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Miscibility of binary VC–MC carbides in quaternary Fe–V–M–C alloys

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Abstract

A series of quaternary (Fe, V, M, C) alloys with different additions (Ti, Zr, Nb, Ta, Mo and W) were prepared. The phases were characterised by scanning electron microscopy. Quantitative electron probe microanalysis was used to analyse the carbides. As in ternary systems, MC_x carbides formed in quaternary alloys are carbon deficient. TiC and VC formed a continuous solid solution, while Zr, which belongs to the same group, showed a solubility below 0.1% Zr in VC and V is less than 1% in ZrC. VC–TaC and VC–NbC formed a continuous solid solution at high temperature, but decomposed during cooling. In the presence of Mo, continuous variations of M and C levels are observed between VC and Mo_2C, while in the presence of W, the formation of an intermediate carbide of M_6C type limits the solubility of W in VC. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: VC carbides; Carbon level; Additions; Miscibility; Microprobe analysis

1. Introduction

Vanadium and other elements forming MC monocarbides are common alloy elements in steels and cast irons. They are used to improve the mechanical properties. In industrial alloys, mixtures of elements are added. Mixtures of VC with TaC or NbC are known to increase the hardness and elastic moduli [1,2]. Knowledge of the mutual miscibility of the carbides of the IV (Ti, Zr), V (V, Nb, Ta) and VI (Cr, Mo, W) groups is of particular interest in hard materials.

MC monocarbides have been extensively studied. Binary carbides as carbides formed in ternary Fe–V–C alloys show a large deviation from stoichiometry. The composition of vanadium carbides changes according to the vanadium content in Fe–V–C alloy [3] and to the presence of additions such as Cu, Si or Al [4].

The purpose of this study was to perform quantitative microanalyses on mixtures of carbides formed in the Fe-rich corner of quaternary Fe–V–M–C systems with additions forming carbides: MC_x and other types of carbides (Cr, Mo and W).

2. Experimental

Series of quaternary alloys (Fe, V, M, C) were prepared by arc melting in an argon environment from electrolytic iron ($C<0.0025\%$), pure metals ($>99.98\%$) and carbon. Carbon was kept at around 13 at.%.

Differential thermal analyses were carried out, under argon, using a thermal analysis apparatus (DTA, Netszch 404 S type). Samples were sectioned, polished and observed by scanning electron microscopy (SEM, Leica S440). Usually, microstructures are observed directly on polished surfaces with backscattered electrons.

Quantitative electron probe microanalysis (EPMA, Cameca SX50) was used to determine accurately the composition of the phases and particularly the carbon level. C Kα X-ray radiation was analysed with a PC2 monochromator. A chromium carbide of known composition was used as the standard for C analysis. The quantitative analyses of the metallic elements were performed with monochromators at 15 keV using standards of elemental Fe, V and M. The C Kα line is shifted only slightly for the different carbides and the standard (44.39 Å). Atomic number, absorption and fluorescence effects were corrected for with a computer program according to the PAP model [5].

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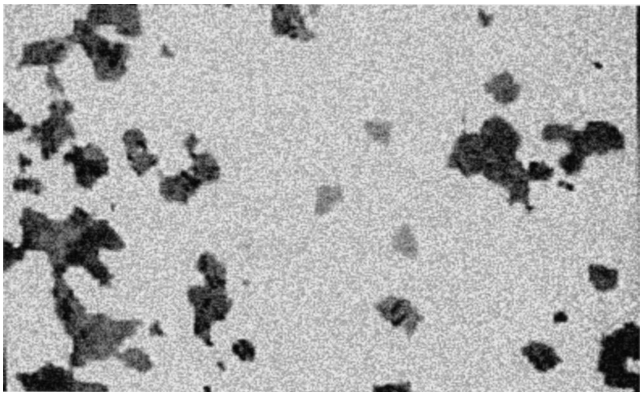

Fig. 1. Microstructure of quaternary FeVCTi alloys showing the MC carbides. V-rich carbides appear with a dark contrast and Ti-rich MC carbides are grey.

3. Results and discussion

3.1. Microstructures of quaternary alloys

Two families of additions were tested:

- Ti, Zr, Nb and Ta, which form MC carbides;
- additions forming other types of carbides such as Cr, Mo and W.

