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PROBLEMS OF PAD WELDING STRUCTURAL STEELS WITH MARTENSITIC FILLER METAL

ABSTRACT

There is a problem in obtaining a suitable impact strength of the padding weld after cladding with a martensitic filler metal. Too low annealing temperature below 580°C and the excessive annealing temperature above 650°C do not provide adequate impact strength of the padding weld. A heat treatment technology for mixed joints has been developed based on the results of the microscopic observations, X-ray diffraction measurements and transmission electron microscope examination. The problem was identified and a special technology of heat treatment for the dissimilar joint was elaborated. This technology provides a high impact resistance of the padding weld and an appropriate properties of the base material.

Keywords: *pad welding, reversed austenite, X3CrNiMo13-4 martensitic steel*, H_p *parameter*

INTRODUCTION

Martensitic steels containing 13% Cr are widely used in the industry due to their high corrosion resistance and strength. Their microstructure vary from pure ferrite to martensite depending on the carbon content. These steels can be divided into four groups [1]:
- the ferritic steels for general use,
- the steels with a low martensite content,
- the steels with soft martensite,
- the new supermartensitic steels.

The strength range for each of these groups depends on the heat treatment applied. During solidification of these steels the primary phase precipitating from the liquid is δ ferrite. This is particularly important in the case of joint not subjected to high-temperature heat treatment homogenizing the chemical composition. Differences in the chemical composition of the weld cause a change in the kinetics of the transformation during cooling and this can result in the occurrence of microstructure components that adversely affect both corrosion and strength. The effect of strength changes during cooling is also observed in the other groups of steels i.e.

in structural steels [2] and in advanced micro-alloyed steels and alloys for high-temperature and high-pressure applications [3, 4].

Supermartensitic stainless steels are based on grades containing 13% Cr, but they have a lower carbon content and additions of 4÷6% Ni and 0.5÷1.5 Mo. These steels have a very good resistance to general corrosion as well as cracking caused by stress corrosion in an acidic environment (H_2S). They also present high resistance to cavitation and abrasion in high humidity conditions. For this reason, they were used in such applications as: parts of water turbines, pumps and valves in power plants, drilling heads in the oil industry, etc. [1,5,6,7].

The influence of heat treatment on the microstructure and mechanical properties of supermartensitic steels has been studied by many authors [8-12]. They found that after tempering the steel microstructure consists of tempered martensite and residual austenite. The amount of austenite decreases above 700°C. De Sanctis [13] noted that relatively low A_{c1} temperatures induce the formation of an austenitic phase above 600°C during tempering. The formed reverse austenite tends to be unstable during cooling, which contributes to increasing the final hardness by converting austenite to virgin (fresh) martensite. Similar behavior of austenite is also observed in other martensitic steels [14, 15].

In case of welding the X3CrNiMo13-4 steels, low-carbon binders of the EN 12072 : G 13 4 grade are used. After welding the microstructure of these steels obtained after tempering contain a lath martensite, austenite and a small amount of residual ferrite. Weldability of these steels is good due to the formation of ductile, low-carbon martensite in both the weld and the heat affected zone (HAZ) [16, 17]. This reduces the susceptibility to hydrogen cracking. The low content of δ ferrite reduces the tendency to grain growth. However, in spite of such good properties, the attention should be paid to the hydrogen content in the weld, which should not exceed 5 ml / 100 g of weld metal. In the petrochemical and mining installations exposed to hydrogen sulfide, high impact strength and low hardness are important. In order to prevent cold cracking caused by the hydrogen sulphide, the hardness of the HAZ and the welded joint should be lower than 23 HRC and the impact energy at room temperature have to be higher than 50 J.

