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## MICROSTRUCTURE OF WELDED JOINTS OF X5CrNiCuNb16-4 (17-4 PH) MARTENSITIC STAINLEES STEEL AFTER HEAT TREATMENT

## MIKROSTRUKTURA ZŁĄCZ SPAWANYCH STALI NIERDZEWNEJ MARTENZYTYCZNEJ X5CrNiCuNb16-4 (17-4PH) PO OBRÓBCE CIEPLNEJ

The paper presents results of microstructure (LM, TEM) investigation and hardness measurements of welded joints in martensitic precipitation hardened stainless steel containing copper, subjected to heat treatment. For the aging temperature up to 540°C even for the very long times, the microstructure of the welded joints is similar to this one at lower temperature aging. After aging at 620°C a distinct change of the microstructure was observed. Non-equilibrium solidification conditions of the weld metal, segregation and the diffusion of copper and the elements stabilizing the austenite cause the occurrence of the reverse transformation of the martensite into austenite as fast as just 1 hour at 620°C. TEM investigations revealed the differences in dispersion of hardening copper precipitates after aging at temperature 620°C for 1 and 4 hours.

*Keywords:* Weld metal, heat treatment, martensitic PH stainless steels , 17-4PH steel

W artykule przedstawiono wyniki badań mikrostruktury (LM, TEM) oraz twardości złączy spawanych stali nierdzewnej martenzytycznej utwardzanej wydzieleniowo miedzią po obróbce cieplnej. Aż do temperatury starzenia 540°C mikrostruktura spoin nie wykazuje istotnych różnic niezależnie od czasu wytrzymania w porównaniu do tej obserwowanej w niższych temperaturach. Po starzeniu w temperaturze 620°C zaobserwowano wyraźne różnice w mikrostrukturze spoin. Nierównowagowe warunki krzepnięcia metalu spoiny, występowanie segregacji oraz procesy dyfuzji miedzi i pierwiastków stabilizujących austenit powodują wystąpienie przemiany odwrotnej martenzytu w austenit już po 1 godzinie starzenia w 620°C. Badania TEM wykazały, różnice w dyspersji cząstek umacniających w temperaturze starzenia 620°C przez 1 i 4 godziny.

### 1. Introduction

The precipitation hardened stainless steels are widely used as a structural material in chemical plants and power plants due to the optimum combination of good mechanical properties and corrosion resistance. Uniform distribution of fine intermetallic phases or alloying elements such as niobium and copper provide good mechanical properties [1-3]. The stainless X5CrNiCuNb16-4 (17-4 PH) steel is a martensitic grade containing 4 wt % of Cu. After supersaturation at 1040°C and cooling in air it is aged at temperature range for 480°C to 620°C. The martensite formed during cooling after solution heat treatment as well as coherent Cu-rich precipitates contribute to high strength of the 17-4PH steel. Low content of carbon (less than 0.07 wt. %) cause that the martensite formed after solution heat treatment is plate-like, ductile. It is due to a low extent of strengthening of the steel with the interstitial atoms of carbon and nitrogen. After solution heat treatment the yield strength of the 17-4PH steel is 750 MPa and increases further up to 1200 MPa after aging at 482°C [4÷6].

Precipitation process in the 17-4PH stainless steel starts with formation of Cu coherent particles [8]. Long-term aging at ca. 400°C causes that the coherent Cu precipitates transform into incoherent Cu-fcc particles. Aging at 480°C for 1 hour cause that the Cu precipitates are coherent with the matrix. The aging at 620°C for 4 hours results in a substantial amount of reversed austenite. The later formation of austenite occurring in the matrix containing fine precipitates of Cu [7] is caused due to the fact that Cu particles precipitate before formation of austenite during a high-temperature aging.

Chromium stainless steels including grade 17-4PH become brittle when the  $\alpha'$  phase forms as a result of spinodal decomposition [9-15]. As the Cr concentration in 17-4PH steel is near spinodal curve, after the long-term aging at temperature below 450°C, a spinodal decomposition of martensite into Fe-rich  $\alpha$  phase and Cr-rich  $\alpha'$  phase is likely to occur. Stainless 17-4PH steel exhibits a high susceptibility to cracking as a result of aging at 400°C. This is due to formation of  $\alpha'$  phase [9÷12]. This phase is observed also after aging at 482°C [12]. Formation of  $\alpha'$  phase in the microstructure is associated with a substantial drop of cracking resistance [11, 12].