Two typical types of carbide microstructures are observed according to the composition: V-rich or M-rich primary carbides and eutectic carbides between the austenite (Fe-rich matrix) and the MC carbides.

Some typical microstructures with different additions are presented in Figs. 1–6. The compositions of vanadium carbides in the presence of different additions and the compositions of other carbides are reported respectively in Tables 1 and 2. As in binary and Fe–M–C ternary systems, MC_x carbides are carbon deficient ($x < 1$).

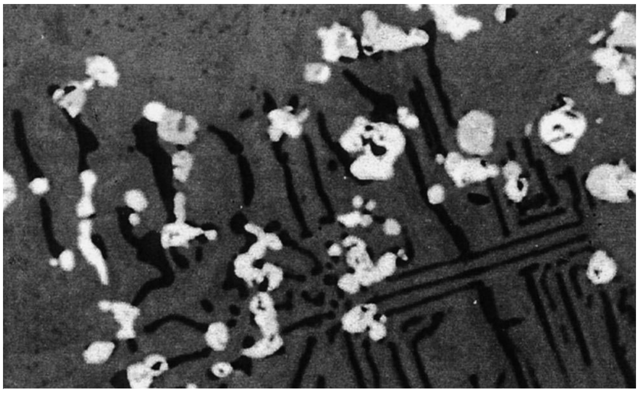

Fig. 2. Microstructure of quaternary FeVCZr alloys showing the MC carbides. V-rich carbides appear with a dark contrast and Zr-rich MC carbides are white.

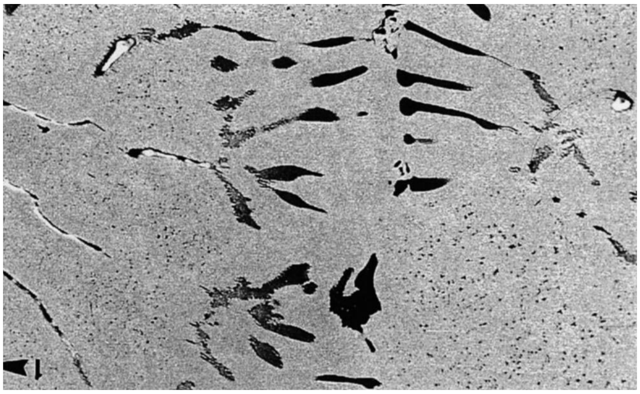

Fig. 3. Microstructure of quaternary FeVCNb alloys showing the transition zone between V-rich carbides (dark contrast) and NbC (white).

Fig. 4. Microstructure of quaternary FeVCTa alloys showing the transition zone between V-rich carbides (dark contrast) and TaC (white).

3.2. Monocarbide compositions in Fe–V–M–C (M = Ti, Zr, Nb and Ta)

With these additions, the C content does not change significantly. The C content increases slightly and continu-

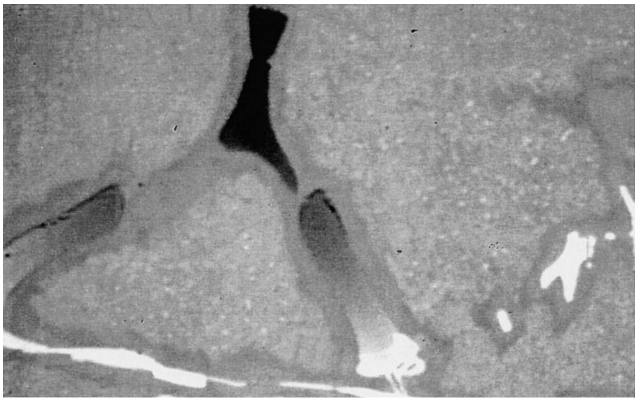

Fig. 5. Microstructure of quaternary FeVCMo alloys showing the transition zone between V-rich carbides (dark contrast) and Mo_2C (white) carbides.

