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COMPOSITIONAL CHANGES IN CARBIDE M_7C_3 UPON ANNEALING

ZMIANA SKLADU WĘGLIKA TYPU M_7C_3 W CZASIE WYŻARZANIA

A lot of work was done on the structure of M_7C_3 in the past. It was found that this carbide contains an extremely high amount of defects and its structure can be interpreted either as a orthorormbic, hexagonal or trigonal crystal structure. Compositional studies, however, have not been done in detail yet. It has been, therefore, our intention to shed further light into the compositional evolution of carbide M_7C_3 upon annealing. Four low alloy steels 0.9Cr, 0.9Cr-0.25V, 2.5Cr-0.25V-0.4Mo, 0.9Cr-0.25V-0.4Mo (compositions given in mass percents) were annealed for 1000 – 5000 h at temperatures 773 – 993 K in evacuated capsules. Secondary phase particles extracted into carbon replicas were identified by the electron diffraction, and their compositions were determined by the energy dispersive x-ray spectroscopy. In parallel, changes in the Fe/Cr ratio for M_7C_3 were predicted using the thermodynamic-database program Thermo-Calc and plotted *versus* the bulk content of carbon, vanadium and chromium. It was shown that the Fe/Cr ratio increases with increasing bulk carbon content for all investigated steels and temperatures considered. On the other hand, it was predicted that the Fe/Cr ratio decreases with increasing bulk vanadium and chromium contents and increasing temperature. Molybdenum was found to stabilize the MC carbide, to reduce the molar fraction of M_7C_3 carbide and to decrease the values of Fe/Cr ratio in M_7C_3 at lower temperatures. The predictions were found to be in a good agreement with experimental observations, mainly for higher annealing temperatures. The only disagreement was found for the 2.5Cr-0.25V-0.4Mo steel.

Keywords: carbide M_7C_3, composition, Cr-V-Mo steels, CALPHAD

Tematyce struktury M_7C_3 poświęcono w przeszłości wiele prac. Stwierdzono, że węglik ten zawiera ekstremalnie dużą ilość defektów, a jego struktura może być interpretowana zarówno jako ortorombowa, heksagonalna lub trygonalna. Jednakże nie przeprowadzono dotychczas badań składu tej fazy. Tak więc, naszą intencją było rzucenie nowego światła na zmiany składu węglika M_7C_3 w trakcie wyżarzania. Cztery gatunki stali niskostopowych 0.9Cr, 0.9Cr-0.25V, 2.5Cr-0.25V-0.4Mo, 0.9Cr-0.25V-0.4Mo (składy podano w % wagowych) poddano wyżarzaniu w próżniowych kapsułach przez 1000 – 5000 godzin w temperaturach 773 – 993 K. Cząstki węglików ekstrahowano do repliki węglowej i identyfikowano za pomocą dyfrakcji elektronowej, a ich skład określono metodą spektroskopii dyspersji energii promieniowania rentgenowskiego (EDX). Równolegle, korzystając z termodynamicznej bazy danych programu Thermo-Calc, obliczono prognozowane zmiany parametru Fe/Cr dla M_7C_3 i przedstawiono je graficznie jako zależności od całkowitej zawartości węgla, wanadu i chromu w stali. Pokazano, że parametr Fe/Cr wzrasta wraz ze wzrostem całkowitej zawartości węgla dla wszystkich zbadanych gatunków stali w rozpatrywanym zakresie temperatur. Z drugiej strony pokazano również, że następuje spadek wartości parametru Fe/Cr ze wzrostem całkowitej zawartości wanadu i chromu oraz obniżaniem temperatury wyżarzania. Stwierdzono, że molibden stabilizuje węglik MC, obniża udział molowy węglika M_7C_3, a dla najniższych temperatur obniża wartość współczynnika Fe/Cr. Obliczenia prognozujące, zwłaszcza dla wyższych temperatur wyżarzania, okazały się być w dobrej zgodności z obserwacjami eksperymentalnymi. Jedyną rozbieżność zaobserwowano dla stali 2.5Cr-0.25V-0.4Mo.

