

Carbon and Nitrogen Redistribution in Weld Joint of Ion Nitrided 15CrMoV 2-5-3 and Advanced P91 Heat-Resistant Steels

J. Sopotšek and R. Foret

(Submitted January 5, 2006; in revised form June 9, 2006)

The present contribution compares the theoretical modeling of the kinetics of the development of chemical composition and phase profiles of heterogeneous laboratory weld joints of heat-resistant steels after long-term annealing with earlier experimental results. The weld joints of ion-nitrided 15CrMoV 2-5-3 low-alloy ferritic steel and the advanced P91 steel (X10CrMoVNb 10-1) are the subject of study. The long-term annealing of the (nitrided 15CrMoV 2-5-3) | P91 weld joint was simulated at 500 to 700 °C (i.e., 773 to 973 K). The simulated results were compared with earlier experimental carbon and nitrogen profile measurements. The phase diagrams of the investigated materials were calculated using the CALPHAD approach making use of the STEEL thermodynamic database. The activities of both carbon and nitrogen were calculated by the same method. The CALPHAD approach complemented with an appropriate diffusion model given in the DICTRA program enabled a simulation of the phase and element profile evolutions inside the diffusion-affected zone of weld joint. The DIF kinetic database was used to describe the diffusion. The coexistence of different phases (carbides, carbonitrides, and so forth) was considered in the simulations. The results show very reasonable agreement between experiment and theoretical simulation, and the method used is very promising for further weld design.

Keywords CALPHAD, carbide, carbonitride, diffusion profile, transformation

1. Introduction

In view of the wide field of application of heat-resistant ferritic steels with different contents of individual alloying elements, welding these steels poses serious technical problems, not only in the design of welds for new creep-stressed equipment but also in the reconstruction of older technological units and machinery. The differences in the chemical composition of welded steels and filler metals have a fundamental effect on the resultant stability of the mechanical properties of weld joints and multilayer weld deposits after long-term exposure. This factor needs to be taken into consideration, in particular for high-temperature technological units in power and incineration plants (repairing the inner walls of combustion chambers by protective weld deposits of corrosion-resistant materials in places damaged by aggressive waste gases) and for chemical technologies, and also for all designs of new technologies that should be more effective, reliable, and environment-friendly (such as gas turbine rotors in power plants under supercritical conditions^[1]). Thus in a great number of technologies the long-

term stability of the mechanical properties of welds influences the reliability and overall service life of a number of technological units, and appropriate weld solutions can fundamentally affect the financial cost of reconstruction.

The present work concerns the effect of nitriding on the behavior of the weld joint of two ferritic heat-resistant steels of different chemical composition (Table 1). One steel 15CrMoV 2-5-3 (referred to hereafter as LA) represents a low-alloy material that has been used frequently in the past. The other steel, X10CrMoVNb 10-1 (referred to hereafter as P91) represents a more advanced series of alloyed steels with high chromium content. The other significant alloying elements of the P91 material are Mo, V, and Nb. Markedly better mechanical properties of the P91 steel can be obtained by a heat treatment that leads to the appearance of a microstructure, which, among other things, is strengthened with fine dispersed particles of mixed carbonitride MX.

In this work it is assumed that long-term stability of the mechanical properties of the weld joints of these two different steels is closely related to the changes in the phase and chemical compositions near the weld joint, which at the temperatures of expected high-temperature exploitation is affected in particular by carbon and nitrogen diffusion. Preceding experimental^[2] and theoretical^[3] studies of welds of nonnitrided initial materials, LA and P91, have shown that during long-term thermal exploitation a wide carbon-depleted zone appears on the low-alloy LA side. The reduced mechanical properties in the carbon-depleted zone of low-alloy material in comparison with the properties in that part of this material that has not been affected by diffusion could be compensated for by a slow dissolution of the

J. Sopotšek, Faculty of Science, Masaryk University of Brno, Czech Republic; and R. Foret, Department of Materials Science, Faculty of mechanical Engineering, Brno University of Technology, Czech Republic. Contact e-mail: sopotsek@chemi.muni.cz.

