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STUDY OF HETEROGENEOUS WELDS OF HEAT RESISTANT STEELS WITH ARTIFICIALLY INCREASED NITROGEN CONTENT BY COMBINATION OF EXPERIMENTAL AND COMPUTATIONAL TECHNIQUES

BADANIE WIELOFAZOWYCH SPOIN SPAWALNICZYCH W STALACH ŻAROODPORNYCH ZE SZTUCZNIE PODWYŻSZONĄ ZAWARTOŚCIĄ AZOTU METODAMI EKSPERYMENTALNYMI I OBLICZENIOWYMI

The paper presents results of experimental and simulational survey of weld joints of steels with enhanced nitrogen content. The steels CSN15128 (13MoCrV6), P91(X12CrMoWVNbN10-1) and 6CrMoV8-3-2 depicted as T25 were nitrided at 500 °C for 80 hours and then homogenized. Experiments and simulations were performed for annealing temperatures rating from 500 to 900 °C and times from 1000 to 16 hours. Thermodynamical calculations showed higher MX and M_7C_3 content in the low alloyed steels after nitriding. For P91 the calculation showed displacing of $M_{23}C_6$ by M_2X and MX. Activity calculations for nitrogen and carbon in all materials yielded activity gradients aiming to the high alloyed steel in temperature range up to 900°C.

Experimentally all the joints showed simultaneous diffusion of carbon and nitrogen to the P91 material. Nitrogen was concentrated close to the welding boundary, while carbon penetrated deeper into P91. MX and M_7C_3 were identified in the low alloyed materials, M_7C_3 being gradually dissolved with lowered carbon content. P91 being further enriched with carbon and nitrogen shows growing population of MX and M_2X. Experimentally acquired values are compared to values achieved by simulations using DICTRA software package.

Keywords: Calphad, Diffusion profile, Creep-resistant steel, Weld joint

Artykuł przedstawia wyniki analizy połączeń spawanych stali o podwyższonej zawartości azotu na podstawie badań doświadczalnych i symulacji. Stale CSN15128 (13MoCrV6), P91 (X12CrMoWVNbN10-1) oraz 6CrMoV8-3-2, oznaczona jako T25 były aztowane w temperaturze 500 °C przez 80 godzin, a następnie homogenizowane. Eksperyment oraz symulacja dotyczyły temperatur wygrzewania z zakresu 500 do 900 °C oraz czasów od 1000 do 16 godzin. Obliczenia termodynamiczne wykazały wyższą zawartość MX oraz M_7C_3 w stali niskostopowej po azotowaniu. Dla stali P91 obliczenia wykazały, że $M_{23}C_6$ jest zastępowany przez M_2X i MX. Z obliczeń aktywności azotu i węgla we wszystkich stalach wyznaczono gradienty ich aktywności w zakresie temperatur do 900 °C. Eksperyment wykazał, że we wszystkich połączeniach wystąpiła dyfuzja węgla i azotu do stali P91. Azot występował w pobliżu granicy spawu, natomiast węgiel penetrował głębiej do stali P91. MX oraz M_7C_3 zostały zidentyfikowane w stalach niskostopowych, przy czym M_7C_3 ulegał stopniowemu rozpuszczeniu w stali niskostopowej. Stal P91, która była dalej wzbogacana w węgiel i azot wykazuje rosnącą populację MX i M_2X. Wartości uzyskane na drodze eksperymentu zostały porównane z wartościami uzyskanymi z symulacji przy pomocy pakietu oprogramowania DICTRA.

1. Introduction

Considering power production demands of present day and the technology available for power production, conventional coal power plants and nuclear power plants play decisive role as main means of power supply. The reconstruction of these facilities or the construction of new ones always has as one goal higher energy transformation efficiency. This largely means higher working temperatures or higher stresses and among others also longer service intervals. Alongside with these demands there is persistent development of creep resistant steels [1,2]. Power generating units represent complicated systems where large number of different steel materials is used and very often, two materials that differ in chemical composition need to be welded together. Moreover, usually such welds need to operate at high temperatures. This enables transport of interstitial atoms in the materials and leads to redistribution of carbon, nitrogen and hydrogen. As a result of this the structure of the

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welded materials and the weld metal can be weakened. Substitutional atoms have much lower mobilities at the conditions that may come into consideration, therefore only the interstitial constituents redistribution is closely studied.