1. Introduction

The M_3C, M_7C_3, and $M_{23}C_6$ carbides belong to the carbide group typical for high-chromium steels and cast irons. A common attribute of the carbides is the dominance of chromium and iron in their metallic parts [1,2]. On the other hand, these carbides exhibit different crystal structures when compared to each other. The M_7C_3 carbide has a complicated structure type due to high density of planar defects [3,4]. A usual way of the M_7C_3 formation resides in the solidification and/or precipitation. The temperature and compositional ranges of the M_7C_3 existence are influenced mainly by the bulk chemical composition and thermal-deformation history of the

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steel. In steels with higher chromium and lower carbon contents, M_7C_3 is usually an intermediate phase, particles of which replace the original M_3C [5] and precede the $M_{23}C_6$ formation at higher temperatures. In some low-chromium steels, however, M_7C_3 was found to exist at higher temperatures than $M_{23}C_6$ [6,7]. This "anomaly" was observed in some low-alloy and high-speed steels, indeed. Another "anomaly" concerns the chemical composition of M_7C_3. In general, chromium dominates over iron in metallic part of this carbide [5,6]. In some low-chromium steels, however, the M_7C_3 particles with the dominance of iron over chromium were found [8,9].

According to the original concept proposed by Westgren [10] the unit cell of M_7C_3 exhibits a trigonal symmetry (space group P31c) with lattice parameters: a = 1.3980 nm and c = 0.4523 nm. Fruchart and Rouault [11] and Herbstein and Snyman [12] considered later the unit cell of M_7C_3 as orthorhombic (Pnma, a = 0.701 nm, b = 1.214 nm, c = 0.452 nm) and hexagonal (P63mc, a = 0.7371, c = 0.4337 [13]), respectively. The orthorhombic unit cell in the (001)-projection is given in Fig. 1 [14,15]. Besides atoms positioned in the projection plane, with z-coordinates equal to zero, all other metal and carbon atoms have relative vertical distances between 0 and 1. 1 is the distance between two neighbouring metal atoms in the direction [001]. The z coordinates of all atoms are close to 0, 0.25, 0.5 and 0.75 and only small deviations from these values are observed. The exact positions of atoms are given in Fig. 1. Symbols a_0 and b_0 represent the lattice parameters of the unit cell parallel to the projection plane. The metal atoms are arranged into two types of octahedra (tilt of 60° along the vertical axis) and two types of tetrahedra (tilt of 90° along the vertical axis). Carbon atoms center the trigonal prisms formed by six metal atoms, three of which belong to an octahedron and other three to the opposite tetrahedron (see doted area in the left upper part of Fig. 1). The carbon atoms are, therefore, referred to as prismatic interstices. Basic structural units of the orthorhombic unit cell are multiatomic octahedras with two different orientations. The octahedras are arranged regularly (Fig. 1) and form a superlattice. The structure of M_7C_3 can be thus presented as a superlattice with orthorhombic symmetry [11,16]. This makes it possible to characterise the planar defects present in M_7C_3 as antiphase and/or twin boundaries [2,14,16].
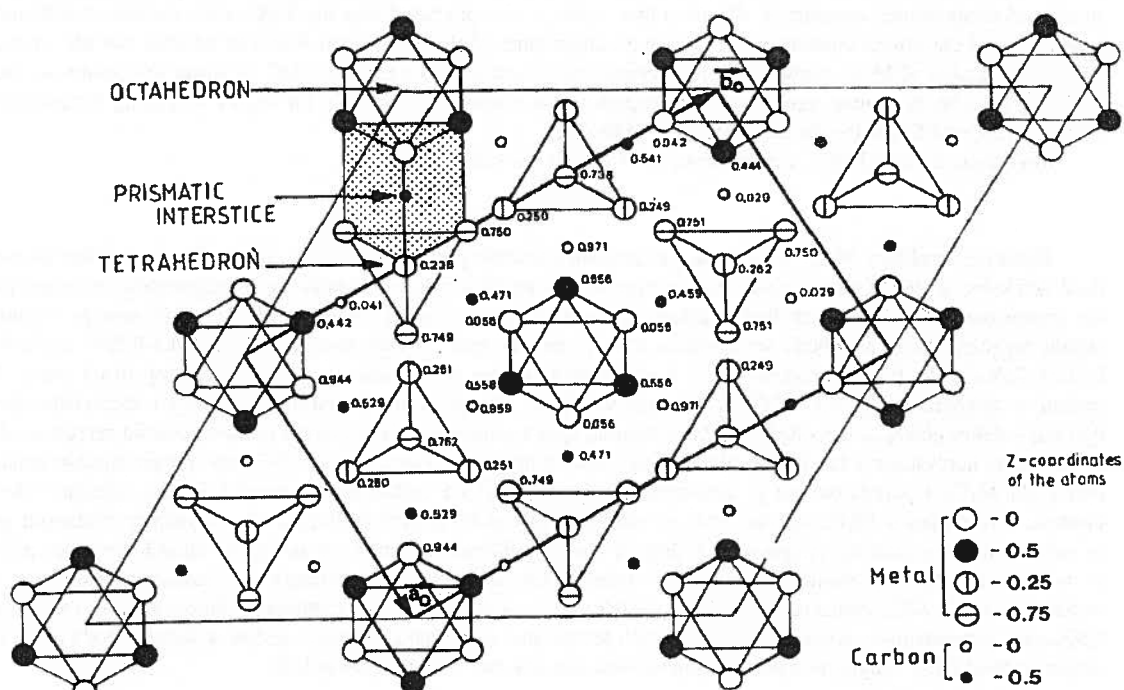