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The 17-4PH steels may be welded with use of such methods as Manual Metal Arc Welding (MMAW), Gas Tungsten Arc Welding (GTAW), Plasma Arc Welding (PAW), Gas Metal Arc Welding (GMAW). Due to the fact that the weld solidifies with formation of  $\delta$ -ferrite, the risk of hot cracks occurrence in the weld is low. The presence of martensitic microstructure causes that the weld and heat affected zone (HAZ) is prone to cold cracking. In order to avoid the cracks, the limitation of hydrogen content in the weld is required. Another possibility is to enable diffusion of hydrogen from the weld is heating of the joint at elevated temperature ca 250°C. Generally, the welding is carried out using the binders of the chemical composition similar to that one of the base material. The welding using austenitic binders is also possible in the case when the welded joint does not require high mechanical properties and the highest corrosion resistance of welded joint is not required. While using the austenitic binder, the welded joint is not subjected to the heat treatment after welding [13].

The welds with thickness below 100 mm are performed without the preliminary heating, however the ductility of the weld is generally low. Therefore, the welding should be careful in order to avoid the factors inducing the stress concentrations in the weld which could be reasons for the preliminary damage.

The welding of 17-4PH steel is carried out in the solution heat treated condition or after the overaging at 580÷620°C, depending on the thickness of the material and the stiffness level. The heavy sections or the elements strongly braced are recommended for welding in an overaged condition. If the tensile strength of welded joints may be lower or if no post-weld heat treatment is possible, then the austenitic steel electrodes are used. [11].

The majority of investigations on 17-4PH steels is focused on the influence of microstructure on mechanical properties of the base material. Although the weldability of this steel is good only a few investigations relate to the influence of the weld microstructure on the properties [14]. The efforts undertaken in this study were focused on more detailed characterization the microstructures of welded joints at different stages of heat treatment e.g. aging at 480°C, 540°C, 620°C, for 1 h and 4 h, in order to better understand the influence of aging time and temperature on the microstructure.

**2. Experimental procedure**

The study was carried out using the 80x25x10 mm specimens of the stainless steel X5CrNiCuNb16-4 (17-4 PH) after overaging at 560°C. Chemical composition of steel 17-4 PH used in the studies is shown in Table 1.

TABLE 1  
Chemical composition of 17-4PH stainless steel

Element	C	Cr	Ni	Cu	Si	Mn	Nb
wt. %	0.06	16.5	4.0	3.4	0.6	0.6	0.3

The welding was performed by GTAW metod without using an additional filler metal with current of 100A, arc voltage of 12V and linear welding speed of 1.5 mm/s. The obtained

sample welded joint was cut into pieces and the sample was subjected to heat treatment. The heat treatment was carried out in syilit resistance furnace in the argon protective atmosphere. The conditions of heat treatment and the sample identification symbols are presented in Table 2.

TABLE 2  
The heat treatment conditions

Sample no	0	4/1	4/4	5/1	5/4	6/1	6/4
Aging temperature, °C	after welding	480	480	540	540	620	62
Aging time, h	0	1	4	1	4	1	4

After heat treatment the samples were included in the termosetting resin, then ground and polished using Struers LaboPol-5 device, using abrasive papers with grit from 100 to 2000 and polishing pastes. Such prepared samples were etched in Fry etchant composed of 120 ml of hydrochloric acid, 20 g of cupric chloride and 100 ml of distilled water. The microstructure was observed with use of light microscope Leica DMLM and transmission electron microscope JEOL 200CX. Hardness of the samples was measured using Vickers method using HPO-250 device. The measurements were carried out on the cross-section of the welded joint using force of 98.07 N.