It is important to choose the appropriate heat treatment parameters after welding to ensure optimum plastic properties and a minimum hardness. In the case of pad welding of structural P265GH steels with a binder corresponding to the composition of X3CrNiMo13-4 steel, the designers usually recommended a stress relief annealing in the range 520÷570°C. Such treatment guarantees obtaining correct properties of the pad welded part, however it does not provide the required impact strength and hardness of the pad welds of the martensitic steel. Due to the problems with obtaining the required plastic properties and hardness, an attempt was made to test the X3CrNiMo13-4 steel pad welds.

EXPERIMENTAL

The research on the influence of heat treatment on the properties of padding was carried out on pad welded samples made of the P255GH steel elements cut from power equipment parts. The pad welds were produced using GMA method applying Thermanit 13/04 wire in M13 mixture. The main purpose of the research was to explain the mechanism of changes in the properties of pads subjected to heat treatment process and to determine the conditions of heat treatment ensuring hardness of the pad weld lower than 23HRC and the highest possible impact strength. The orientation of the pad weld in the P265GH steel element and the cutting of the impact test samples are shown in Figure 1.

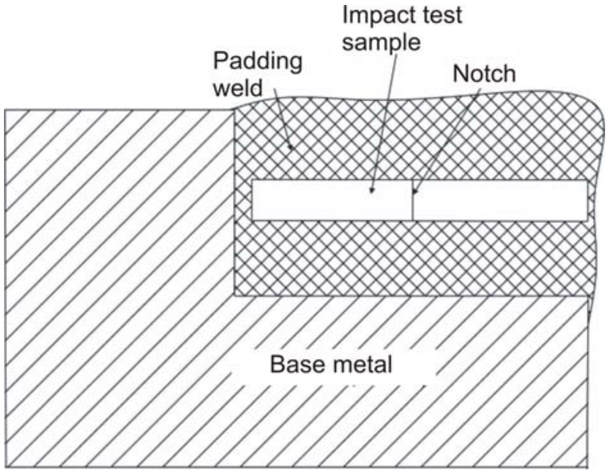

Fig. 1. The schematic diagram of the part with the pad welding and the method of cutting out impact samples

The impact test samples (without V notch) were heat treated at 580 ÷ 690°C for 2, 5, 10 and 20 hours. After heat treatment, the V notches were cut and the samples were broken at +20°C using Charpy impact test. For each individual temperature and time of the heat treatment the three samples were used. The values of the impact energy are the average from three measurements. In addition to testing the impact strength of the weld pads, hardness was measured using Rockwell (HRC) and Vickers (HV) using 294,3 N load. The results of hardness are calculated as the average of nine measurements. Both methods: Rockwell and Vickers hardness measurements were used. The welded joint hardness is measured by the Vickers method, while the acceptance criteria of the welded construction usually give the HRC number as a reference value.

Annealing temperatures and heat treatment times were varied throughout the investigations. Therefore in order to determine the effect of these parameters on the properties, the H_p parameter was calculated. The references [18 ÷ 21] showed that the properties of steel after heat treatment are described by a specific function of the H_p parameter.

$$H_p = T(20 + \log t) \cdot 10^{-3}$$

where:

T – annealing temperature, K
t – annealing time at given temperature, hours

Microstructure of the pad weld samples was investigated using LM light microscope Leica DMLM. TEM microstructural analysis was carried out using a transmission electron microscope JEOL 200CX. The XRD studies were performed on a Siemens D500 Diffractometer, using the monochromatic radiation of a copper X-ray tube (λ_{Cu} Kα = 1.54 Å). Diffraction pattern was determined with the use of Bragg-Brentano method, using step-counting ($\Delta 2\theta$ = 0.02°, time per step τ = 5s) in the angle range 2θ from 35° to 90°.