Fig. 1. The orthorhombic unit cell of M_7C_3 (a = 0.701 nm, b = 1.214 nm, and c = 0.452 nm) projected in (001)-plane. Z-coordinates are given for both the metal and carbon atoms in the legend and the exact values are listed beside the individual atoms. Lattice parameters parallel to the projection plane are marked with a_0 and b_0. Figure was prepared according to Fruchart and Rouault [11]

Although the concept of orthorhombic superlattice fits the crystal structure of M_7C_3 very well, the original trigonal concept has not been definitely declined. S. D. Carpenter and D. Carpenter [17,18], for instance, considered the M_7C_3 as an undisputedly hexagonal phase, even if they conceded indexing of diffraction patterns with orthorhombic symmetry. From this formulation one

can conclude that the crystal structure of M_7C_3 is still open for discussion.

The main aim of this work is the characterisation of the M_7C_3 carbide in selected Cr-V-Mo steels. The structural studies were completed by the analysis of the carbide particles performed by the energy dispersive X-ray spectroscopy (EDX). The experimental results were compared with thermodynamic predictions of the M_7C_3 metal compositions at equilibrium. The attention was paid to the determination of conditions at which iron becomes a dominant element in the metallic part of M_7C_3.

2. Experimental part

Cast ingots of nominally 0.9Cr (1), 0.9Cr-0.25V (2), 2.5Cr-0.25V-0.4Mo (3) and 0.9Cr-0.25V-0.4Mo (4) low alloy steels were forged between 1373 K and 1123 K into bars with a cross section of 12 × 12 mm and normalized at 1423 K to achieve a mean austenite grain size of approximately 150 μm. The samples were then water quenched, tempered at 953 K for 2 hours, water cooled and finally annealed. The exact compositions of the steels are given in Table 1. The annealing conditions are listed in Table 2.