Table 1 Chemical compositions of base 15CrMoV 2-5-3 steel (Czech standard CSN 15128 (LA), X10CrMoVNb 9-1 steel (P91), and nitrided material LA (LA + N)

Material	Abbreviation	Composition, wt. %											
		C	Mn	Si	P	S	Cr	Ni	Mo	V	Nb	N(a)	N(b)
15CrMoV 2-5-3	LA	0.13	0.60	0.31	0.015	0.022	0.58	0.07	0.47	0.52	0.00	0.000	0.48 exp(-1.348x)
X10CrMoVNb 9-1	P91	0.10	0.40	0.43	0.012	0.006	8.50	0.10	0.88	0.23	0.018	0.045	0.045

(a) Nitrogen content in base steels. (b) Nitrogen content in the LA + N material; x (in mm) gives the distance from the surface for the LA + N material.

Table 2 Phase abbreviations used in the figures

Phase	Austenite	Ferrite	M ₂₃ C ₆	M ₇ C ₃	Cementite	M ₆ C	M ₂ X carbonitride	MX carbonitride
Abbreviation	fcc	bcc	M23	M7	M3	M6	M2	MX

strengthening carbide phase of the type of MX. On the other hand, a carbon-enriched zone forms near the weld interface on the P91 side. Although carbon redistribution in the initial LA/P91 welds after different periods of thermal exposure was experimentally proved and measured,^[2] nitrogen redistribution could not be proved by the analytical methods used (wavelength dispersive analysis of x-ray, or WDAX). In the next stage, surface nitriding of low-alloy material LA was undertaken with the aim of examining the behavior of nitrided materials (referred to hereafter as LA + N) in weld combination with material P91 that was not treated by nitriding. The successfully measured experimental redistributions of carbon and nitrogen in LA + N/P91 weld joints under different exposure conditions were presented in a research report with further detailed experimental results.^[4]

This article follows up on the aforementioned experimental work^[4] on a theoretical level by applying an approach described below,^[5,6] which makes it possible to simulate the behavior of the experimental weld joints under examination, exposed to different thermal conditions, and to explain the experimentally established facts.

2. Experiment

The joints were prepared from base low-alloy ferritic steel LA (15CrMoV 2-5-3) and the advanced chromium steel P91 (X10CrMoVNb 10-1). See Table 1 for composition.

The shortened experimental procedure was as follows. Samples of coinlike shape (about 12 mm in diameter and 4 mm in width) were prepared from the low-alloy ferritic steel LA and from the advanced chromium steel P91. The samples of the LA steel were ion-nitrided 60 h at 510 °C. A nitride case of about 2 mm in thickness and a maximum surface nitrogen concentration of 0.48 wt.% N (see the exponential fit function in Table 1) was prepared by such procedure. These samples (LA + N) were individually joined with the P91 samples by electric discharge welding. The prepared LA + N/P91 weld joints were annealed at 500 °C/1000 h, 575 °C/320 h, 625 °C/160 h, and 700 °C/65 h, and quenched in water.

The heat treated weld joints were cut perpendicular to weld joint interface and investigated. The detailed microstructures after grinding, polishing, and etching have been reported^[4] along with carbon and nitrogen analyses and microhardness measurements.

3. Equilibrium Prediction

The CALPHAD approach^[5] and the STEEL thermodynamic database^[7] were used for the solution of both local and global phase equilibrium problems concerning the base steels (LA and P91), nitrided material (LA + N), and weld joints [(LA + N) | P91]. The approach allows the calculation of chemical compositions of equilibrated phases at a given temperature as well as cross sections of the phase diagram for these steels. Also very important is the possibility of calculating the chemical potentials and activities of elements. A detailed description of the method has been included in previous reports.^[3,8-10]

The base steels, nitrided material, and weld joints were approximated as the Fe-Cr-Mn-Mo-V-N-C thermodynamic system (compare with elements in Table 1). The remaining elements were neglected or excluded from calculations for reasons previously given.^[11] A list of phases is given in Table 2, and the procedure for treating these phases is the same as earlier applied to other phases.^[3]