RESULTS

The values of the impact energy of the pad welds and corresponding hardness measured by Rockwell and Vickers methods as a function of H_p parameter are presented in Figures 2 and 4. The dependence of the impact energy and the hardness of the pad weld sample on annealing treatment temperature for 5 hours are illustrated in Figures 3 and 5. These figures show that the lowest hardness and the highest impact energy is obtained for H_p parameter between 18 and 19. Assuming the parameter $H_p = 18.5$, it can be calculated that at 600°C, the minimum annealing time to obtain a hardness of 275HV is about 11 hours, while for 620°C it is about 5 hours. Thus, heat treatment after welding in the temperature range 600 to 620°C for 5 hours will ensure a maximum impact energy of 90 ÷ 100 J (Fig. 5). For the parameters of heat treatment mentioned above a minimum hardness of 275 HV is obtained (Fig. 3).

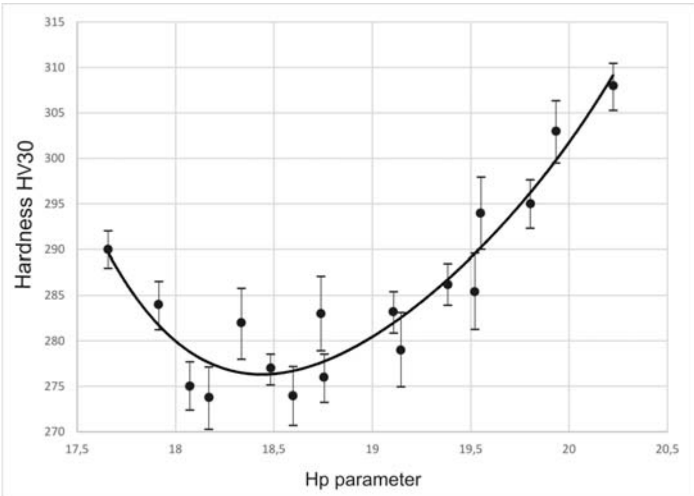

Fig. 2. The dependence of HV30 hardness on the Hp parameter. The averaged experimental data points are marked as black dots, the error bars are shown on the graph. The thick solid line represents the resulting fitting curve (HV30=252973.1-51841.46·Hp+3992.741·Hp2-136.8755·Hp3+1.762915·Hp4)