TABLE 1

Chemical compositions (in weight %) of the systems investigated

No.	Denomination	C	Mn	Si	Cr	V	Mo	N (ppm)	P/S(ppm)
1	0.9Cr	0.115	0.331	0.232	0.894	–	–	41	450/45
2	0.9Cr-0.25V	0.136	0.337	0.238	0.879	0.258	–	40	470/35
3	2.5Cr-0.25V-0.4Mo	0.133	0.329	0.225	2.490	0.247	0.406	45	420/39
4	0.9Cr-0.25V-0.4Mo	0.126	0.321	0.223	0.851	0.254	0.405	32	450/36

Carbon extraction replicas were used to characterize the secondary phases in the investigated steels. The crystal structure was determined by means of selected area electron diffraction. Electron microscopy analysis was performed using a Phillips CM12 transmission electron microscope (TEM), equipped with an EDAX 9900 (EDX) analyser system. Neither the corrections for absorption nor the corrections for the fluorescence were made. The secondary phases were investigated in the as-quenched, as-tempered and annealed conditions of investigated steels. At least 15 particles of each phase type were analyzed to determine the average metal content.

3. Results and discussion

The presence of carbide M_7C_3 was experimentally found for several temperatures. The ageing conditions and the experimental Fe/Cr ratio in M_7C_3 for the investigated steels 1-4 are given in Table 2. The Fe/Cr ratio varies according to the temperature and the bulk content of Cr, Mo and V in the alloys.

TABLE 2

The annealing conditions and the experimental Fe/Cr ratio (wt.%/wt.%) found in carbide M_7C_3 for steels 1-4. Standard deviations are also given

T(K)	t(h)	1	2	3	4
773	100	–	–	0.6 ± 0.0	–
773	1000	–	–	0.7 ± 0.0	–
773	5000	–	–	0.8 ± 0.1	–
853	100	–	1.7 ± 0.2	0.6 ± 0.0	–
853	1000	–	1.4 ± 0.1	0.5 ± 0.0	1 ± 0.1
853	5000	–	0.8 ± 0.1	0.6 ± 0.0	1.1 ± 0.1
953	1000	1.3 ± 0.1	1.2 ± 0.1	0.5 ± 0.0	1.1 ± 0.1
993	1000	1.3 ± 0.2	1.4 ± 0.2	0.6 ± 0.0	1.3 ± 0.2

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The experimental results summarized in Table 2 show that no regularities exist between the values of Fe/Cr ratio for M_7C_3 and changes in temperature, except for steel 4. In the latter case the Fe/Cr ratio increases with increasing temperature.