Figure 1 shows a temperature composition plot illustrating the effect of changing carbon composition on phase stability in an LA steel, the composition of which is shown in Table 1. This shows that the phase composition of this low-alloy steel is generally very sensitive to the balance of alloying elements. Putting it very simply, it can be stated that the phase diagram of the basic Fe-C system is modified mainly by the presence of: chromium (which stabilizes the chromium-rich M₇C₃ carbide in the LA steel), vanadium (which forms MX carbonitrides but here, in the nitrogen-free base LA material, the composition corresponds to the MC carbide phase), molybdenum (which stabilizes the molybdenum-rich M₆C carbides in the lower temperature range), and manganese (which stabilizes the M₂X carbonitride and which in the base LA steel is present in the form of nitrogen-free M₂C carbide).

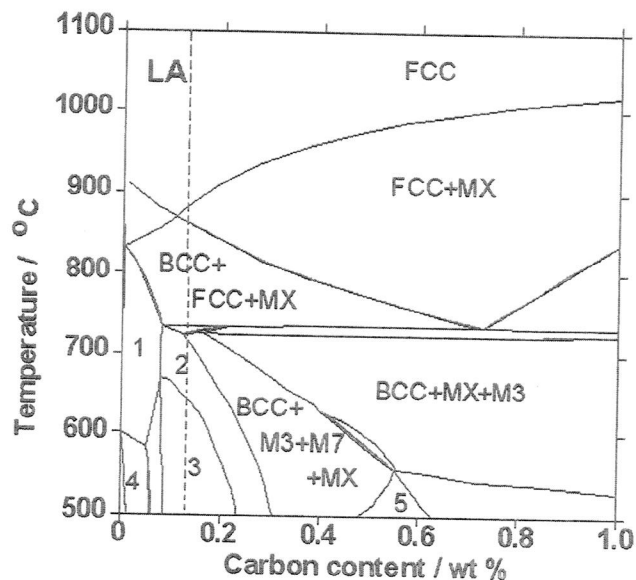


Fig. 1 Phase diagram for base LA steel (Fe-Cr-Ni-Mo-Mn-V-C-N thermodynamic system). Dashed line represents carbon content. Phase fields: 1, bcc + MX; 2, bcc + MX + M7; 3, bcc + MX + M7 + M2; 4, bcc + MX + M6; 5, bcc + MX + M23 + M7

The equilibrium calculations show that the phase composition of material LA + N is similar to that found in Fig. 1 for steel LA. The main difference between LA and LA + N materials is the increasing amount of MX and M_2X carbonitride phases and the progressive replacement of carbon with nitrogen in carbonitride lattices (see Sopoušek et al.^[11] for details at 625 °C).

The phase diagram of the P91 steel (having composition identical to that given in Table 1) can be also calculated in the same way. If the equilibrium state is reached for P91, the coexisting phases are bcc + MX + $M_{23}C_6$ at 530 to 810 °C. In addition, the M_6C phase can be found below 525 °C. The P91 diagram has been presented in Ref 11 together with an example of isothermal (625 °C) phase diagram cross section showing the equilibrated phases inside the P91 material for different nitrogen and carbon contents. Equilibrium calculations show that the M_2X carbonitride is stable in P91 at 625 °C if the nitrogen content exceeds 0.08 wt.% of N. The MX carbonitride dissolves in P91 at approximately 1150 °C.

The evaluation of the thermodynamic activities of individual elements in the steels and nitrided materials with respect to standard element reference (SER)^[12] is an important result of phase equilibrium calculations. Each element tends to diffuse to a place that lowers its activity, and its diffusion flux is proportional to element mobility.^[13] The activity difference of a given element in the two different materials can be used as a rough approximation for judging weld joint stability judgment.^[14] In the case of the microstructural evolution of the weld joints LA + N/P91, carbon and nitrogen are most important because they diffuse most quickly. It has been experimentally verified that the chemical concentrations of the individual substitute metals change in a region within a weld interface of less than 5 μm in thickness.