**3. Results and discussion**

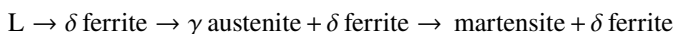
**3.1. Light Microscopy**

The microstructure of base metal used for the welding consists on tempered martensite with fine carbides precipitates inside the martensite laths and at their boundaries (Fig. 1).



Fig. 1. Microstructure of the base metal after welding; martensitic microstructure

The solidification mode of the 17-4PH weld is ferritic, therefore during the welding and the subsequent cooling the sequence of the phase transformations in the weld is the following:



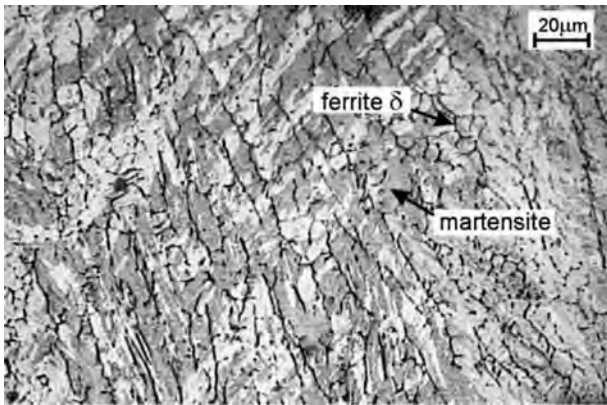


Fig. 2. Weld microstructure without heat treatment

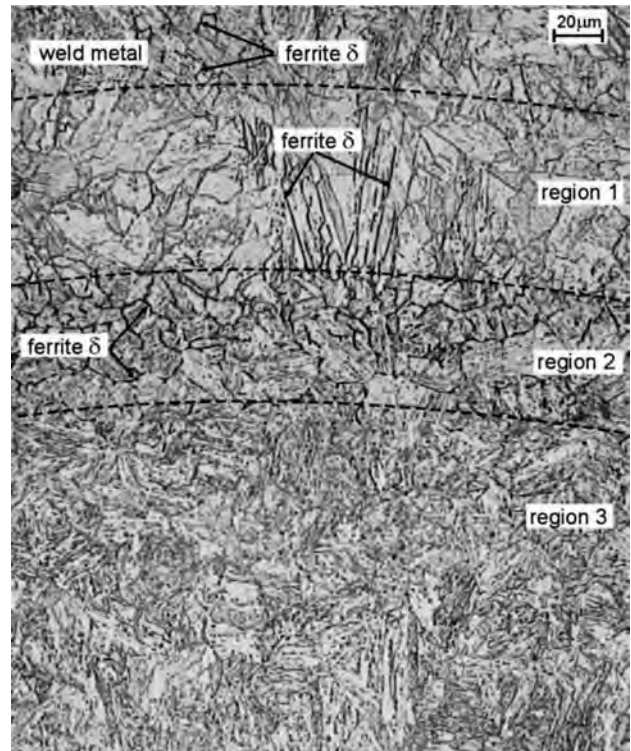


Fig. 4. Microstructure near the fusion line and the high-temperature regions of the HAZ from the place marked "A" in Fig. 3

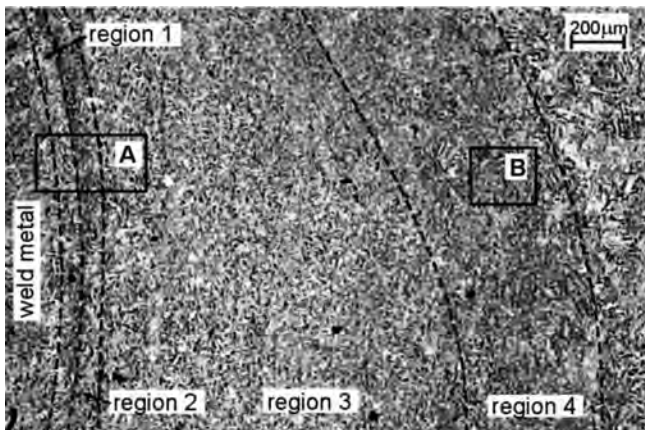


Fig. 3. HAZ microstructure with the characteristic regions marked with dashed lines