The characteristic morphologies of M_7C_3 particles in annealed states are documented in Figs. 2a, c, and e for respective steels 1, 2, and 4. The corresponding EDX-spectra are illustrated in Figs. 2b, d, and f. The spectrum of M_7C_3 in steel 3 was similar to the one obtained for the steel 4, and thus, it is not presented in this work. As follows from Figs. 2b, d, and f, there is accordance between the occurrence of metallic elements in M_7C_3 and in the bulk. In the 0.9Cr steel, for instance, chromium and iron are present, and the same metallic elements were also found in M_7C_3 (compare Table 1 and Fig. 2). This trend was also confirmed for other three steels investigated.
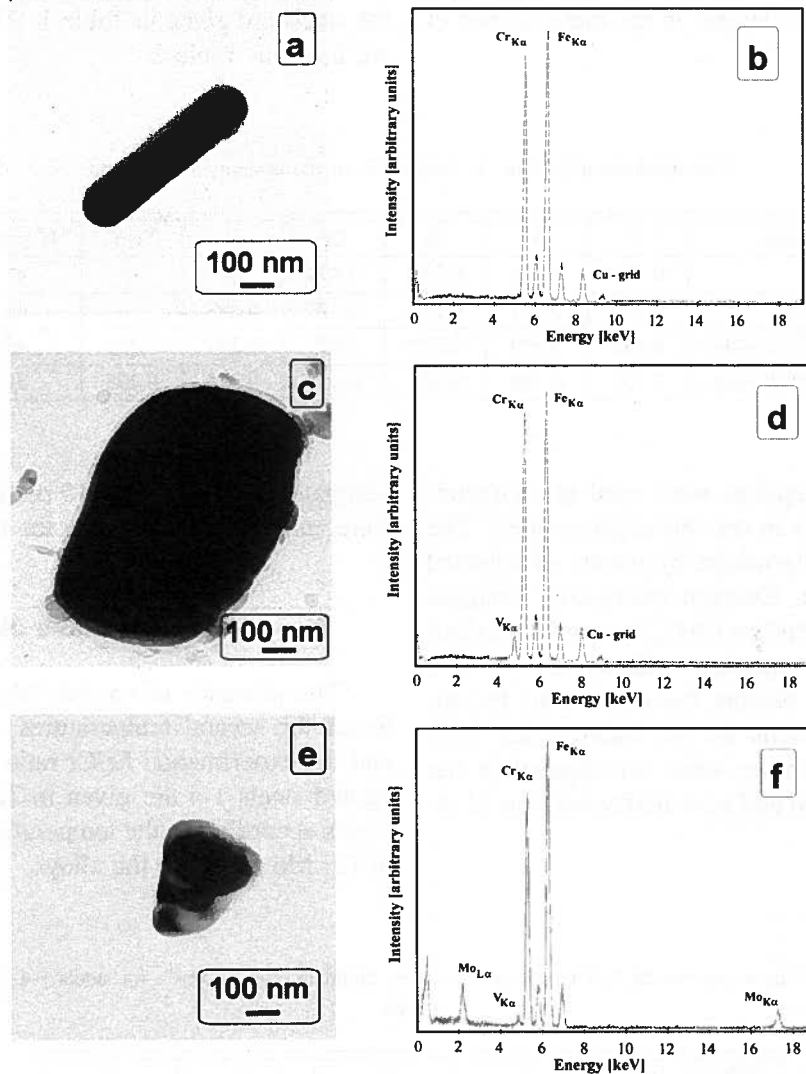

Fig. 2. Characteristic morphologies and EDX-spectra of M_7C_3 particles in steels: 0.1C-0.9Cr after annealing for 1000 h at 993 K (a, b), 0.1C-0.9Cr-0.25V after annealing for 5000 h at 853 K (c, d), and 0.1C-0.9Cr-0.25V-0.4Mo after annealing for 5000 h at 853 K (e, f); TEM of carbon extraction replica

The program Thermo-Calc [19] and the steel database comprising 16 elements STEEL16 [20,21] were used to predict the equilibrium contents of metallic elements in M_7C_3 for the systems corresponding to the investigated steels at different temperatures. In the first step, the phase equilibrium was calculated in the temperature range 773-993 K. In the thermodynamic predictions the phosphorus and sulphur contents were neglected. The results are presented in Table 3.

TABLE 3

The calculated molar fractions of equilibrium phases in steels 1-4 at temperatures between 773 and 993 K

T (K)	ferrite	MC	M_3C	M_7C_3	$M_{23}C_6$
Steel 1					
773	98.20	–	–	1.77	–
853	98.22	–	–	1.75	–
953	98.30	–	0.073	1.60	–
993	98.1	–	1.18	0.62	–
Steel 2					
773	98.18	–	–	1.29	–
853	98.20	–	–	1.27	–
953	98.27	–	–	1.19	–
993	98.35	–	–	1.11	–
Steel 3					
773	97.65	–	–	0.501	1.47
853	98.11	–	–	1.50	–
953	98.12	–	–	1.53	–
993	98.14	–	–	1.52	–
Steel 4					
773	98.45	0.0264	–	0.774	–
853	98.45	0.00893	–	0.820	–
953	98.48	–	–	0.859	–
993	98.54	–	–	0.832	–

Beside the ferrite matrix, M_7C_3 was predicted to be stable at all investigated temperatures. The $M_{23}C_6$ was predicted to be stable only in steel 3 (high chromium content) at 773 K. This carbide disappeared when the temperature increased. The M_3C carbide, on the other hand, was found to be stable only in steel 1 at high temperatures. From these observations it may be concluded that M_7C_3 is the most important secondary phase present in all the investigated steels. The highest relative content of M_7C_3 was found at low temperatures in steel 1. At temperatures 773 and 853 K, however, no carbide M_7C_3 in steel 1 was detected experimentally (Table 1).