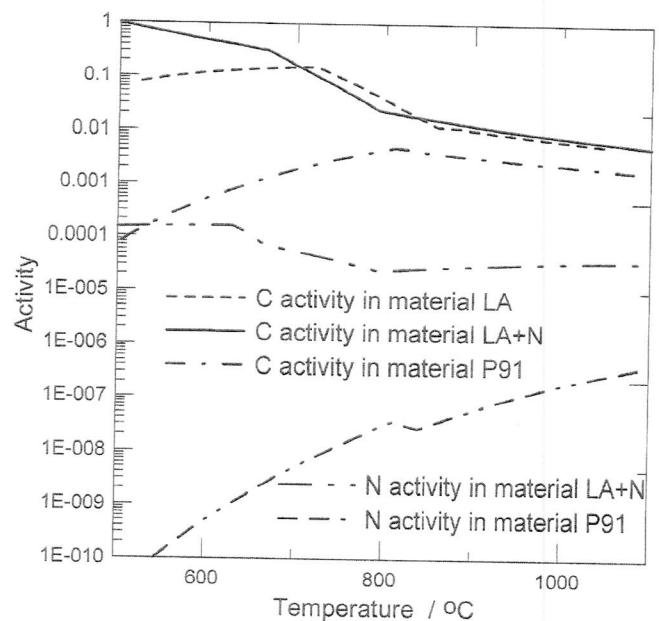


Fig. 2 Simulated temperature dependencies of carbon and nitrogen activities of investigated base steels (LA, P91) and surface-nitrided steel LA-N for maximum nitrogen on the surface.

The temperature dependence of the carbon and nitrogen activities for the two base steels (LA, P91) and of the surface of nitrided material LA + N are shown in Fig. 2. Despite of the higher carbon content (0.13 wt.%) in the P91 material and the lower carbon content (0.10 wt.%) in the LA + N material, formation of a couple from these materials (Fig. 6) shows that the carbon will diffuse from LA + N to P91 (i.e., an “uphill” diffusion of carbon). The absolute value of nitrogen activity is much less than that of carbon activity. The nitrogen activity in LA + N is higher than in the P91 steel. The nitrogen tends regularly to diffuse from the nitride case to the P91 steel in agreement with the sign of the concentration difference between nitrogen contents in P91 and LA + N. The high phase fraction of nitrogen-rich fine precipitates was observed using electron microscopy near weld interface in material P91. It should be noted that the nitrogen diffuses simultaneously also to the opposite side—to the nitrogen-free bulk of the LA + N material because the nitrogen activity is equal to 0 in such a region at any temperature, and the nitrogen solubility in the body-centered cubic (bcc) diffusion matrix is very low.

4. Diffusion Simulations

The different experimental heat treatments (500 to 700 °C) of the (LA + N) | P91 weld joints were computer simulated. Each joint was approximated as two dissimilar Fe-Cr-Mo-V-C-N systems being in diffusional contact (the so-called diffusion couples). Steplike overall starting element profiles were assumed for all elements excluding nitrogen in the nitrogen case of the LA + N material (see the fit function in Table 1). The DICTRA program,^[15] which contains subroutines for the CALPHAD method,^[5] was used as a tool for such simulations.

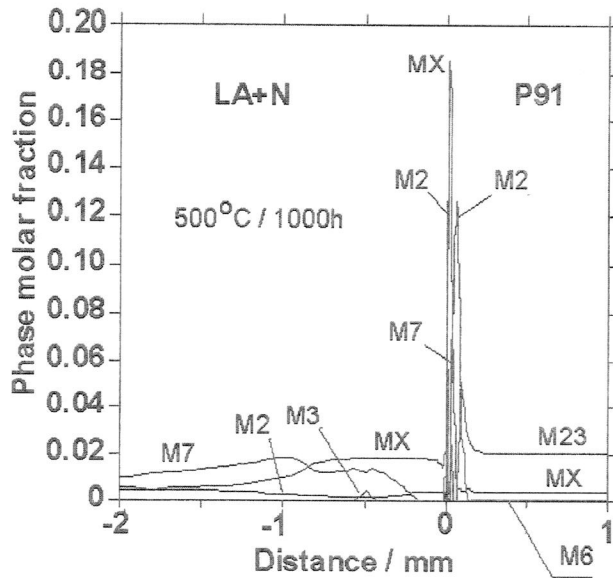


Fig. 3 Simulated phase profiles of LA + N/P91 weld joint after annealing at 500 °C/1000 h

