Crystallographic structure of vanadium carbide precipitates in a model Fe–C–V steel

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(Received 2 August 2007; in final form 11 October 2007)

The crystallographic structure of vanadium carbide precipitates in iron is investigated using High Resolution Transmission Electron Microscopy (HRTEM) and conventional Selected Area Diffraction (SAD) analysis. After a two-step precipitation treatment (10 hours at 700°C and 10 days at 800°C) and different annealing treatments (from 870 to 920°C) performed on an ultra-pure Fe–V–C model alloy, carbides exhibit unambiguously the ordered monoclinic form \( V_6C_5 \). The often reported \( V_4C_3 \) structure, that refers to the pioneering work by Baker and Nutting is not encountered in the present investigation. Reasons for this contradiction are discussed, and the conclusion is drawn that no literature data are available to unambiguously support the existence of precipitates with the \( V_4C_3 \) structure.

1. Introduction

Microalloyed steels have received considerable interest over many years because of their extensive use for many industrial applications [1]. As an example, the addition of vanadium and/or niobium is a well-known way to control the mechanical properties of the alloy: (i) in Interstitial Free (IF) steels, carbonitride precipitation traps C and N atoms out of the solid solution, thus improving the formability [2]; (ii) in High-Strength Low-Alloyed (HSLA) steels, the grain size is controlled by a fine dispersion of carbonitride precipitates [1]. In this context, understanding the evolution of the precipitation state during the elaboration process of steels is a key to optimizing its final properties. From an experimental point of view, it is then required to proceed to a detailed microstructural characterization of the size, volume fraction, chemistry and crystallography of the precipitates. Such data are required for any attempt to model the kinetic evolution of the precipitation state versus temperature and time, as is being achieved more and more in modern thermodynamic approaches [3–6]. In the case of the well-documented Fe–V–C system, conflicting results can be found in the literature concerning the crystallography of vanadium carbide precipitates in ferrite: indeed, the B1, Na–Cl type
stoichiometric VC or substoichiometric VC\(_{1-x}\) fcc structure, and the ordered V\(_6\)C\(_5\) and V\(_4\)C\(_3\) phases have been frequently reported (see below). It is the purpose of this paper to clarify the structure of the vanadium carbide precipitates encountered in the course of a thorough experimental and thermodynamic investigation of model Fe–V–C alloys [7, 8].

2. Electron microscopy work

TEM observations of precipitates were performed on both thin foils and carbon extraction replicas. Thin foils serve to observe the location and orientation relationship, with respect to the matrix, of the precipitates, whereas extraction replicas allow easier statistics about the size of the precipitates. Thin foils were obtained by the conventional method of careful grinding to produce a thin disk of less than 50\(\mu\)m (in order to minimize the undesirable magnetic effects in the TEM), followed by final thinning to electron transparency by ion beam thinning with argon ions at 4–2.5\,keV under grazing incidence of 6–3\(^\circ\) in a Gatan PIPS instrument. Extraction replicas were obtained by a classical carbon film deposition (of an estimated thickness 15–30\,nm) on the surface of samples polished to \(1\,\mu\)m finish with diamond paste and slightly etched with a 0.4% Nital solution. The final dissolution of the matrix is performed in an ethanol–nitric acid bath.

Electron microscopy was essentially performed using a JEOL 2010F field emission gun transmission electron microscope operating at 200\,kV and equipped with an Oxford EDX device. The microscope was fitted with a JEOL annular detector allowing High Angle Annular Dark Field (HAADF) imaging in the scanning mode (STEM).

3. Alloy and treatments

An ultra-pure model alloy, the composition of which is given in table 1, was specifically prepared by direct melting at 1450\(^\circ\)C in an induction furnace under a mixed Ar/H\(_2\) atmosphere (PECM laboratory of the Ecole des Mines de Saint-Etienne – lecoze@emse.fr).