Since the metal composition of M_7C_3 was measured experimentally (Table 2), we have calculated the theoretical Fe/Cr content in the carbide for each temperature. The equilibrium Fe/Cr content in each of the investigated steels is presented in Table 4. The agreement with the experimental values is good for data at high temperatures. It can be concluded that annealing times of 1000 h at high temperatures were mostly sufficient to achieve the equilibrium in samples.

TABLE 4

The equilibrium ratio of Fe and Cr mass contents in investigated steels

T (K)	Fe/Cr			
	1	2	3	4
773	0.549	0.359	0.0818	0.247
853	0.817	0.606	0.163	0.499
953	1.23	1.017	0.334	0.976
993	1.21	1.210	0.421	1.208

A remarkable disagreement between the equilibrium and experimental metal compositions of M_7C_3 was observed for steel 3. The experimental values were higher than the calculated values and they were temperature-independent. The reason can reside in the higher alloying of this steel, preventing from the diffusivity of metallic species and reaching the equilibrium quickly. A better agreement between the experimental

and theoretical values at higher temperatures confirms this suggestion.

The bulk content of carbon is expected to reflect the amount of carbides present in the investigated steels. The composition of carbide was, therefore, predicted with respect to temperature and bulk contents of carbon, vanadium and chromium. The results are presented in Figs. 3-5. The equilibrium iron content in M_7C_3 increases with increasing temperature and bulk carbon content. The only disagreement was found the steel 2 at 993 K where the iron content decreased with increasing carbon content. The iron content, on the other hand, decreases with increasing chromium and vanadium contents. The decrease is most pronounced in the case of chromium. It can be reasonably concluded that iron replaces chromium in the crystal lattice of M_7C_3. Since vanadium and chromium have smaller ionic radii than iron [22], one may expect a reasonable lattice expansion and other structure changes upon substitution.
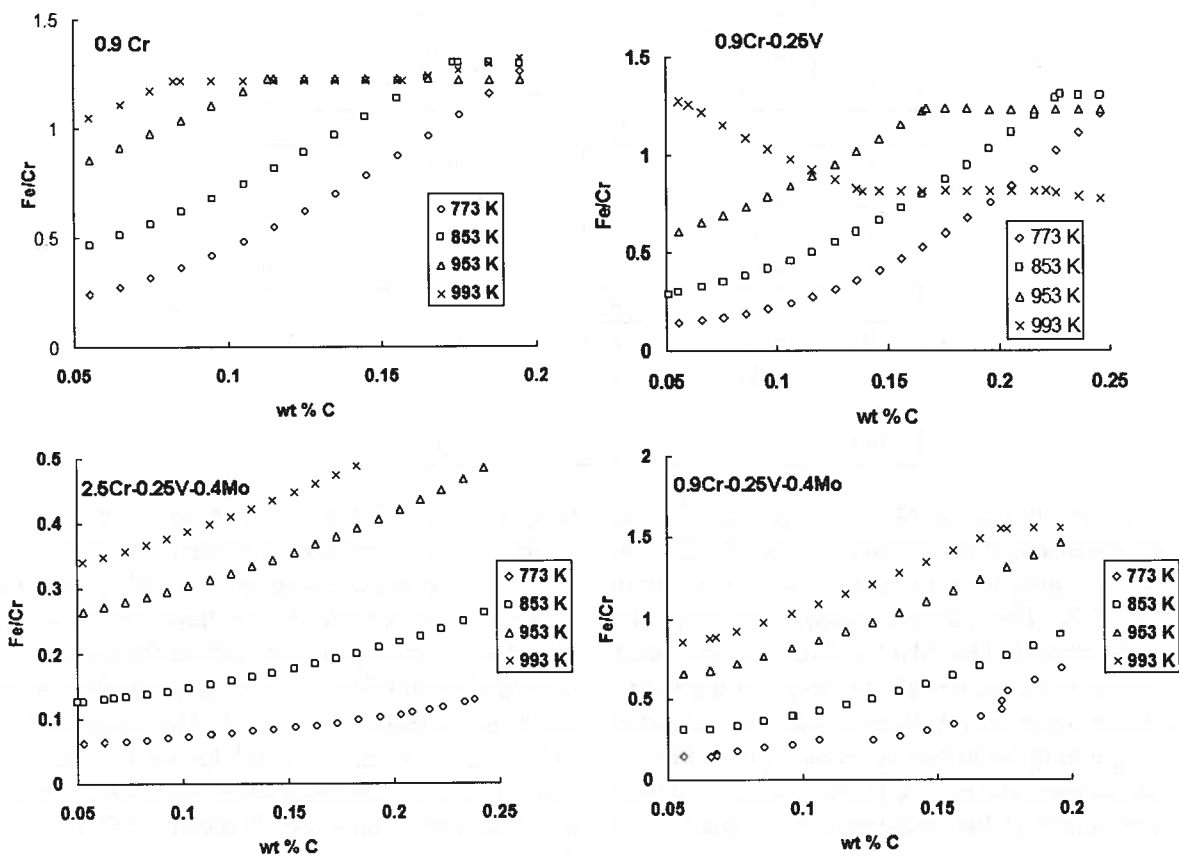