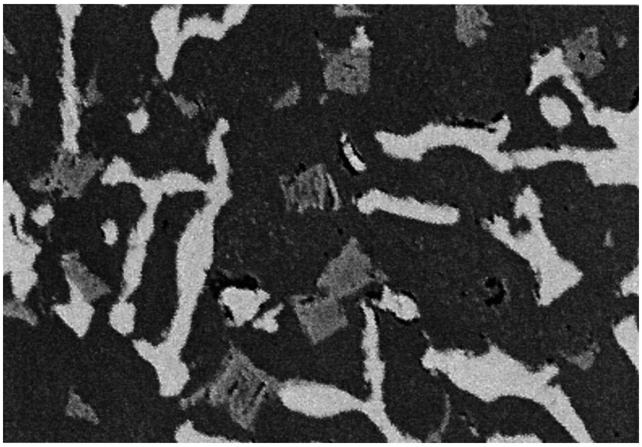

Fig. 6. Microstructure of quaternary FeVCW alloys showing the transition zone between V-rich carbides (dark contrast) and M_6C (grey) carbides.

Table 1
Carbon content, stoichiometry and solubility of M and Fe in V-rich $(VM)C_x$ carbides

M	C (at.%)	$x = C/M$	M (at.%)	Fe (at.%)
Ti	43–44	0.70–0.75	–	1.5
Zr	45–46	0.80–0.85	<0.1	1.0
Nb	41–43	0.70–0.75	9.0	1.5
Ta	42–44	0.70–0.80	5.0	1.5
Cr	42–43	0.70–0.75	1.5	1.5
Mo	41–43	0.70–0.75	1.5	3.0
W	39–40	0.65–0.70	7.0	2.0

ously from VC_x $(0.75 < x < 0.80)$, which seems to contain the lowest C level, to higher values: TiC_x $(0.85 < x < 0.90)$, ZrC_x $(x > 0.90)$ and TaC_x $(0.75 < x < 0.90)$. In these carbides, the Fe level is below 1 at.%.

Fig. 7 shows the compositions of the mixed carbides formed in alloys with different M/V ratios. With Ti, Nb and Ta additions a linear variation exists between the M and V levels; as V decreases, M increases. Between VC and MC carbides, all M/C ratios were analysed, indicating a continuous solubility in the temperature range of formation of these carbides.

In BSE images, VC carbides appear with a dark contrast while MC carbides formed with heavy elements show a white contrast. It is therefore easy to distinguish between the two types of V-rich and M-rich carbides.

Table 2
Carbon content, stoichiometry and solubility of V and Fe in M-rich MC carbides

M	Carbide	C (at.%)	M (at.%)	V (at.%)	Fe (at.%)
Ti	TiC_x	46.0–47.0	44.0–49.0	–	0.5
Zr	ZrC_x	47.5–48.5	48.0–49.2	<1.0	2.0
Nb	NbC_x	38.3–40.5	52.5	8.5	0.5
Ta	TaC_x	46.0–47.5	25.5–27.0	25.0	2.0
Cr	M_7C_3	26.0–28.0	10.0–15.0	5.0–9.0	40.0–48.0
Mo	Mo_2C	29.0–35.0	54.0	6.5	0.5
W	M_6C	15.0–15.8	34.0–38.0	4.0–10.0	40.0–45.0

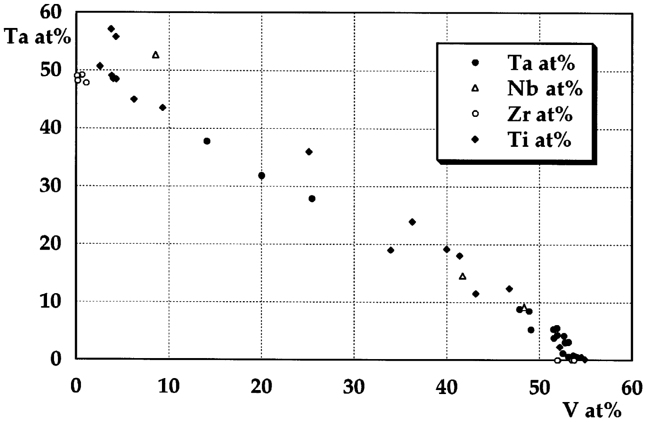

Fig. 7. The miscibility of mixed VC–MC carbides in quaternary FeVMC alloys with M = Ti (continuous solubility), Zr (very low solubility), Nb and Ta.