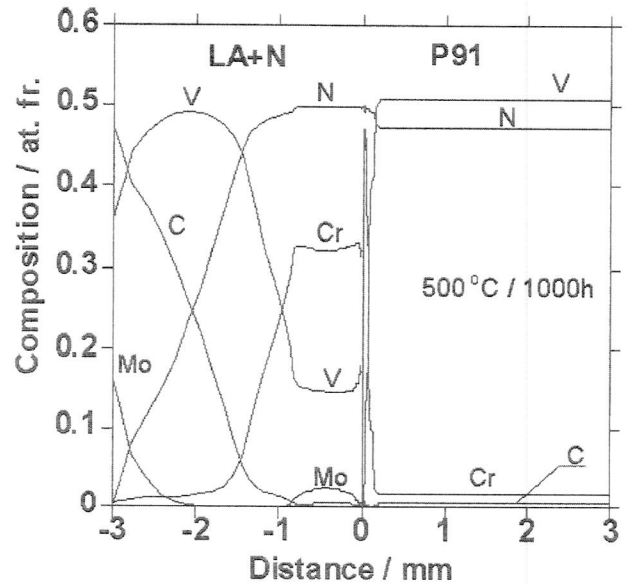


Fig. 4 Simulated MX phase composition profiles of LA-N/P91 weld joint after annealing at 500 °C/1000 h

The DICTRA program embodies the assumption of local equilibrium, the assumption that diffusion is the controlling process of the phase transformation rate,^[16,17] multicomponent diffusion theory,^[13] and the gradients of chemical potentials (activities) of the elements are considered for mass flux evaluations. The individual diffusion couples were treated by the same approach as described in Ref 3 and 14. A diffusion matrix formed from the bcc (500 to 700 °C) phase was assumed. It used one-dimensional geometry with a double-geometric grid.

The carbides and carbonitrides in Table 2 were treated as diffusion-free phases in local phase equilibrium with the bcc diffusion matrix. The STEEL thermodynamic database^[7] and the DIF kinetic database^[31] were used to simulate the LA + N | P91 weld joints. The simulation results have been plotted to show the dependence of selected values (mole fractions of phases, overall concentrations of elements, phase composition) on distance at selected times (Fig. 3-9).

The results of the simulation for 500 °C and 1000 h are given in Fig. 3 to 6. The uphill carbon diffusion and the regular nitrogen diffusion division between the P91 steel and the nitrogen-free bulk of the LA + N material can be observed at this temperature and also at higher temperatures. More detailed results of simulations at 625 and 700 °C have been presented in a previous report.^[11]

Nitrogen diffusion is slow due to a low nitrogen content in the diffusion bcc matrix (nitrogen solubility: 10^{-7} to 10^{-6} wt.%) in consequence of the high thermodynamic stable MX carbonitride in the nitride case. The same effect occurs in P91 steel, where nitrogen forms highly stable MX and M_2X carbonitrides with chromium and vanadium. This results in a high nitrogen peak close to the weld interface on the P91 steel side.

The carbon-depleted zone (CDZ) is formed close to the weld joint interface in the LA + N material (Fig. 6 to 9). The width of CDZ depends on annealing conditions. The for-