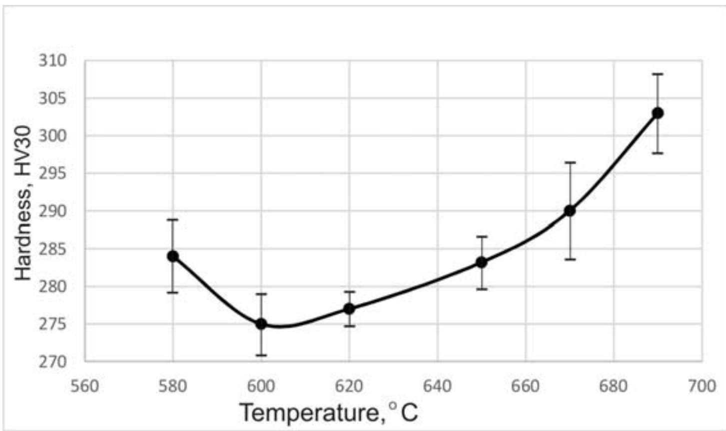

Fig. 3. The dependence of hardness on the annealing temperature for 5 hours

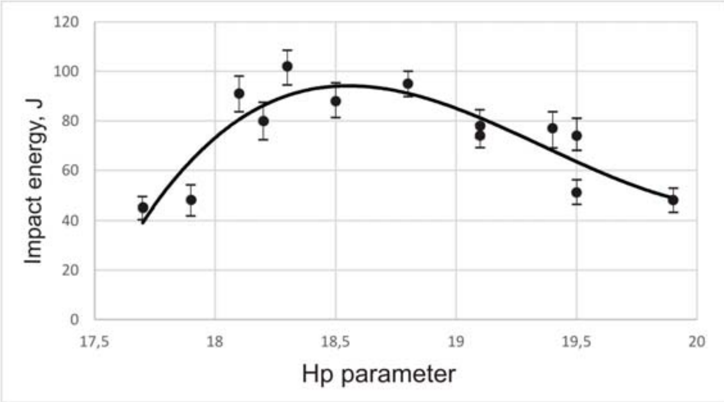

Fig. 4. The dependence of the impact energy on the Hp parameter

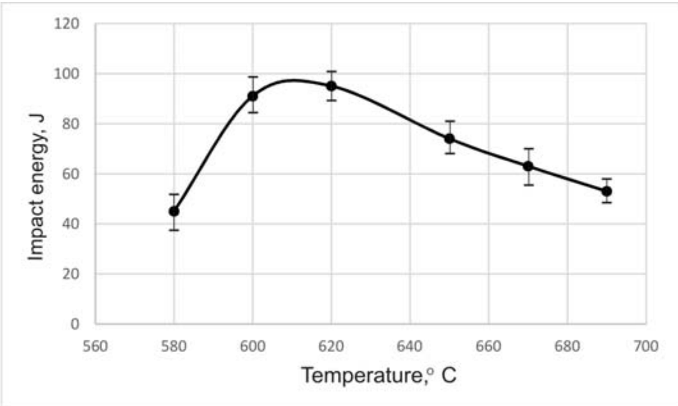

Fig. 5. The dependence of the impact energy on the annealing temperature

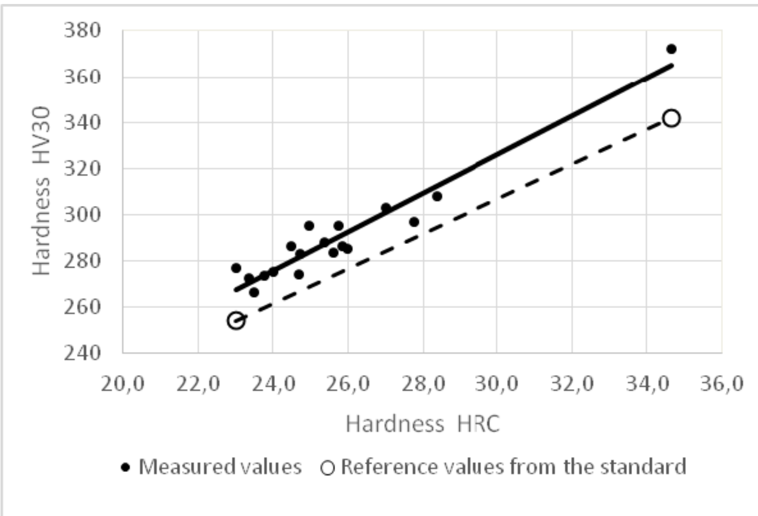

Fig. 6. Relationship between HV30 hardness and HRC hardness

Hardness measurement results allowed to make a graph of the relationship between hardness measured by the Vickers and Rockwell method. This relationship is shown in Fig. 6 and it can be seen that there is no match between the obtained hardness results and the relationship given in the EN-ISO 18265:2013.

Microscopic examination shows that there is martensite and δ ferrite located in the cores of the cells within the pad weld microstructure (Fig. 7). Annealing at the range of temperatures of 580÷690°C does not change the microscopic image of the structure significantly. The only change concerns the blur of the martensite - δ ferrite interface boundary as a result of diffusion processes (Fig. 8).

The XRD examinations showed that after pad welding only α phase (martensite and δ ferrite) is present. After annealing in the temperature range 580-620°C, the additional phase is austenite. After annealing at higher temperatures, only α phase is present in the microstructure [21]. Figure 9 shows the changes of the austenite volume fraction in the microstructure.