Fig. 3. Predicted values of Fe/Cr ratio for M_7C_3 (wt.%/wt.%) in dependence on the bulk carbon content and temperature
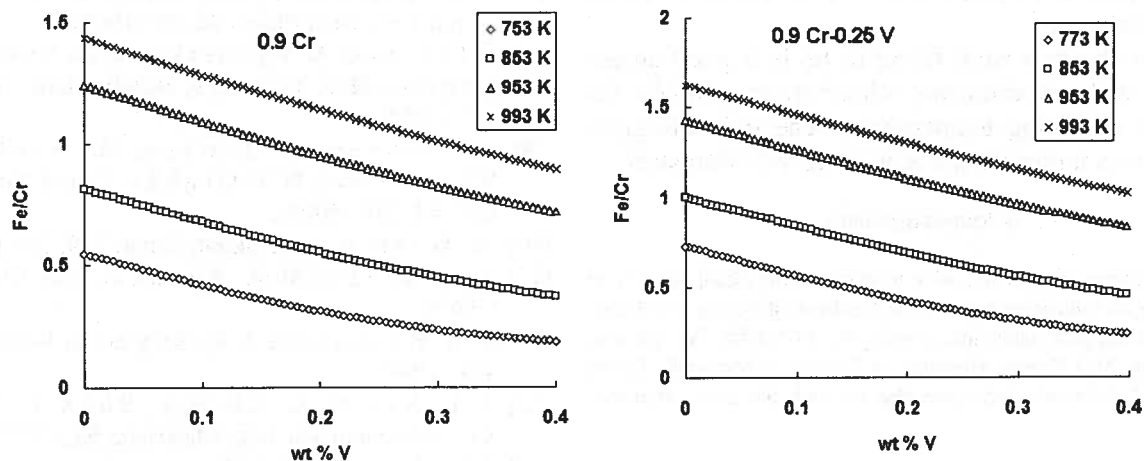
Fig. 4. Predicted values of Fe/Cr ratio for M_7C_3 (wt.%/wt.%) in dependence on the bulk vanadium content and temperature. Vanadium content was changed during the calculation, contents of other elements were held constant
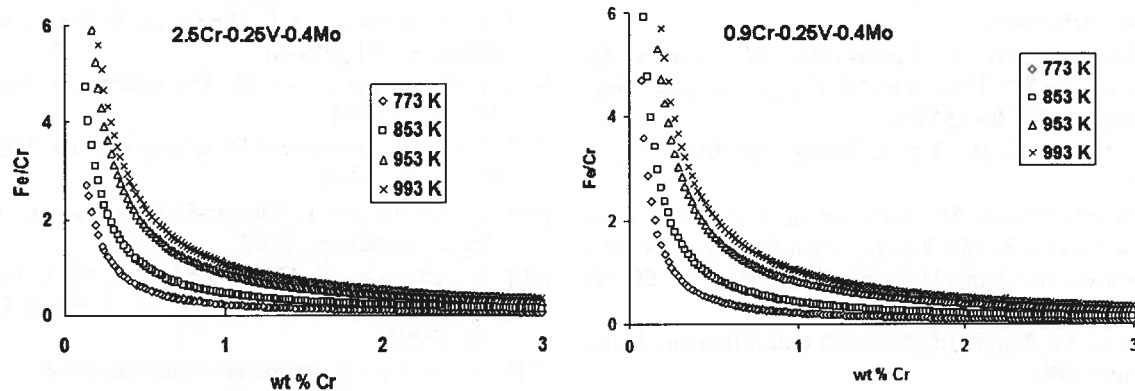

