CARBON DIFFUSION IN CARBON-SUPERSATURATED 9Cr-1Mo STEEL: ANOMALOUS TEMPERATURE DEPENDENCE OF CARBON DIFFUSIVITY

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Abstract

Carbon diffusion was studied in temperature interval 573 - 1073 K in carbon-supersaturated surface layer of 9Cr-1Mo steel P91 and in model Fe-15Cr binary alloy. Extremely low carbon diffusion coefficient D (by 3 orders of magnitude lower than the value D_{eq} in material with equilibrium carbon concentration) was observed in carburized surface region of Fe-15Cr. Similar results were obtained for P91 above the temperature $T_n \sim 800$ K. However, below T_n, the values of D measured in P91 increased and approached the value of D_{eq}. It seems that the non-Arrhenius behaviour of P91 steel around T_n may be ascribed to the $\alpha \rightarrow \alpha + \alpha'$ phase decomposition. Possible effect of nitrogen upon the low-temperature increase in D in P91 steel was excluded.

Keywords: Diffusion; Carbon; phase decomposition; Carbon-supersaturation, Cr-Mo steels

1. INTRODUCTION

The stability of structures involving carbon-supersaturated regions and their behaviour during thermal treatment is determined to a great extent by the carbon diffusivity, characterised quantitatively by the carbon diffusion coefficient D. However, reliable value of D is usually not at hand because it depends strongly on carbon concentration. Studies of carbon diffusion in carbon-supersaturated lattices are not too numerous in the literature and carbon diffusion characteristics in carbon-supersaturated matrices are not fully understood as yet.

In our previous works [1-3], we studied carbon diffusion in carbon-supersaturated surface of chosen ferrite materials: model alloy Fe-15.17 Cr (hereafter referred to as Fe-Cr) and commercial steel P91 (0.10 C, 0.40 Mn, 8.5 Cr, 0.10 Ni, 0.88 Mo, 0.23 V, 0.10 Nb, 0.045 N, bal. Fe - all in wt. %). In the latter case, we observed a significantly non-Arrhenius temperature dependence of D. Whereas at higher temperatures (above about 800 K), the measured values of D were close to those known for carbon diffusion in carbide phase, below 700 K, D's approached the higher values, D_{eq}, reported for carbon diffusion in BCC lattice with equilibrium carbon concentration [4]. Between 700 and 800 K, the transition diffusion behavior was observed. Low values of D were ascribed to carbon diffusion in supersaturated matrix [1-3,5], but the increase in D at low temperatures remained as an open question. It was presumed only that it originated in - at least local - lost of carbon supersaturation. Similar break in the Arrhenius dependence of D in Fe and in Fe-Cr was not observed in [1-3].

In the present paper, we propose a possible explanation of anomalous carbon diffusion behavior in carbon supersaturated P91. We carried out supplementary carbon diffusion measurements at the temperature 673 K with P91 and with the binary ferrite alloy Fe-Cr as a reference material.

2. EXPERIMENTAL

2.1 Verification of known results

Repeated diffusion measurement with a new series of P91and Fe-Cr samples was carried out to verify the low-temperature difference in D reported earlier in the both materials [1-3]. The present measurement of D was conducted at temperature 673 K only, where the significant carbon diffusivity difference could be expected

and, at the same time, where the experiment can be performed in reasonably short time, because of not too low D's.

For details of experimental technique used to measurement of carbon concentration depth profiles $c(x,t)$ (c, x, t - carbon concentration, depth co-ordinate and diffusion time respectively) and procedure applied to D evaluation, see in [1-3].

2.2   Nitrogenation

An *ad hoc* hypothesis that the origins of non-Arrhenius diffusion behaviour might stem from different content of nitrogen (and/or from the presence of carbonitrides MX) in P91 and in Fe-Cr was tested. The test was conducted with two groups of Fe-Cr samples: The samples in the first group were nitrogenated, the other served as the reference samples. The nitrogenation was carried out from the pure N_2 gas (purity of N_2 was 4N) under condition 893 K/1 h/30 bar.