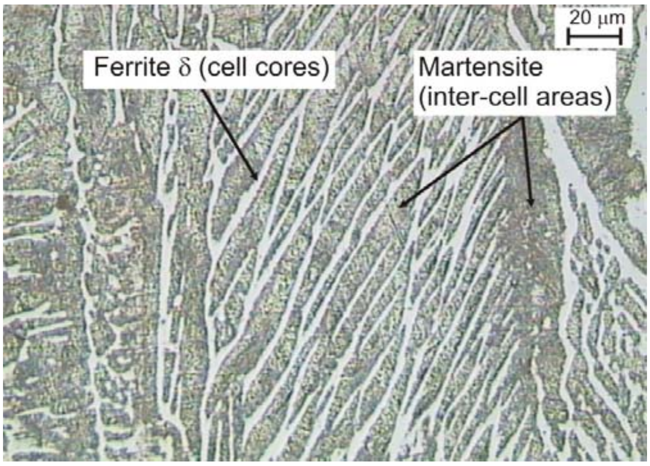

Fig. 7. Microstructure of the pad weld without heat treatment

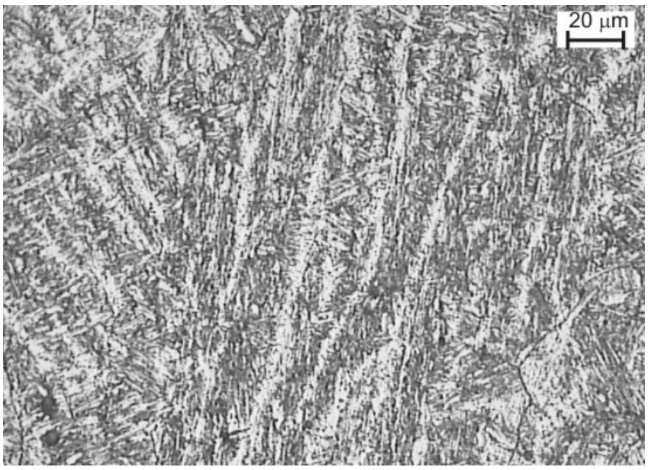

Fig. 8. Microstructure of padding weld after heat treatment (6000C, 10h)

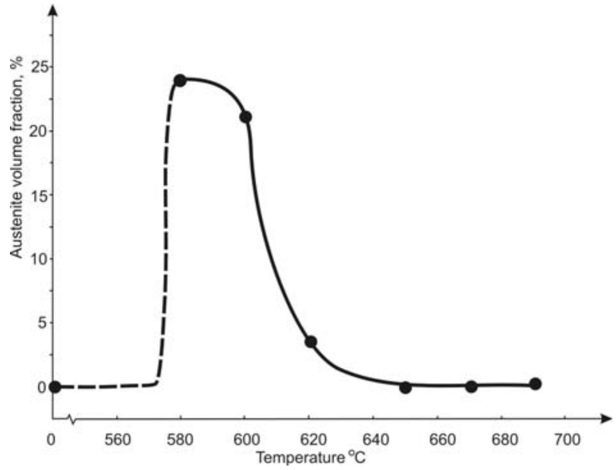

Fig. 9. Dependence on the austenite volume fraction on heat treatment temperature. Annealing time10 h

In order to explain the cause of the drop in impact strength after annealing at 650°C and above, the microstructure of the pad weld was examined in a transmission electron microscope using thin films. Examples of microstructures after pad welding and after heat treatment observed in an electron microscope are shown in Fig. 10. Observations of the microstructure show existence of a lath austenite after pad welding (Fig. 10a). After heat treatment at 580÷620°C, austenite occurs in the microstructure between the laths of tempered martensite (Fig. 10b, c). After annealing at higher temperatures, austenite does not occur, whereas there is "fresh" martensite between the laths of tempered martensite (Fig. 10d).