The light microscopy study shows the evidence that there are the phase transformations in the HAZ during the welding of the 17-4PH steel. The four areas can be distinguished in the HAZ (Fig. 3). Directly at the fusion line a coarse grained  $\delta$  ferrite can be observed. The  $\delta$  ferrite transforms into austenite during cooling and below the  $M_s$  temperature turns into martensite (Fig. 4). Finally, some remnants of non-transformed  $\delta$  ferrite may be found in the microstructure. At lower temperatures the area that was heated during welding to the range of  $\gamma$  austenite +  $\delta$  ferrite can be found (region 2). The  $\delta$  ferrite is located at the grain boundaries and during the subsequent cooling sequence will not transform into austenite and in the martensite. The martensite with a network of intergranular  $\delta$  ferrite can be visible on Fig. 4. Below  $1200^\circ\text{C}$  there is an area which is heated during welding to the temperature range of austenite. After cooling the martensite can be observed in the microstructure (region 3). The region heated up to the temperature range  $Ac_1$ - $Ac_3$  consists of the austenite coexisting with martensite, and after cooling transforms into the newly formed martensite and the tempered martensite. Figure 5 shows the example of the region heated up to the temperature slightly higher than  $Ac_1$ . The grains of the newly formed martensite (difficult for etching) martensite within the tempered martensite are observed.

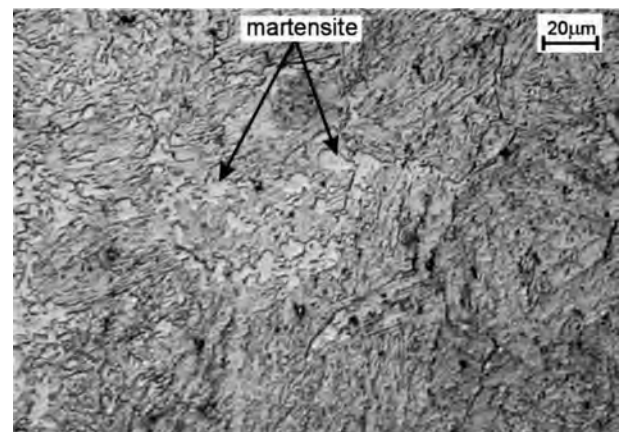


Fig. 5. Microstructure of the region no 4 from the place marked "B" on Fig. 3 heated to the temperature slightly higher than  $Ac_1$ . The "fresh" martensite within the tempered martensite

Microstructure of the base metal after aging at  $480^\circ\text{C}$  and  $540^\circ\text{C}$  (Fig. 6) does not show any distinct differences from that one in the as-welded state. However, only a lightly stronger etching of the grain boundaries is observed. For of the sample aged at  $620^\circ\text{C}$  for 1h and 4h the stronger etching is visible. This is most probably related with precipitation of the hardening phases. The dilatometric studies shown that the  $Ac_{1s}$  onset temperature is  $614^\circ\text{C}$  (Fig. 7). The heat treatment temperature at  $620^\circ\text{C}$  is higher than the temperature of austenite formation and during the subsequent cooling the austenite may transform into martensite. In the case of high stability of austenite, the  $\gamma$ - $\alpha'$  transformation will not occur.