Usually a depleted zone develops on the side of the low-alloyed material and high population of new phases form on the high alloyed side of the weld. Both these effects are considered as negative. The depleted zone lacks precipitation strengthening and suffers grain coarsening; in the enriched zone phases that tend to grow rapidly can evolve thus weakening the weld even more [3-5]. Since apart from carbon, nitrogen is also being intentionally introduced in creep resistant steel materials, its behaviour in heterogeneous welds during high temperature exposition is gaining relevance [5,6]. However, the nitrogen contents are usually not high enough to enable reliable analyses of chemical changes in welds. The present work shows results of study where materials were treated in such way, that detection of both nitrogen and carbon were well possible

2. Experimental material

ČSN 15128 (13MoCrV6), T25 (6CrMoV8-3-2) and P91 (X12CrMoWVNbN10-1) steels were nitrided at 500 °C for 80 hours and then homogenized by means of annealing. The chemical composition of the base non-nitrided materials can be found in tab.1.

TABLE 1

Chemical composition of the used materials [weight%]

	C	Mn	Si	P	S	Cr	Mo	V	B	Al	N	Nb	Fe
T25	0,06	0,42	0,34	0,012	0,011	1,91	0,31	0,22	0,003	0,009	0,024	0,058	bal.
15128	0,13	0,60	0,31	0,012	0,022	0,58	0,47	0,25	–	–	–	–	bal.
P91	0,12	0,38	0,44	0,010	0,003	9,96	0,89	0,22	–	0,010	0,069	0,070	bal.

After the steels were homogenized, the nitrogen content in the T25 steel was at 0,113±0,07 wt %. For the simulation purposes, this value was set to 0,113wt%. The content of nitrogen in the 15128 steel after nitridation was set to 0,08wt%. P91 steel showed even after homogenization uneven distribution of nitrogen over the sample thickness. Areas near the surface showed values as high as 0,9wt%, while the value decreased towards middle of the specimens to original untreated state value of 0,07wt%. For the simulation purposes, the nitrogen content profile could be represented by exponential function $N^{**} = 0,85\ \exp^{-1,83x}$ where x is the distance form sample surface in millimetres. This function was found to be valid till the depth of 1,5mm from the sample surface.

3. Used methods

Small cylindrical samples of 12mm diameter and 5mm height were prepared from all of the materials. Samples of T25 and 15128 were subsequently nitrided. The samples were then welded by means of electric current shock so that no detectable mixing zone was formed. [1] These diffusion pairs were then sealed in evacuated glass capsules and annealed. All measurements after the annealing were carried out on metallographic samples prepared perpendicularly to the weld plain. WDX analyzer of the electron microscope Philips XL30 was used for measuring both interstitial and substitution elements content. Thermodynamical calculations and simulations were carried out using the Thermocalc-DICTRA software package [7,8]. DICTRA software is widely recognized as standard tool for simulations of changes in dissimilar welds [9]. It makes use of the CALPHAD [7] approach assuming the local equilibrium condition and handles diffusion as the process that controls the phase transformation rate in the weld. For handling the diffusion, the theory of multicomponent bulk diffusion, atomic mobilities and gradients of chemical potentials of the elements are considered [10,11]. Thermodynamic database Steel16 and Dif kinetic database were used for the calculations [12-14].

4. The acquired results:

Two types of welds were prepared from the samples. Combinations of the nitrided T25 and nitrided P91 and pairs consisting of nitrided 15128 and P91 in original state were selected. Annealing experiments for following temperature and times were carried out on nitrided 15128 / P91 pair: 900°C/16h, 625°C/160h, 575°C/320h and 500°C/1000h. The nitrided T25 / nitrided P91 pair was subdued to annealing at 900°C/18h, 600°C/ 240h and 500°C/1000h. Each weld was quenched in water after the annealing period. Results for the annealing experiments and simulations of 625°C/160h and 600°C/ 240h applicable to the respective weld pairs are shown in this paper.