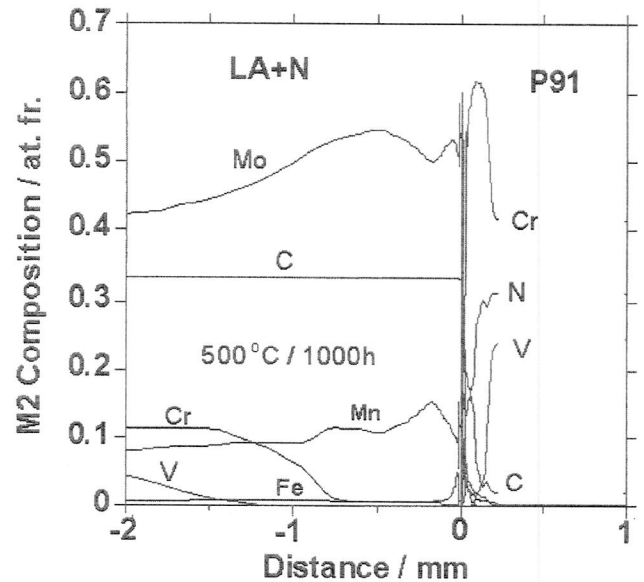


Fig. 5 Simulated M2 (i.e., M_2X) composition profiles of LA + N/P91 weld joint after annealing at 500 °C/1000 h

mation of the CDZ is primarily caused by the dissolution of M_7C_3 carbide (Fig. 3). The carbon-enriched zone (CEZ) inside the P91 material results from the nitrogen-rich region (Fig. 6 to 9). The CEZ is formed due to formation of $M_{23}C_6$ and M_7C_3 carbides (Fig. 3).

It is obvious that one of the most important results of the simulations is the phase composition profiles (example in Fig. 3) because the mechanical properties are closely related to phase composition. It can also be demonstrated that the composition of an individual phase in equilibrium with the other phases varies with the distance from weld joint interface. As for composition, the most variable phases are the

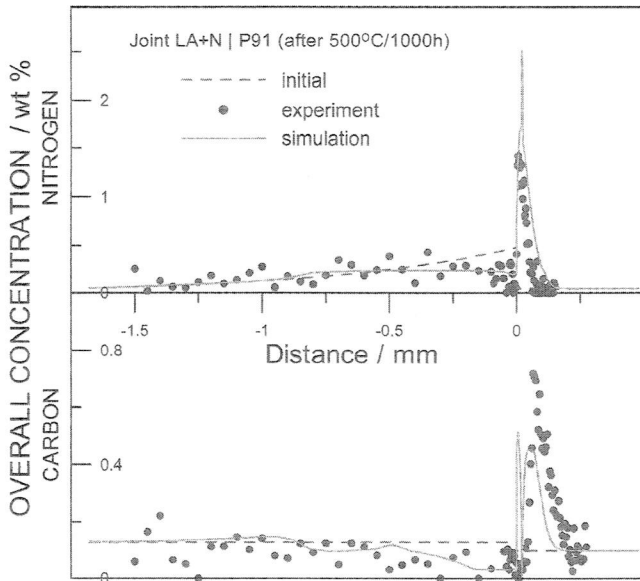


Fig. 6 Simultaneous carbon and nitrogen diffusion. Initial (starting), experimental, and simulated overall carbon and nitrogen profiles of LA + N/P91 weld joint (annealing at 500 °C/1000 h)

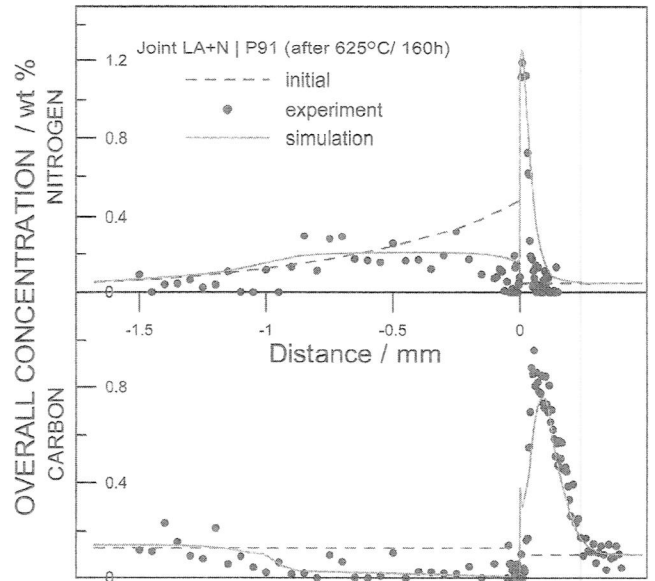


Fig. 8 Simultaneous carbon and nitrogen diffusion. Initial, experimental, and simulated overall carbon and nitrogen profiles of LA + N/P91 weld joint (annealing at 625 °C/160 h)