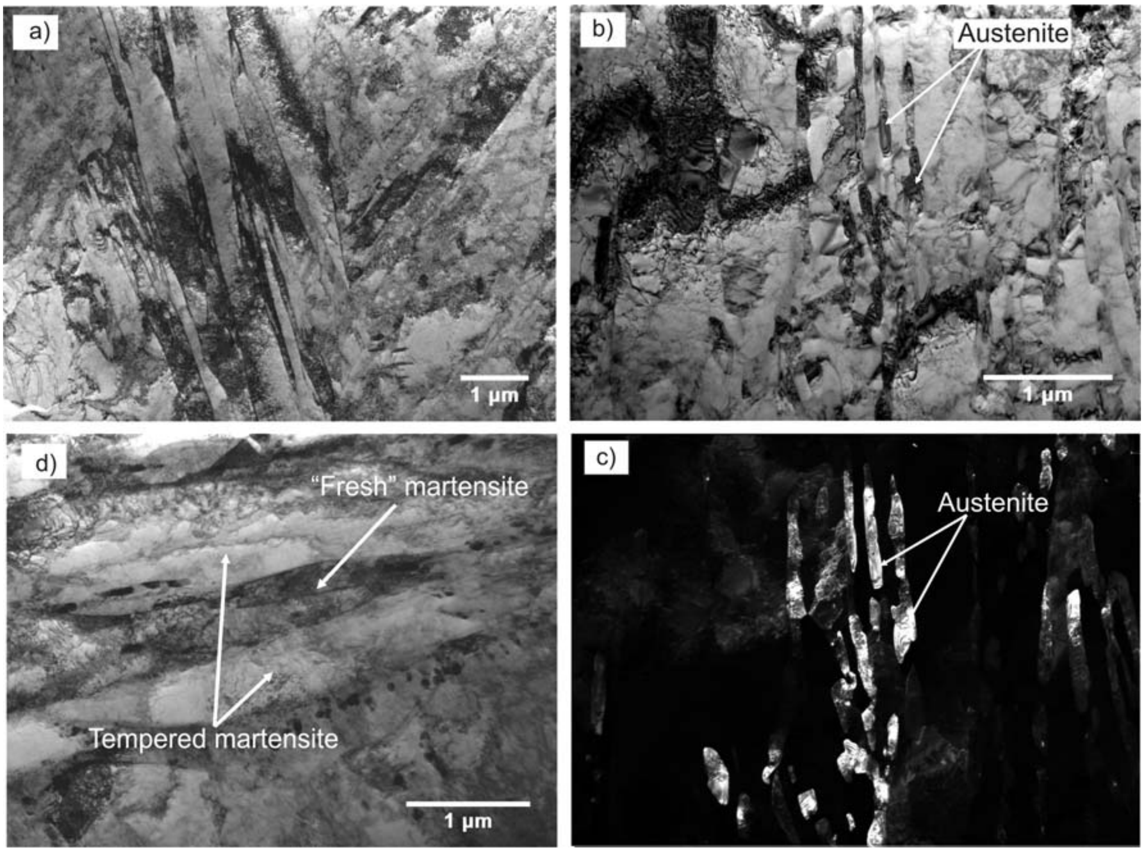

Fig. 10. Padding weld microstructure observed in a transmission electron microscope: a) lath martensite after pad welding, b - lath martensite with austenite after heat treatment at 600°C for 10 h, c – austenite in the dark field contrast, d - tempered martensite and "fresh" martensite after heat treatment at 670°C for 10 hours

DISCUSSION

The investigations have shown that the highest impact strength is obtained in temperature range of 600÷620°C after 10 hours of annealing. An increase in temperature above this range causes a continuous drop in impact strength. The annealing time is of no great importance, as this decrease is observed both for the annealing time of 5 hours and 10 hours. Therefore, behavior of this material is discrepant to the generally known relationships for other groups of steels. The change in impact strength also involves a corresponding change in hardness. The minimum hardness of pad weld at the level of 23HRC (275HV) is obtained after heat treatment in the same temperature range. However, below 600°C and above 620°C, the hardness is higher. Considering the combined effect of temperature and time (H_p parameter), it can be concluded that H_p parameter is between 18 and 19, the impact energy has a value of 90 to 100J (Figure 4). Low impact strength and high hardness after tempering up to 580°C can be explained by too slow diffusion process and a large dispersion of carbides. On the other hand, the decrease in impact energy and increase in hardness associated with the increase of the annealing temperature above 620°C can be explained as follows: There is a large segregation of alloying elements, especially nickel, in the X3CrNiMo13-4 steel padding welds. The ferritic cores of cells (marked in Fig. 7), contain 13.7% Cr and 3.76% Ni, while martensitic inter-cell areas contain 13.2% Cr and 5.44% Ni [22]. In Gooch research [7] it was shown that steel containing 3.8% Ni has an A_{c1} temperature of about 600°C, whereas steel containing 6%Ni has an A_{c1} temperature of about around 575°C. Since there is around 5.5% of nickel in the microsegregation areas, at around 580°C a local phase transformation takes place and austenite is formed. Carbon and nickel diffuse into the austenite areas. In the martensitic inter-cell areas with the increased nickel content (5.44%), the A_{c1} temperature is lower than in the ferritic cell cores.