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According to previous work on a similar steel, carbides as small as 3\,nm have been successfully extracted [9].
A solutionizing treatment (30 minutes at 1000°C) followed by a water quench was performed. A dedicated treatment to achieve a ‘fully-precipitated state’ was designed according to the following considerations:

- To ensure homogeneous nucleation, it was preferred to perform nucleation and growth stages in ferrite α-Fe; according to the Fe–V–C phase diagram (see figure 1), a treatment of 10 hours at 700°C in vacuum (quartz encapsulation), followed by a slow air cooling, was chosen.
- In order to investigate a wide range of sizes, it was necessary to perform either long-term treatments, or high-temperature heat treatments.
- In order to maximize the precipitated volume fraction, it was necessary to perform low-temperature treatments.

From all the preceding points, it is tempting to perform long-term treatments at 700°C. Figure 2 shows that the typical precipitate size after the initial nucleation treatment remains very small, of the order of a few nanometres. It also confirms that VC carbides adopt a fcc structure in the expected Baker–Nutting orientation relationship [10]:

\[[100]_\text{Fe} / /[110]_\text{VC} \]
\[(002)_{\text{Fe}} / /(002)_{\text{VC}}.\]

Trying to perform coarsening at 700°C would lead to unfeasible treatment times (see below). Thus, an additional coarsening treatment of 10 days at 800°C (followed by slow air cooling†) was decided upon. Choosing lower temperatures, a ferrito-perlitic microstructure forms.

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†The iron austenitic matrix at 800°C turns into a ferrito-perlitic microstructure after slow air cooling.
as suggested by consideration (iii) above, would lead us to penetrate the rather complex three-phase domain ($\alpha$-Fe + $\gamma$-Fe + carbide) between the AC$\textsubscript{1}$ and AC$\textsubscript{3}$ temperatures (see figure 1), which is not desired. Figure 3 shows the resulting microstructure, and figure 3a demonstrates a distribution of roughly spherical precipitates, in the range 15–60 nm, within a ferritic grain. In order to get comparable precipitate sizes at 700°C, heat treatments as long as 100 days would have been necessary.$^\dagger$

As a conclusion, 10 hours at 700°C followed by 10 days at 800°C and slow air cooling (designated as the ‘fully-precipitated state’$^\ddagger$ below) represents the best compromise to satisfy the three preceding points (i)–(iii). In order to further investigate a wide range of sizes, the alloy was subjected to different isothermal reversion treatments in the austenitic domain at 870°C (2 minutes and 60 minutes in a molten salt bath) and 920°C (60 minutes in a molten salt bath and 10 days in quartz capsules), followed by a water quench.

4. Results

The crystal structure of vanadium carbide precipitates has been studied for each heat treatment (see section 3) on both thin foils and extraction replicas.

As already presented, figure 3 is a montage from the ‘fully-precipitated state’. All the precipitates that have been observed in thin foils appear to have a similar rounded-shape and were identified as fully incoherent with the matrix, owing to the

$^\dagger$According to the basic assumptions that (i) the coarsening is limited by vanadium diffusion, and (ii) the characteristic diffusion distance ranges as $\sqrt{D}t$, where $D$ is the diffusion coefficient at a given temperature $T$ ($D = 0.6110^{-4}\exp[-267100/RT]$ for $V$ in ferrite, and $D = 0.2510^{-4}\exp[-264200/RT]$ for $V$ in austenite $\gamma$-Fe [1], with $R$ equal to 8.32 J/K), 100 days at 700°C is ‘equivalent’ to 10 days at 800°C.