First, the Thermocalc software was used to calculate equilibria in all of the materials both in nitrided and original state. The materials were approximated by using system with following constituents: Fe-Cr-Mo-V-Nb-N-C. The calculations showed that due to nitriding of the 15128 and T25 steels the content of MX and M_7C_3 minority phases in these materials is enhanced. The same calculation for P91 steel showed that with the nitrogen content rising the $M_{23}C_{+}6$ carbide is being substituted by carbo-nitride M_2X and at higher temperatures by carbo-nitride MX. Calculations of activity values for nitrogen (fig. 1,2) and carbon (Fig.3,4) were done for all materials at original composition and after nitriding. All the samples were analyzed to determine the chemical profiles after the annealing experiments and to determine the phase composition across the weld boundary. In all cases, diffusion of nitrogen and carbon from the low alloyed material was detected, forming a complex chemical profile on the high alloyed side with nitrogen fixed close to weld interface and carbon diffusing deeper into the high alloyed material. Experimental values and simulation results of chemical profiles for annealing at 600°C/ 240h of nitrided T25-nitrided P91 weld can be seen at fig.5 (carbon profile) and fig.6 (nitrogen profile). Experimental values and simulation results of chemical profiles for 625°C/160h annealing conditions of nitrided 15128- P91 pair are in fig.8 (carbon profile) and fig. 9 (nitrogen profile). Figs.7 and 10 show the calculated phase profiles for the two experiments.

