or total decomposition in the welds and in the overlay welds. The dissolution (during welding) of the remaining precipitates (primarily carbides) was favoured by their lower stability and smaller dimensions than those of titanium nitride. The values of the free enthalpy (ΔG) related to the formation of the nitrides and carbides of titanium, niobium and vanadium (in relation to pure components) at a temperature of 20°C and 1600°C are presented in Table 3.

Table 3. Free enthalpy of the formation of the carbides and nitrides of titanium, vanadium and niobium [29]

Phase	Free enthalpy	
	ΔG_{20} , kJ/mole	ΔG_{1600} , kJ/mole
TiN	-765.5	-516.2
TiC	-180.9	-160.6
VN	-646.8	-412.9
VC	-98.2	-80.8
NbN	-662.3	-417.4
NbC	-136.9	-133.2

The metallographic tests performed using the transmission electron microscope and the scanning electron microscope did not reveal the presence of carbide and nitride precipitates in the welds directly after welding (Fig. 7 and 9). The above-named observation was consistent with the results presented in publication [25] stating that the high-temperature area of the HAZ of welded joints made in steel P24 did not contain MX type phases. The 30-minute long tempering of the test welds at a temperature of 600°C did not lead to the formation of precipitates. Observations performed using the transmission electron microscope revealed that the structure of the welds contained characteristic striated anomalies having dimensions restricted within the range of 5 nm to 10 nm (Fig. 10). The above-named anomalies could constitute the initial stages of MX type precipitates. The aforesaid state corresponded to the maximum hardening $R_m = 1148$ MPa and the very low toughness (9.3 J/cm²) of the weld (Fig. 3, 4). The formation of precipitates (having dimensions restricted within the range of 100 nm to 150 nm) in the weld after tempering at a temperature of 750°C (Fig. 11) was accompanied by a decrease in hardness restricted within the range of 230 HV₁ to 240 HV₁ as well as a decrease in mechanical properties to 750 MPa. However, it was possible to observe an increase in the elongation, area reduction and the toughness of the welds (Fig. 3, 4 and 5).

Taking into consideration the test results concerning susceptibility to secondary hardening (Fig. 1 and 2) as well as the results obtained in the metallographic tests it can be stated that the welds in the as-welded state contained significant amounts of alloying components dissolved in the matrix having lattice α (Fig. 9).

The welding of steel is characterised by many factors favouring the dissolution of hardening phases and the saturation of the weld with alloying components, i.e. the high temperature and the intense convection of the liquid metal combined with high cooling rates. In welds

made of steel 7CrMoVTiB10-10 dissolution processes involve alloying elements used intentionally to harden the solid solution (Cr, Mo), elements following the decomposition of the hardening phases and the primary precipitates of the base material (V, Ti, Nb, B, C and N) as well as hydrogen and nitrogen (constituting impurities entering welds during the welding process). Some of the above-named elements (C, N, Ti, Nb, and B) form solutions with ferrite (characterised by limited solubility). High cooling rates combined with the presence of elements (in the solution) impeding diffusion and diffusive transformations provide conditions for the supersaturation of welds.

Metals containing lattice A2 (bcc) tend to be less plastic than those having face-centred cubic lattice A1 (fcc). The foregoing results from the internal friction stresses of lattice A2, significantly higher than those observed in lattice A1. Particularly at low temperatures, in metals containing lattice A2, the slip of dislocations is blocked by the internal friction of the lattice. The overlapping of the high internal friction of lattice A2 with the effect of dislocation with the components of the solid solution leads to the additional hardening of the alloy, unfortunately at the expense of plastic properties. Knowledge concerning the solid solution hardening and the deterioration of the plastic properties of ferrite is usually related to dual-component systems such as Fe α -C, Fe α -N, Fe α -Mn, Fe α -P, Fe α -Cr etc. F. B. Pickering [26] noticed that the hardening of ferrite through the deformation of lattice triggered by the presence of interstitial constituents (C and N) is approximately 100 times stronger than in cases of substitution solutions. It is commonly known that the supersaturation of ferrite with carbon or nitrogen has a very negative effect on the plastic properties of solution α . A question that arises in such a situation is how the properties of welds made in steel 7CrMoVTiB10-10 are affected by the transition of significant amounts of alloying agents and impurities to the solution

during welding and what is the simultaneous interaction of components, e.g. substitution atoms with interstitial atoms, in the solid solution. Some of the aforesaid atoms form limited solubility solutions with ferrite, which additionally complicates the situation. The interaction of substitution and interstitial atoms in iron α affects their solubility and diffusiveness [27] and, consequently, influences the kinematics of the precipitation of phases from the solid solution as well as affects amounts of alloying components in the solution.