Table 1 Carbon diffusion coefficients D

Fe-Cr	P91	Remark
D	D	
m²/s	m²/s	
4.2×10^{-21}	6.3×10^{-19}	
7.9×10^{-22}	6.4×10^{-19}	
2.3×10^{-21}		
1.8×10^{-20}		
1.1×10^{-20}		
5.8×10^{-21}		with N_2
3.3×10^{-21}		with N_2
6.5×10^{-22}		with N_2
2.2×10^{-20}		with N_2

3.   RESULTS AND DISCUSSION

3.1   D's measured at T=673

Measured values of D are listed in **Table 1** and plotted in Arrhenius diagram in **Fig. 1** together with D's obtained in [1-3] and with D_{eq}'s for diffusion in carbide phase [6,7] and in P91[4]. The most probable value of the measured coefficients D lies typically in interval ($\frac{1}{2}D$; $2D$). Bearing in mind this experimental uncertainty, it is obvious that the present measurements confirm the conclusions drawn in our preceding studies, namely that there is a break in temperature dependence of D in P91: At higher temperatures, the values of D are close to carbon diffusion in carbide phase, at low temperatures they tend to D_{eq} (**Fig. 1**).

3.2   Nitrogenated Fe-Cr

Equilibrium nitrogen content in Fe-based ferrites may reach the solubility limit of about ~10^{-1} wt. % N_2 [8, 9] and it forms nitrides ε-$M_{2-3}N$ and/or γ'-M_4N [8]. After the nitriding of the present Fe-Cr samples, it may be expected that their surface was nitrided up to the nitrogen solubility limit down to the depth x of tens of micrometers [8]. In the **Fig. 2**, SIMS depth profiles are shown that document increased average of N concentration and its invariance with respect to x within the layer, which thickness was sufficient for the present

carbon diffusion measurements (tens of nm). The SIMS signal was registered at channel m/e = -14, i.e., where the negative nitrogen ions were detected. Rietveld analysis of XRD pattern obtained with nitrogenated Fe-Cr samples revealed, before all, ferrite (90.7%) and austenite (6.0 %) and traces of two minority phases - ε-$Fe_{2-3}N$ (0.6 %) and Fe_3O_4 (2.7 %).
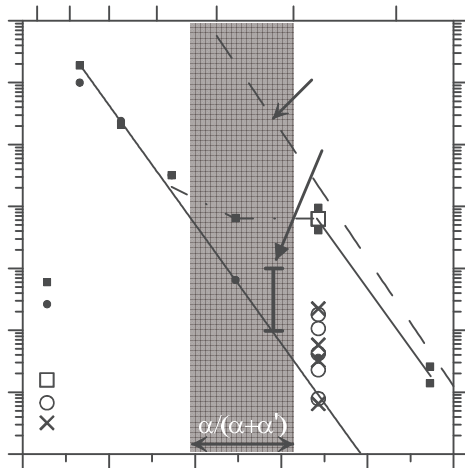

Fig. 1 Arrhenius diagram of carbon diffusion coefficients in matrices with equilibrium carbon concentration (D_{eq}) and in carbon super-saturated materials (D). Temperatures within shaded band comprise assessments of starting temperatures T_{tr} of the α → α + α' decomposition [11-17].
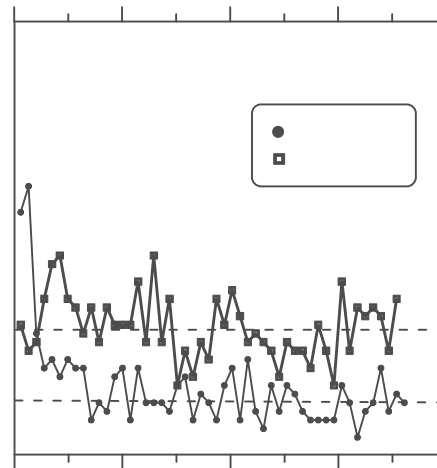
Fig. 2 Concentration - depth profiles of nitrogen in nitrogenated and in non-nitrogenated reference samples of Fe-Cr.

Nitrogen introduced into the lattice of Fe-Cr, however showed no significant effect upon the measured values of D (**Table 1** and **Fig. 1**). It means that the different content of N_2 in the P91 steel and Fe-Cr reference alloy cannot explain the carbon diffusion anomaly observed in P91.