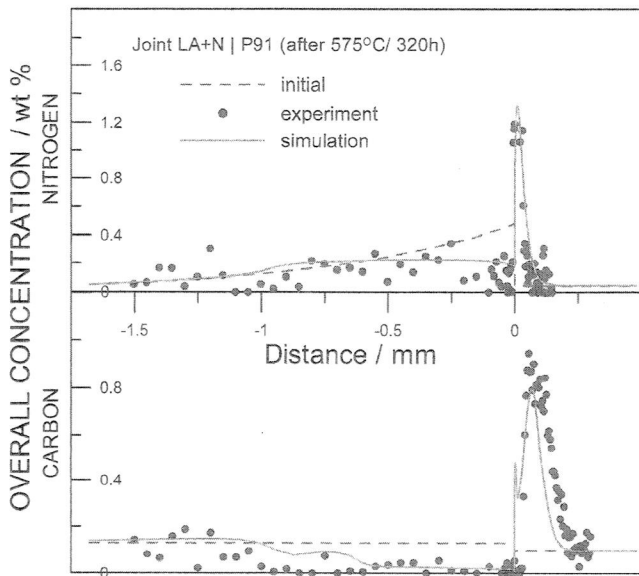


Fig. 7 Simultaneous carbon and nitrogen diffusion. Initial (starting), experimental, and simulated overall carbon and nitrogen profiles of LA + N/P91 weld joint (annealing at 575 °C/320 h)

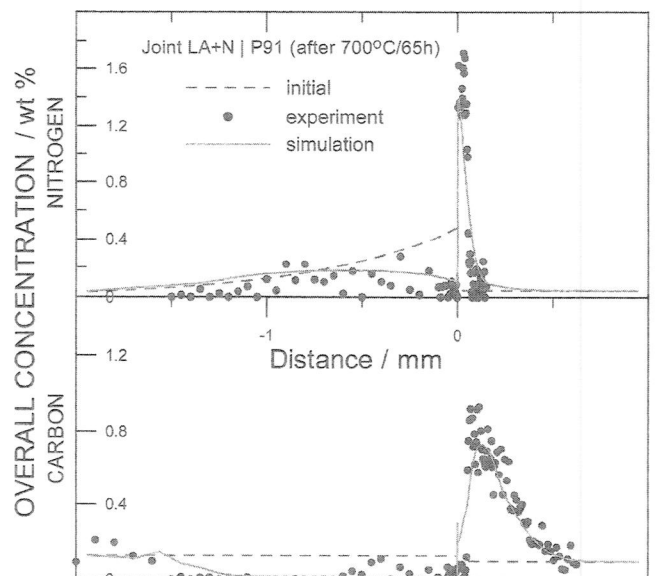


Fig. 9 Simultaneous carbon and nitrogen diffusion. Initial, experimental, and simulated overall carbon and nitrogen profiles of LA + N/P91 weld joint (annealing at 700 °C/65 h)

MX and M_2X carbonitrides (Fig. 4 and 5) near an LA + N/P91 weld joint. For example (Fig. 4), the composition of the nonstoichiometric MX carbonitride in the bulk of material LA + N corresponds to V_1C_{1-x} , in the diffusion-affected zone of material LA + N corresponds to $(CrV)_1N_{1-x}$, and in the bulk of P91 corresponds to V_1N_{1-x} (where $x \rightarrow 0$ for low temperatures). A similar distance-dependent behavior of composition can be derived for the M_2X carbonitride from Fig. 5.