The knowledge concerning the above-named subject is rather limited. It is commonly known that carbon and hydrogen affect the plastic properties and the cold crack formation susceptibility of welded joints made in steels subjected to hardening. In publication [28] J. Węgrzyn demonstrated that the primary reason for the brittleness of supersaturated ferritic steel 17Cr is carbon, nitrogen and hydrogen arrested in the interstitial solution and titanium, which after exceeding the limit value, forms the substitution solution. A significant improvement of the plastic properties and weldability of the above-named steels can only be obtained after decreasing the total content of C+N < 0.03%.

The supersaturation Fe α of welds made of steel 7CrMoVTiB10-10) with interstitial components (N, C) favours the deterioration of plastic properties as a result of post-solutioning ageing. At the same time, welding strain cycle increases the density of dislocations in the welds, providing conditions for post-strain ageing. However, it seems that more important issue is the interaction of interstitial atoms with local strain areas formed near the bottoms of the notches (microcracks, incomplete fusions, lacks of penetration etc.) in welded joints during welding, transport, assembly and the start-up of power engineering systems. The foregoing may exhaust the ductility of steels and result in the formation of cracks.

Unlike steel P/T 22 (2.25%Cr, 1%Mo), successfully used for many years, welds made in

steel 7CrMoVTiB₁₀₋₁₀ contain additives of V, Ti, Nb and B. The contents of titanium and niobium depend on the degree of dilution (of the filler metal with the base material).

In steels used in power engineering systems, vanadium significantly increases susceptibility to the formation of annealing cracks. In the high-temperature part of the HAZ it is possible to observe the decomposition of relatively unstable vanadium carbides (Table 3) and the transition of vanadium and carbon to the solution. The reheating of the joint triggers mechanisms similar to those inducing secondary hardness, which, combined with the relaxation of stresses, lead to formation of cracks.

In chromium-molybdenum-vanadium steels, titanium and niobium significantly increase the effect of secondary hardness [20] and, with ferrite, form solutions characterised by limited solubility. In addition, in lattice Fe α , niobium is characterised by a significant lattice misfit degree (+6.1%).

Because of the small atom diameter, boron was initially regarded as an element forming the interstitial solution with ferrite. Subsequent works [21] imply that boron and iron α form the substitution solution characterised by limited solubility. The fact that interstitial site is possible at higher temperature [22], could explain previously contradictory results of experiments concerning the behaviour of boron in iron α . The primary reason for which boron was added to steel 7CrMoVTiB₁₀₋₁₀ was the improvement of creep resistance through affecting the nucleation of hardening phases [14]. At the same time, boron increases the hardenability of the steel impeding the diffusive transformations of austenite and, consequently, favouring the saturation of the Fe α matrix with alloying components. Many research publications emphasize that, to prevent the worsening of the plastic properties of welds and their resistance to notch effect, the content of boron in the welds should be determined very precisely [23, 24].

Summary

The assessment of the weldability of steel 7CrMoVTiB₁₀₋₁₀ is a very complex issue. The above-named situation results from incomplete knowledge concerning the effect of alloying components and impurities on properties of welds. In particular, the foregoing applies to the effect of the interaction of substitution and interstitial atoms in solution Fe α on their diffusivity and solubility. This, in turn, affects the kinematics of the precipitation of phases from the solid solution and has an impact on amounts of alloying components and impurities remaining in the solution. In the above-presented situation, the application of traditional weldability assessment criteria and treating the content of carbon as well as the maximum hardness of the HAZ as the primary criteria underlying procedures concerning the welding of the steel proved a mistake. In spite of the low content of carbon and relatively low hardness, welds not previously subjected to heat treatment were brittle. The foregoing resulted from the solution hardening and the supersaturation of welds having lattice A₂ (bcc) not only with carbon but also with other alloying components and impurities forming (along with Fe α) substitution and interstitial solutions. The supersaturation of welds appeared to be a thermodynamically unstable state, unable to provide joints with structural stability during operation. The reheating (repair, start-up, operation) of welded structures made of steel 7CrMoVTiB₁₀₋₁₀ not subjected to heat treatment leads to the further worsening of the plastic properties of welds because of their significant susceptibility to secondary hardness. The plastic properties of welds may also decrease as a result of post-solutioning ageing and after cold work. Welding procedures not including the heat treatment of welded joints made of steel 7CrMoVTiB₁₀₋₁₀ do not provide conditions ensuring weld structure stability and the proper dispersion of MX type phase precipitates.

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