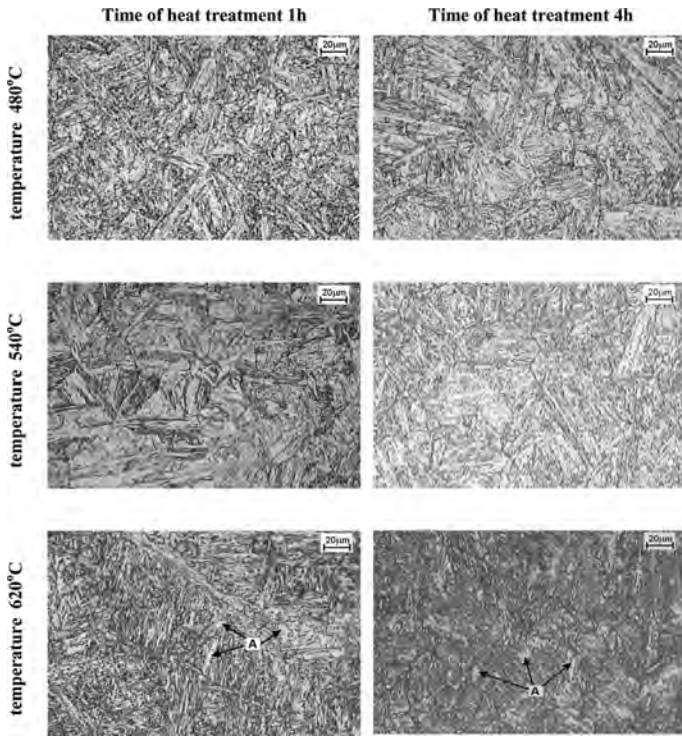


Fig. 6. Base metal microstructure after heat treatment. The bright regions visible between the plates of austenite (marked by arrows and capital letter “A”)

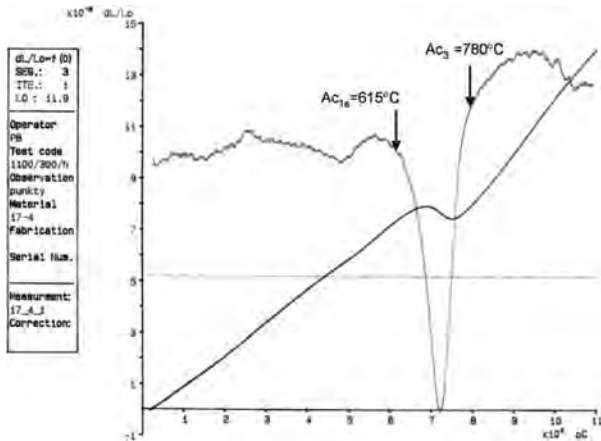


Fig. 7. Dilatometric heating curve (heating rate 0.1°C/s) and differential curve with the temperature values of the critical points  $A_{c1}$  and  $A_{c3}$

Aging up to 540°C does not affect significantly the microstructure of the weld metal observed by light microscopy (Fig. 8). The only effect is a slightly more pronounced etching due to the precipitation of carbides and hardening phases. Starting from the aging temperature of 620°C the microstructural changes are observed. In areas where the segregation is observed at the grain boundaries and cell boundaries where  $A_{c1}$  temperature is lower the austenite is formed. The austenite transforms into martensite after cooling. In the case of high stability of austenite, it cannot undergo phase transformation, similarly to base material.

3.2. TEM study

Transmission electron microscopy studies of the weld metal heat treated at 620°C for 1 hour revealed the typical

microstructure of the lath martensite with  $M_{32}C_6$  precipitates at the grain boundaries (Fig. 9). No precipitates within crystallites are observed. This can be related with an extensive segregation of chromium occurring upon the solidification treatment. Such segregation promotes the nucleation of precipitates on boundaries of the primary crystallites. The small amounts of the  $\delta$  ferrite (Fig. 10) are observed near the boundaries of the crystallites. The tin film of the retained austenite occurs on the boundaries of lath martensite (Fig. 11). In the regions where segregation of the chemical elements occurred, a stable austenite is formed as a result of  $\alpha \rightarrow \gamma$  transformation. The aging process proceeds in martensite. A numerous nanoparticles of Cu-rich fcc precipitates are observed (Fig. 12a). Prolongation of the time of annealing up to 4 hours at 620°C leads to further progress of the aging process. The fcc Cu-rich precipitates are growing (Fig. 12b). The  $M_{23}C_6$  precipitates and a few remnants of  $\delta$  ferrite are still observed at the crystallite boundaries. The austenite, stable down to the room temperature, formed during  $\alpha \rightarrow \gamma$  transformation exhibits a lower dislocation density (Fig. 13). The increase of copper solubility in the austenite causes dissolution of the fcc-Cu precipitates and stabilization of austenite.