Except for quaternary alloys with a very low Nb or Ta content, solidification shows two binary eutectics: first the austenite–MC eutectic (white) then the austenite–VC eutectic (dark). A transition zone was clearly observed where the contrast changes continuously from dark for V-rich carbides to white for M-rich carbides (Figs. 3 and 4). In this area, a continuous variation of composition follows the contrast variation. Microanalyses show the substitution of M atoms by vanadium in the carbides. The V/M ratio increases rapidly from one point to another part of the carbide.

The behaviour of these additions agrees with what is known of the ternary V–M–C systems at high temperature. In ternary V–M–C systems, MC–VC mixtures form a continuous solid solution at high temperature, as shown in isothermal sections and quasi-binary sections reported by Holleck [2]. The presence of Fe seems to have no significant influence.

At low temperature, the behaviour is different. In the cases of Nb and Ta, decomposition of the M-rich carbides is well evidenced. The V-rich carbides are stable and no decomposition is observed. Our results show a larger solubility of V in MC than M in VC.

Experimental data are not available for the solid state, but thermodynamic calculations show that a miscibility gap exists at low temperature. These calculations suggest, either for NbC–VC [6] or TaC–VC [7] systems, a miscibility gap over the whole range of compositions between MC and VC. In the presence of Fe, the miscibility gap is not symmetrical, and extends to the M-rich region.

No indication of decomposition is observed in the presence of Ti additions, indicating complete solubility over the whole composition range between VC and TiC at low temperature as in the ternary system [8].

Ti and Zr belong to family IV and form MC carbides. At high temperature, TiC and VC form a continuous solid solution, while a binary eutectic exists in the VC–ZrC system [9,10] due to the large difference in radii of the metals Zr and V. The microstructure is more complex with the formation of a ternary eutectic between the austenite and the two carbides VC and ZrC. The difference in microstructure is well evidenced in the micrographs presented in Figs. 1 and 2.

In quaternary Fe–V–Zr–C alloys, ZrC_x monocarbide with a high C content ($x > 0.90$) is an almost stoichiometric compound. The mutual solubility is low between VC and ZrC. The solubility of V in ZrC is less that 1 at.%, while the solubility of Zr in VC is much lower (<0.1 at.%).

3.3. Composition of carbides in Fe–V–M–C with M = Cr, Mo or W

Cr, Mo and W belong to the same family of elements (VI) and form carbides with different crystallographic structures (Figs. 5 and 6).

The solubility of Cr in VC_x is about 1.5 at.%, while the solubility of V in M_7C_3 carbides reaches 10 at.% without decomposition in the solid state. VC carbides are often surrounded by a shell of M_7C_3 carbides. The interface is abrupt and no transition zone is observed between these two carbides.

The addition of Mo leads to a more complex situation. Between the solidification of the binary eutectic austenite/VC (dark) and the binary eutectic austenite/Mo_2C (white needles), a transition zone appears with a variable contrast.

Accurate microanalyses show simultaneously a continuous variation of the V/Mo ratio and a continuous decrease of the carbon level, from 42 at.% in V-rich carbides to 30 at.% in Mo_2C carbides.

The maximum solubility of W is about 9 at.% in vanadium carbides. A small transition zone is observed with a variation in the W level in the carbide from 1 to 9 at.%. The C level is found to be between 43.5 and 40.0 at.%, but no correlation was found between the W substitution and the C level. No decomposition of V-rich carbides is observed.

Due to the formation of an intermediate quaternary carbide, W-rich carbides were not observed in our alloys. The formation of carbides of M_6C type is well established. This carbide has a low and fixed carbon level (about 15 at.%). Vanadium seems to substitute for W according to the formula $(WV)_{2.6-2.9}(Fe)_{2.8-3.0}C$ as in the ternary Fe–W–C system. A vanadium level of about 10 at.% is found in some of the M_6C carbides. The (W + V) level seems to remain constant.

4. Conclusion

In quaternary Fe–V–M–C systems, V-rich carbides seem to be stable in the presence of all types of additions. On the contrary, decomposition occurs in Nb-rich and Ta-rich MC carbides in the presence of vanadium, indicating that a miscibility gap exists at low temperature between VC and MC (M = Nb or Ta). In the presence of Mo, continuous variations of the M and C level are observed between VC and Mo_2C, while in the presence of W, the formation of an intermediate carbide of M_6C type limits the solubility of W in VC.

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