$^\ddagger$According to electrolytic dissolution and plasma spectroscopy, 80% of the vanadium is precipitated in that state [8].
Figure 3. Precipitation structure in the as-received state. (a): Low magnification image showing ‘spherical’ precipitates in a grain of ferrite. The inset is a typical EDX spectrum acquired with a nano-probe on a single particle. (b): Diffraction pattern showing the α-Fe matrix near the [111]fcc orientation (dashed ‘hexagon’) and additional spots due to a precipitate (the (111)fcc reflection is labelled – see text for details). (c): [100]M diffraction pattern from a V₆C₅ ‘standard’ ordered in the monoclinic (M) form [11], with a_M = 0.509, b_M = 1.018, c_M = 0.882 nm, γ = 109.47° (space group B2/m). (d): [100]H ([2110]H in four-indexes) diffraction pattern from a Nb₆C₅ ‘standard’ ordered in the hexagonal (H) form [12], with a_H = 0.546, c_H = 1.545 nm (space group P3₁) – this pattern has been rescaled to be directly comparable to (c). (e): Cell of the M₆C₅ monoclinic superstructure. Interstitial (111) carbon planes are labelled α, β and γ; the symbol □ stands for planes containing vacancies. (f): Idem (e) for the hexagonal superstructure (for clarity, M atoms have been omitted).
absence of any orientation relationship† as revealed in diffraction mode. It was thus quite difficult to get crystallographic information on the precipitates in diffraction, since tilting experiments in magnetic materials is a very delicate task. However, in the case of figure 3, it has been possible to observe both matrix and precipitate reflections in a single diffraction pattern for one particle (b). The faint, vertically aligned spots arising from the precipitate are the unambiguous signature of the ordered \( \text{V}_6\text{C}_5 \) phase as explained by figure 3(c)–(f). In (c) and (d), well-oriented diffraction patterns, respectively obtained on a \( \text{VC}_{\approx0.84} \) single crystal [13], and on a \( \text{Nb}_{6}\text{C}_5 \) powder [14], are reported to serve as ‘references’ for the monoclinic \( \text{B}2/\text{m} \) [11] and hexagonal \( \text{P}3_1 \) [12] \( \text{M}_6\text{C}_5 \) superstructures (\( \text{M} = \text{V} \) or \( \text{Nb} \)), depicted in (e) and (f) respectively‡.

From a simple comparison between the experimental diffraction (b) and the ‘standard’ ones in (c) and (d), the monoclinic \( \text{M}_6\text{C}_5 \) ordered form is unambiguously identified for the precipitate of interest.

Figure 4 is a montage of conventional TEM and HAADF images after different thermal treatments, which further confirm the \( \text{V}_6\text{C}_5 \) monoclinic ordered form (e.g. figure 4(g)). The diffraction patterns in figure 4(e) and (f) show two variants of the \( \text{V}_6\text{C}_5 \) superstructure observed along equivalent \( \langle 110 \rangle_{\text{fcc}} \) directions, but in this case the monoclinic form cannot be unambiguously identified since the hexagonal \( \text{V}_6\text{C}_5 \) cell exhibits reciprocal lattice sections with the same symmetry for both patterns (see the appendix).

During our extensive TEM observations, the positive identification of a \( \text{M}_6\text{C}_5 \) ordering (either the \( \text{M} \) or \( \text{H} \) phases, and preferably the \( \text{M} \) phase) has been systematic for all precipitates that could have been oriented along an adequate direction, in which superlattice reflections are expected. However, an undesirable irradiation effect was observed, as demonstrated in figure 5. Owing to knock-on damage arising from the incident primary electrons, disordering of the carbon-vacancy distribution occurred in a few seconds with the intense beam of the FEG-TEM. This phenomenon is well-known in the \( \text{V}_6\text{C}_5 \) [15] and \( \text{V}_8\text{C}_7 \) [16] ordered superstructures.

5. Discussion

From the above, the crystal structure of vanadium carbide precipitates has been positively identified as the \( \text{M}_6\text{C}_5 \) ordered phase, and most probably the monoclinic form proposed by [11].

Nevertheless, some ambiguity remains concerning the precipitates observed in \( \langle 110 \rangle_{\text{fcc}} \) orientations, directly after the nucleation treatment of 10 hours at 700°C (see figure 2). Indeed, it has been shown in figure 5b that unirradiated ordered \( \text{V}_6\text{C}_5 \) particles exhibit a doubling of the \( \langle 111 \rangle_{\text{fcc}} \) lattice fringes in \( \langle 110 \rangle_{\text{fcc}} \) HRTEM images. This feature is not observed in figure 2, which could suggest that the