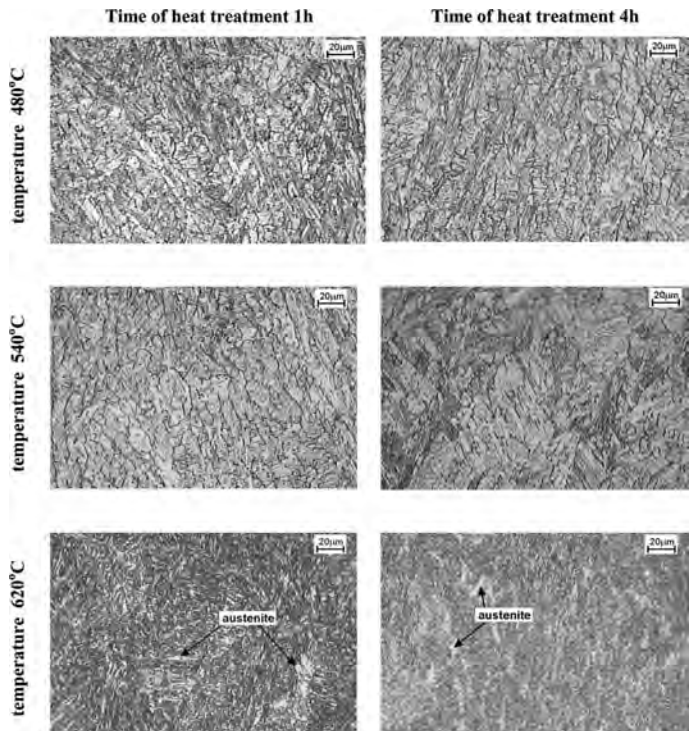


Fig. 8. Weld metal microstructure after heat treatment

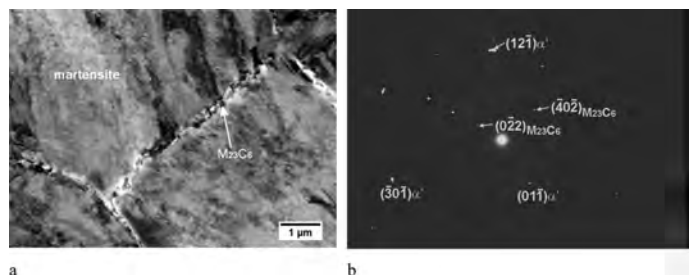


Fig. 9. Weld microstructure after annealing 620°C / 1 hour, b) electron diffraction pattern,  $[\bar{1}22]M_{23}C_6$ ,  $[\bar{1}23]_{\alpha}$

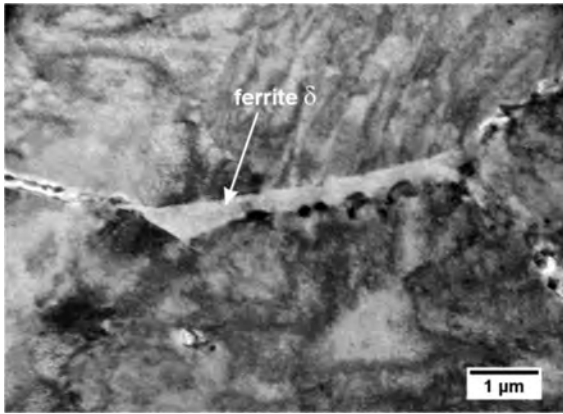


Fig. 10. Weld microstructure after annealing at 620°C for 1 hour. The remnants of  $\delta$  ferrite are indicated by arrow

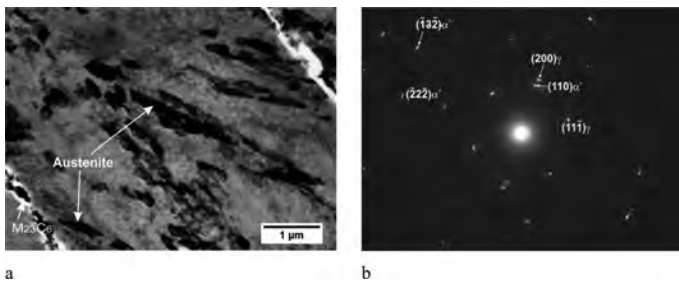


Fig. 11. Retained austenite in the middle of the grains of the weld of 17-4PH steel after annealing at 620°C for 1 hour; a) bright field, b) electron diffraction pattern  $[011]_{\gamma}$ ,  $[\bar{1}12]_{\alpha}$ ,  $[011] M_{23}C_6$