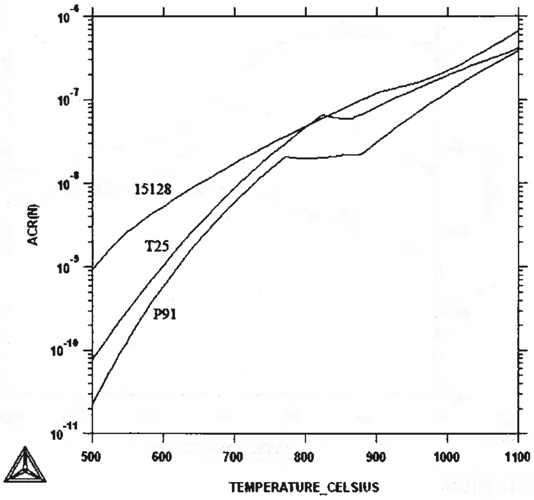

Fig. 1. Nitrogen activity in the steels in original chemical composition

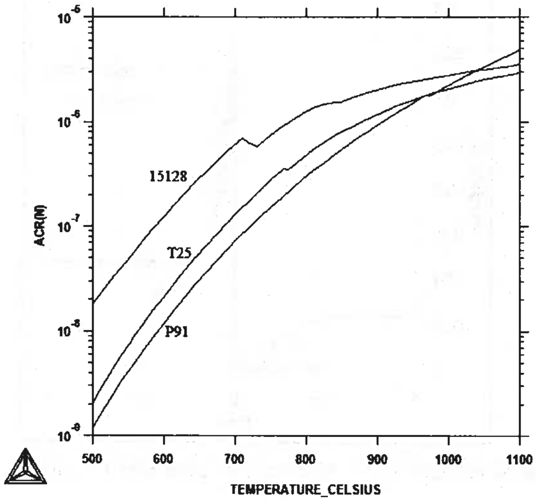

Fig. 2. Nitrogen activity in the steels after nitridation

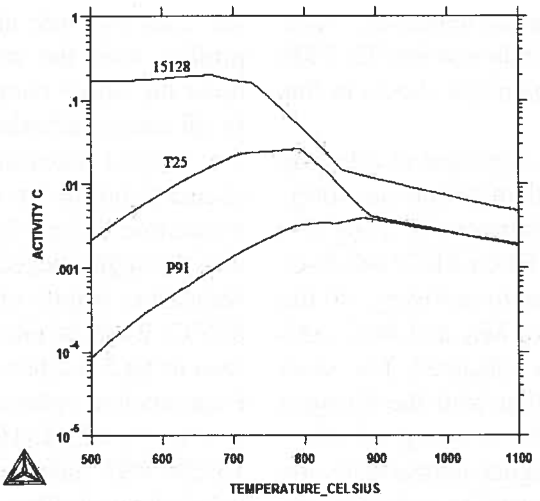

Fig. 3. Carbon activity in the steels in original chemical composition

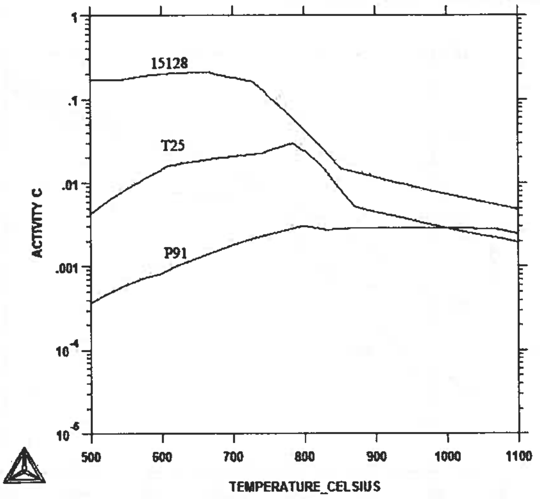

Fig. 4. Carbon activity in the steels after nitridation

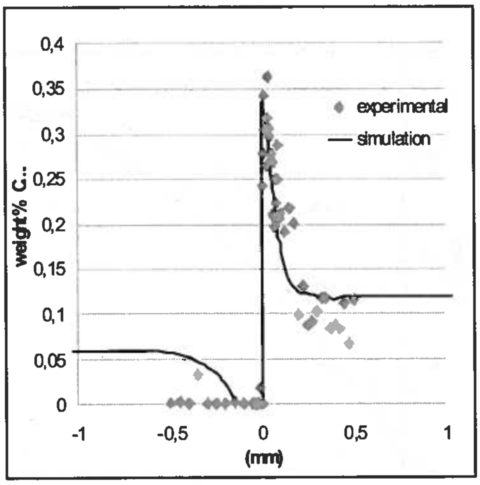

Fig. 5. Carbon weight% profile in the weld of nitrided T25 – nitrided P91 after 600°C/ 240h

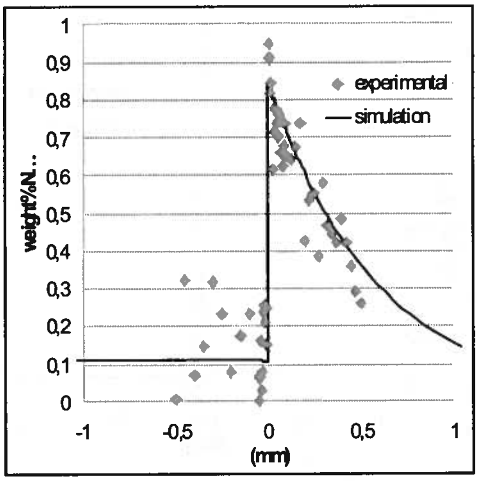

Fig. 6. Nitrogen weight% profile in the weld of nitrided T25 – nitrided P91 after 600°C/ 240h

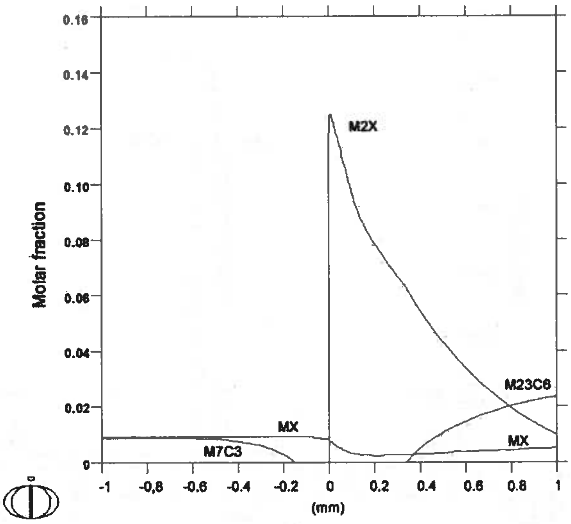

Fig. 7. Phase content profile in the weld of nitrided T25 – nitrided P91 after 600°C/ 240h

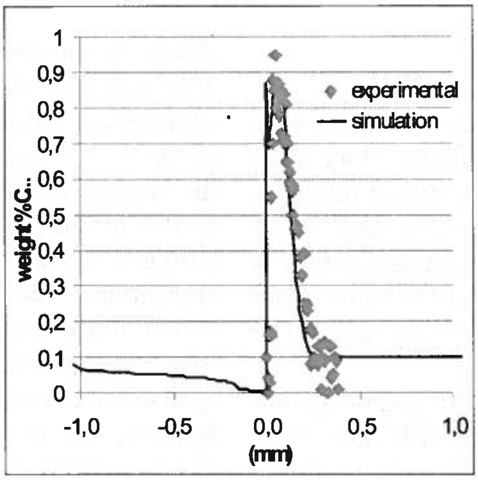

Fig. 8. Carbon weight% profile in the weld of nitrided 15128 – P91 after 625°C/160h