5. Discussion

Analysis of the calculated phase diagram in Fig. 1 leads to a better understanding of the heat resistance of the LA steel. At elevated temperatures, this effect may be attributed to a fine dispersion of the MC and below ~ 650 °C the M_2C phase may also be contributory. Nitrogen addition to LA steel increases the mole ratio of the high-strength carbonitride phases. The MX and M_2X phases in the P91 steel have

a similar effect. This statement assumes an equilibrium state, of course.

The thermodynamic and kinetic stability of the LA + N/P91 weld joints can be estimated from the temperature dependence of carbon and nitrogen activities given in Fig. 2. Here the signs of diffusion fluxes of interstitial elements can be derived. The sign determines whether the "uphill" carbon diffusion or the regular nitrogen diffusion will be found for the investigated temperature range. The nitriding increases the carbon activity of the LA steel, but this negative effect is predicted only for temperatures below 700 °C, and it is suppressed by nitrogen decrease in the nitride case during weld joint aging. The results of the diffusion simulation are illustrated in Fig. 3 to 9. These results are more accurate than the basic estimation, which can be obtained from the activity dependence.

The experimental and the simulated carbon and nitrogen profiles of weld joints after prolonged diffusion times at selected temperatures within the interval of 500 to 700 °C and having ferrite matrix (bcc phase) are shown in Fig. 6 to 9. The profiles for the same element exhibit waveforms that are very similar from one temperature to another. For example, each simulated carbon profile reveals a broad global minimum representing the carbon depletion of material LA + N near the LA + N/P91 weld interface and a peak maximum in the region of carbon enrichment of the P91 steel.

In Fig. 3 to 5 the phase profiles and the phase composition profiles of MX and M₂X carbonitrides are given for an LA + N/P91 weld joint subsequent to annealing at 500 °C for 1000 h. The simulation results for temperatures of 575, 625, and 700 °C are analogous.^[11]

A detailed phase analysis using electron microscopy methods (TEM, RTG diffraction) was carried out for an LA + N/P91 weld joint held at 625 °C for 160 h. In agreement with the simulation results the expected phases MX, M₂X, M₂₃C₆, and M₇C₃ were found in the corresponding regions (compare this list of phases with the phases in Fig. 3 established for a temperature of 500 °C). It can be said that in the 500 to 700 °C temperature interval there is very good agreement between the experimental and the simulation results.

6. Conclusions

The behavior of experimentally examined weld joints of ion-nitrided 15CrMoV 2-5-3 low-alloy ferritic steel (LA + N) and the advanced chromium steel X10CrMoVNb 10-1 (P91) were compared with equilibrium calculations and kinetic simulations in the temperature range 500 to 700 °C for the same weld combination. As a first approximation, the direction of carbon and nitrogen diffusion can be determined from the activity difference. In this simple manner the "uphill" diffusion of carbon from the surface-nitrided LA + N materials into the P91 steel was explained.

A correct picture of the phase stability of LA + N/P91 weld joints at different annealing temperatures was performed on the basis of advanced kinetic simulations. The simulation results were presented as graphic profiles, which enabled prediction of phase compositions, carbon and nitrogen distributions inside the diffusion-affected zone, and

time and temperature dependence of those distributions. The experimental occurrence of carbon-depleted and carbon-enriched regions was predicted, and the existence of a nitrogen peak close to the weld interface in material P91 was explained. The nitriding of the LA low-alloy steel before welding yields carbonitride MX in the carbon-depleted zone, which may have a positive effect on mechanical properties.

Agreement between the experimental and the simulation results justifies using the assumption of the existence of local equilibrium states in the diffusion-affected regions of the welds under examination. In this way, results can be obtained that contain information about redistribution of elements and about the appearance of phase regions in the course of long-term exposure of welds to high temperatures. Information on the development of phase regions allows drawing conclusions as to the mechanical properties of a weld joint and possible failure appearing during creep of a heterogeneous weld joint. The results of kinetic simulation can be used with success in the design of new weld joints of heat-resistant steels as well as in the prediction of service life of existing welds in technological units currently in operation.

Acknowledgment

The support of the Ministry of Education, Youth and Sports (Project No. MSM/0021622410) is gratefully acknowledged.

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