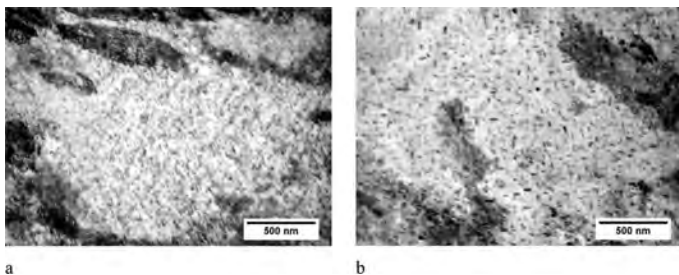


Fig. 12. a) Fine highly dispersed fcc-Cu precipitates inside the laths of martensite after annealing at 620°C for 1 hour, b) Larger fcc-Cu precipitates inside the laths of martensite after annealing at 620°C for 4 hour

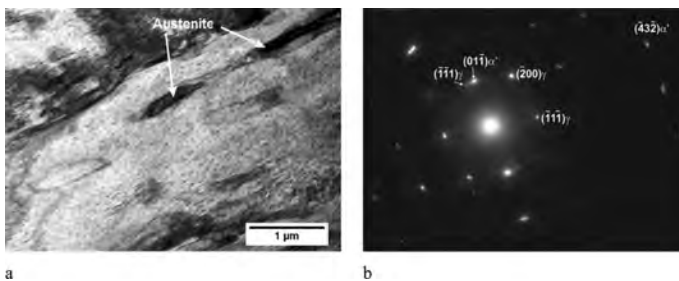


Fig. 13. Retained austenite in the of 17-4PH steel after annealing at 620°C for 4 hour; a) bright field, b) electron diffraction pattern  $[011]_{\gamma}$ ,  $[\bar{1}44]_{\alpha}$

### 3.3. Hardness measurements

The results of hardness measurements are presented on Figs. 14-16. The hardness profile for the examined samples shows that after aging at 480°C hardness of the weld is the

largest. The significant drop of hardness at 540°C is observed in the weld and HAZ. The weld metal did not changed its hardness in comparison with the sample heat treated at 480°C. The overaging at 620°C caused significant decrease of hardness in the weld below 400 HV10, while the corresponding value in the weld metal decreased to ca. 350 HV10.

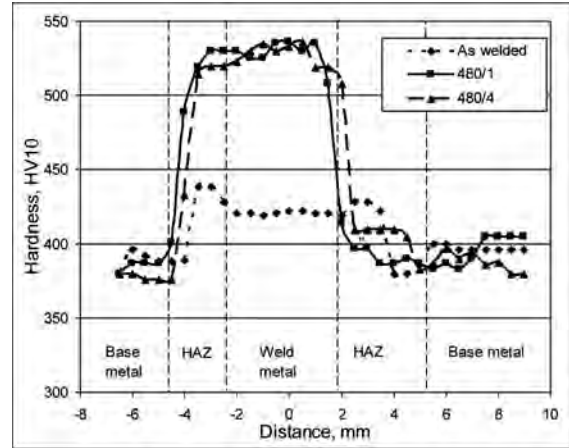


Fig. 14. Distribution of hardness vs. distance after welding and aging 480°C /1h, 480°C/4h

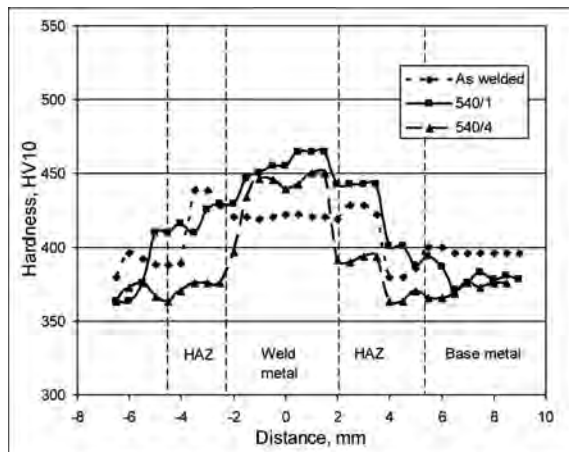


Fig. 15. Distribution of hardness vs. distance after welding and aging 540°C/1h, 540°C/4h