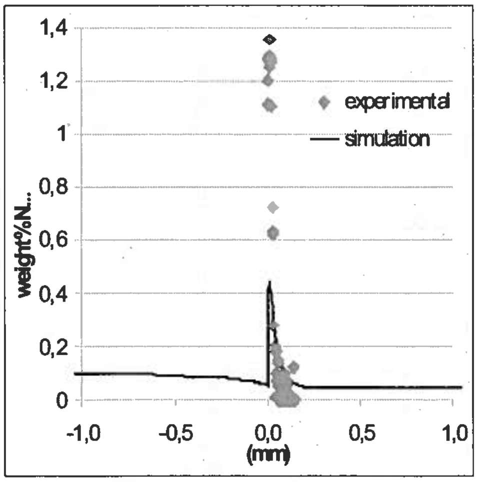

Fig. 9. Nitrogen weight% profile in the weld of nitrided 15128 – P91 after 625°C/160h

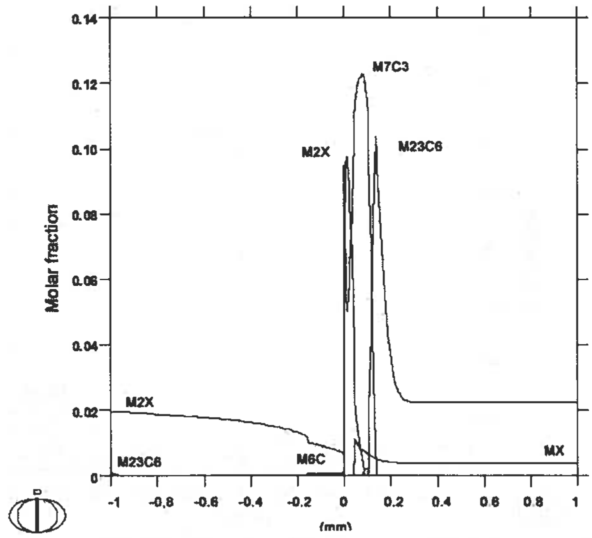

Fig. 10. Phase content profile in the weld of nitrided 15128 – P91 after 625°C/160h

5. Discussion:

From the calculations of carbon and nitrogen activity calculations it is apparent, that in the case of the studied systems, chromium content has the highest influence on these interstitial element's activities. The direction of gradient slope of both the carbon and nitrogen activity is during the high temperature exposition till 900°C from the low alloyed materials in to the P91or nitrided P91 in both examined weld combinations.

During the simultaneous diffusion of carbon and nitrogen from the lower alloyed materials T25 and 15128 into the high alloyed P91 the two interstitial elements concurred and the resulting chemical profiles were result of mutual influence. Nitrogen is being fixed near the weld boundary in carbo-nitrides M_2X and nitrides MX and thus forces carbon to diffuse further in the P91 material. This interaction of carbon and nitrogen was experimentally observed in all of the examined welds. While the nitrided P91 steel could not be homogenized after nitriding, the diffusion profile of nitrogen and the concurence with carbon is not as distinctive in the nitrided T25- nitrided P91 welds [15]. On the other hand, the nitrided 15128-P91 pairs showed distinct shift of the carbon profile away from the weld boundary. This concurrence was in agreement with the results of diffusion simulations. The resulting phase profiles from this diffusion always carry the same characteristic features. On the side of the lower alloyed steel, the carbides can totally dissolve and content of nitrides and nitro carbides is lowered, also at lower temperatures, Mo rich M_6C carbides can form near the weld boundary. The high alloyed material forms M_2X phase directly at the weld boundary, followed by carbide sequence of M_7C_3 and $M_{23}C_6$. MX carbonitride, being thermodynamically very stable, either forms a sequence with M_2X on the high alloyed side (as in nitrided15128-P91) or is present in the whole weld during all annealing experiments, which is the case of nitridedT25 – nitridedP91 pairs [15]. The increase of nitrogen content in P91 steel can be considered to reduce the diffusion of carbon from lower alloyed steels and the formation of depleted zones in the low alloyed parts of the welds.

6. Summary

The experiments and computational simulations were aimed at description of changes of chemical composition in heterogeneous welds during situations, when measurable diffusion of both nitrogen and carbon occurs. To achieve this, experiments used materials that considering their high nitrogen content do not correspond to industrially used materials. Nevertheless, the use of these altered materials allowed reliable identification of nitridic phases and the measurements of nitrogen and carbon concentration profiles over the weld boundary. The acquired experimental results are in good accordance with computations results of phase compositions and chemical profiles with exception of nitrogen maximum concentration in nitrided15128-P91 weld. However the phase profile does correspond to experimental results well. Regarding this, we can expect that the simulations results can be used as valuable information also in cases when real materials whit realistically low nitrogen content are involved

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