Fig. 5. Predicted values of Fe/Cr ratio for M_7C_3 (wt.%/wt.%) in dependence on the bulk chromium content and temperature. Chromium content was changed during the calculation, contents of other elements were held constant

The influence of bulk molybdenum content on both the occurrence of phases and the values of the Fe/Cr ratio can be well specified when the results for steels 2 and 4, differing significantly only in the molybdenum content, are compared. Molybdenum was found to stabilize the MC carbide at lower temperatures, to reduce the molar fraction of M_7C_3 (Table 3) and to decrease the values of the Fe/Cr ratio at lower temperatures (Table 4).

The thermodynamic predictions showed that changes in temperature influence the Fe/Cr ratio for M_7C_3 more significantly than those in the bulk carbon content (Fig. 3). The lower the total contents of alloying elements in the steel, the stronger the influence of the bulk carbon content. Similar trends were also observed for the bulk vanadium content if considered its influence on the Fe/Cr ratio. On the other hand, a transition behaviour was predicted for the influence of the bulk chromium content on the Fe/Cr ratio. It can be concluded that significant changes in the Fe/Cr ratio may be expected already when chromium content in low alloy steels does not exceed 1 wt.%.

4. Conclusion

The characterization of M_7C_3 in four low alloy steels 0.9Cr, 0.9Cr-0,25V, 2.5Cr-0.25V-0.4Mo, 0.9Cr-0.25V-0.4Mo annealed for 1000 – 5000 h at temperatures 773 – 993 K by means of experimental techniques and thermodynamic calculations revealed the following result:

- The Fe/Cr ratio for M_7C_3 increases with increasing bulk carbon content for all investigated steels and temperatures considered. The lower the total contents of alloying elements in steel, the stronger the influence of the bulk carbon content.

- The Fe/Cr ratio for M_7C_3 decreases with increasing bulk vanadium and chromium contents and decreasing temperature. Significant changes in the Fe/Cr ratio can be expected when chromium content in low alloy steels does not exceed 1 wt.%.

- Molybdenum was found to stabilize the MC carbide, to reduce the molar fraction of M_7C_3 and to decrease

the values of Fe/Cr ratio in M_7C_3, mainly at lower temperatures.

● The predictions were found to be in a good agreement with experimental observations, mainly for higher annealing temperatures. The only disagreement was found for the 2.5Cr-0.25V-0.4Mo steel.

Acknowledgements

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