The changes in hardness depend on the temperature and time of tempering. At the temperature 480°C the highly dispersive coherent precipitations of copper are strongly contributing to hardening of the alloy. This influences the high hardness at this temperature. Due to the fact that the drop of hardness at 540°C was small, it can be concluded that the coherence of the hardening precipitates at this temperature is still preserved. A distinct decrease of hardness after treatment at 620°C is caused by overaging of the martensite and formation of austenite. After the prolonged overaging at this temperature, copper diffuses to the grain boundaries and boundaries of the martensite laths. This is the reason of the depletion of martensite in copper and other chemical elements stabilizing the austenite [4]. Furthermore, the character of weld solidification is attributed with strong segregation of the elements that promote formation of austenite at grain boundaries. This causes that these regions are enriched in the elements decreasing the  $A_{c1}$  temperature. Depending on the stability, the austenite formed during the

cooling transforms into “fresh” martensite or remain as the austenite in the vicinity of martensite.

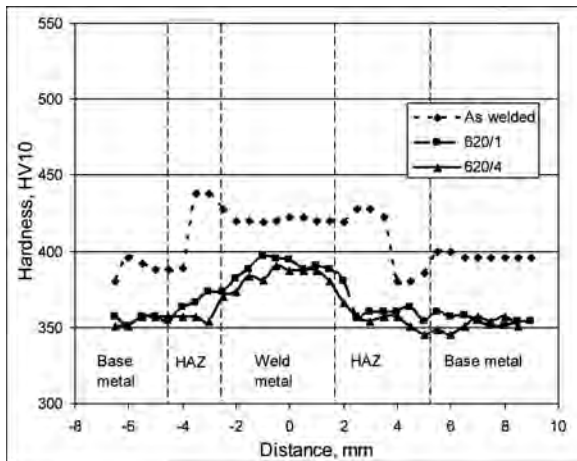


Fig. 16. Distribution of hardness vs. distance after welding and aging 620°C/1h, 620°C/4h

#### 4. Summary

The aging of X5CrNiCuNb16-4 (17-4 PH) steel leads to the tempering of the martensitic microstructure and precipitation of the carbides and strengthening phases. The hardness decreases with the increase of the aging temperature above 540°C. The reason of the hardness decrease is the drop of the dislocation density and the reverse transformation of martensite into austenite. The maximum hardness will occur in the welds aged at 480°C and 540°C where the copper-rich strengthening particles coherent with the matrix are uniformly distributed in the alloy. The increase of the aging temperature leads to intensification of the precipitation processes and the increase of the diffusion rate of alloying element in the steel. Non-equilibrium solidification conditions of the weld metal, segregation and the diffusion of copper and the elements stabilizing the austenite promote the occurrence of the reverse transformation of the martensite into austenite even after only 1 hour at 620°C. As the base material was in the as-aged condition at 540°C, its hardness during the heat treatment at 570°C did not change significantly. Annealing at 620°C caused the decrease of the hardness in the base material down to 350 HV10.

Transmission electron microscopy investigations showed that the aging of the welds with the martensitic microstructure at 620°C causes an intensive precipitation of the strengthening copper-rich particles. The size of the particles increases with the aging time. There are  $M_{23}C_6$  carbides precipitate on the boundaries of the primary crystallites what is accompanied by

the presence of the thin film of austenite. The retained austenite occurs inside the grains and at the grain boundaries of martensite laths. The increase of the aging time up to 4 hours results in the formation of the austenite due to the  $\alpha \rightarrow \gamma$  transformation. Such austenite is stable after cooling down to the ambient temperature.

#### Acknowledgements

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