Extending the annealing time results in austenite saturation with nickel and carbon, and thus an increase in thermal stability. After cooling to ambient temperature, thermally stable austenite is not transformed into martensite. The presence of residual austenite between the martensite laths has a positive effect on the impact strength of the padding weld.

XRD phase analysis (Fig. 9) showed that after cooling from the tempering temperature of 580°C there is 24% residual austenite in the microstructure, while after cooling from 620°C there is only 3%. The remaining austenite was transformed into "fresh" martensite. However, at 620°C, the amount of "fresh" brittle martensite is small and does not significantly affect the impact strength and hardness increase. The increase of the annealing temperature results in a larger amount of austenite with a lower concentration of nickel and carbon, which reduces its thermal stability. After cooling, the tempered martensite and "fresh" martensite are formed. The annealing temperature of 690°C is so high that virtually all of the austenite is transformed into a “fresh” martensite. This results in a decrease of impact strength by almost half as compared to the impact strength obtained after annealing at 600°C.

The EN-ISO 18265:2013 assumes that values of the hardness measured with different methods can be converted using appropriate tables. The tests carried out on the joints of martensitic steel showed that the dependences given in the standards are not correct. This is especially important in the case of pads or welds that are in contact with hydrogen sulfide. Hardness below 23HRC and high impact strength is required for these materials. In the welded and pad welded joints hardness measurements are made using the Vickers method. The conversion table presented in EN-ISO 18265:2013 gives that the hardness value of 23 HRC corresponds to Vickers hardness number 254 HV. On the other hand, in the present study, it was found that the hardness of 23 HRC corresponds to 275 HV. The results obtained in the present work are confirmed by previous studies of Hayes and Patrick [23] and Gooch [7], who also showed that the results of hardness measurements with the conversion given in ASTME 140-88 and BS 860:1967 were not compatible. The acceptance criterion permitting martensitic chromium-nickel steel constructions to be allowed, should be based on the following conversion formula 23HRC = 275HV.

CONCLUSIONS

1. During solidification of GMA pad welds produced with Thermanit 13-4 wire in M13 mixture gas there is a clear segregation of alloy components. Ferritic cell cores contain more chromium and less nickel, while inter-cell regions are richer in nickel and poorer in chromium. The enrichment of inter-cell areas with nickel and carbon results in lowering the A_{c1} conversion temperature. For areas containing about 6% Ni, the A_{c1} temperature is about 580°C.
2. The change of hardness and impact resistance of the X3CrNiMo13-4 padding welds with an increase in tempering temperature is not monotonic. The highest impact strength (90 ÷ 100J) is obtained after tempering in the range of 600÷620°C for 10 hours. The highest toughness corresponds to the lowest hardness at 23HRC (275HV). An increase in the tempering temperature above 620°C, regardless of time, results in lower impact strength and higher hardness.
3. The hardness tests have shown that the dependence of 23HRC = 253HV recommended in the case of pad welds made of X3CrNiMo13-4 steel according to the EN-ISO 18265:2013 standard is not correct. For these steels one should assume that 23HRC = 275HV.

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