3.3   Influence of phase composition

Another possible explanation of the C diffusion anomaly could be based on phase transformation of P91 at temperatures around T_{tr} ~ 750 K. The samples P91 were annealed before the diffusion measurement (for details of sample preparation - see in [1]). However, the MX carbonitrides (M = Nb, V; X = C, N) were not dissolved during this pre-treatment and were stable during the C diffusion measurement in the whole temperature interval 573 - 1073 K.

Particles of Laves phase A_2B (A = Fe, Cr; B = Mo) and low-temperature carbide M_6C (M = Fe, Mo, Cr) that form (M_6C) or increase (Laves phase) their volume fraction [9,10] around the temperature T_{tr} , were indicated neither in solution annealed P91 nor in Fe-Cr (by XRD and EBSD). It follows that also these phase reactions cannot explain the observed C diffusion anomaly.

3.4   Alpha phase decomposition in P91

The observed carbon diffusion anomaly invokes an idea that - at least in a certain volume fraction of P91 - domains without carbon super-saturation appear below T_{tr}. This is supported by comparison of D's with D_{eq}'s reported in [4]. It is clear from **Fig. 1**, that above T_{tr}, D's are close to very low values known for C diffusion in

carbide phase [6,7], but below T_{tr} , they approach 'common' values D_{eq} measured for P91 with equilibrium C concentration [4].

Impressive connotation follow from Mössbauer study of P91 annealed above and below T_{tr} [3]. We obtained that next-neighbor sites of Fe atoms in P91 annealed above T_{tr} are populated almost exclusively by Fe atoms, but in P91 annealed below T_{tr}, these sites are occupied also by other atoms. These facts points to possible influence alpha phase decomposition α → α + α'. This reaction occurs close to T_{tr} , but unfortunately, the location of the phase boundary α/(α+α') is known exactly neither for Fe-Cr binary alloy [11-14] nor for P91 [15-17], therefore, it is difficult to coincide convincingly its critical temperature with T_{tr}. Cr-rich precipitates of α' are totally coherent [18,19]. It is easy to imagine that the (α + α') structure undergoes an extensive atomic rearrangement, which may contain regions with lowered carbon concentration and, therefore, channels of rapid carbon diffusion (see the structures simulated in refs. [18,19]).

Of course, it could be objected that the Fe/Cr de-mixing reaction α → α + α' runs very slowly [18, 19] and that it may not proceed to a significant volume fraction of α' during the present diffusion measurement. On the other hand, the characteristics of carbon diffusion may be very sensitive to very beginning stages of the transformation, similarly as, e.g., the heat capacity c_p measured as low as at the room temperature with quenched Fe-Cr samples [20]. The measurement of c_p was carried out after a relatively short delay following the quenching. Despite this fact, the obtained values of c_p show distinct irregularities at Fe-Cr composition that can be coincided with α/(α + α') or (α + α')/α phase boundary.

Interpretation of the carbon diffusion anomaly in C super-saturated P91 in terms of α → α + α' decomposition leads to a question, why a similar anomaly was not observed also in Fe-Cr reference alloy that should also decompose into (α + α') phase mixture [21]. Present results of repeated measurement with Fe-Cr alloy at T = 673 K (**Table 1**, **Fig. 1**) have shown that resulting D values were scattered in a wide interval that was much broader than the experimental error of a single measurement. Hence, it is most likely that the scatter of D's at T = 673 resulted from an instability just in the close vicinity of the α/(α + α') phase boundary. The possible shift of the transformation temperature T_{tr} in Fe-Cr compared to that in P91 may consist in the influence of alloying elements [15, 22]. Comparison of low-temperature decomposition in Fe-Cr model binary alloy and relevant complex commercial Cr steel was made also in ref. [23], where the variation of characteristics depending on the decomposition extent on chemical composition were reported.

It is obvious that the proposed explanation of carbon diffusion anomaly in terms of Fe/Cr demixing could be verified by carbon diffusion measurement with Fe-Cr alloy at temperatures T < 673 K. However, this remains for the further study.

CONCLUSION

Carbon diffusion anomaly in P91 is most likely caused by the α → α + α' decomposition. It was deduced that the anomaly is induced or controlled neither by the presence of nitrogen nor by any nitride/carbonitride reaction.

ACKNOWLEDGEMENTS

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