†The initial Baker–Nutting [10] orientation relationship between precipitates and the ferritic matrix at 700°C (see figure 2) has been lost during the subsequent coarsening treatment at 800°C in the austenitic domain.
‡More details on the \( \text{M}_6\text{C}_5 \) ordered phases are given in the appendix.
Figure 4. Evolution of precipitation during ageing. (a): Detail showing a precipitate in thin foil after 2 minutes at 870°C (TEM bright field). (b): *Idem* (a) after 60 minutes at 920°C. (c): Extraction replica of the same state as in (b) observed in HAADF-STEM. (d) and (e): SAD patterns from two precipitates from (c) showing the unambiguous evidence of the V₆C₅ superstructure (the indexing is given for the monoclinic form, see text for details). (f): HAADF image of an extraction replica after 10 days at 920°C; larger and more cuboidal precipitates are observed. (g): Further SAD evidence of the M-V₆C₅ ordered phase in state (f).
corresponding precipitates are not ordered and consequently with a composition possibly different from V₆C₅. However, this conclusion cannot be ascertained for the following reasons:

(i) In the monoclinic M₆C₅ form, some (110)ₚfcc-type zone axes do not exhibit any superlattice reflection (as discussed in the appendix), which obviously prevents the observation of any doubling of (111)ₚfcc lattice fringes.

(ii) For those precipitates lying in rather thick matrix regions (figure 2a), the existence of Moiré fringes makes it difficult to visualize the possible doubling of the (111)ₚfcc lattice fringes.

(iii) For those precipitates lying in rather thin regions, without any significant overlapping matrix (figure 2b), the low thickness can prevent the observation of any fringe doubling. Although the quality of the micrograph in figure 2a is not

Figure 5. Irradiation damage of precipitates (after 60 minutes at 870°C). (a): [1T0]fcc HRTEM image of a precipitate on an extraction replica. (b): Enlargement of the central part of the particle shown in (a): note the contrast re-enforcement every two (111)fcc lattice fringes (arrows), due to carbon ordering in the V₆C₅ structure. (c): Numerical diffractogram from (b) showing the $\frac{1}{2}(111)_{fcc} = (020)_{fcc}$ superlattice reflection responsible for the fringe doubling in (b). (d)–(f): Same as (a)–(c) after 30 seconds under the electron beam: note that the (020)fcc superlattice fringes and reflection have almost vanished in (e) and (f), respectively. Note that the HRTEM contrast of images (b) and (e) is not excellent because of the thick particle and the additional carbon replica layer.
sufficient to allow HRTEM image simulation, indicative computations can be performed as a function of reasonable thicknesses and defoci for both ordered V₆C₅ and disordered VC (or VC₁₋ₓ/C₀ₓ). Figure 6 shows that for thin precipitates, the ordered phase can easily be confused with the disordered one for many defocus values, where the \( \frac{1}{2}(111)_{\text{fcc}} \) superlattice fringes are too faint to be discerned.

(iv) As clearly shown by figures 5d–f, electron irradiation promotes disordering, obviously all the more easily than the crystal is thin.

In complement to high-resolution imaging, one may think of performing nanodiffraction. It should be emphasized that such observations remain rather difficult owing to (i) the size of the particles embedded in the matrix, and (ii) the high electron beam flux inherent to this mode, which would promote fast irradiation effects.

As a conclusion, the smallness of vanadium carbides present after 10 hours at 700°C prevents any positive interpretation of the ordering state and consequently of the chemical composition. Note that in all other states where precipitates were large enough to allow a classical electron diffraction analysis, the ordered V₆C₅ phase was unambiguously identified.
Surprisingly, although some previous works on the precipitation of vanadium carbide in steels report the existence of the $V_6C_5$ structure [18–20], or simply refer to the fcc, B1-type $VC_{1-x}$ structure [21–24], a lot of authors, moreover rather recently, claim evidence for the ‘$V_4C_3$’ structure [25–31] in most cases with the simple indication of a fcc lattice parameter near or equal to 0.416 nm, as already mentioned in the pioneering work on precipitation of metallic carbides in low-alloy steels (e.g. [32, 33]). Even in the well-known work by Baker and Nutting on (Mo,V)C precipitates in steel [10], $V_4C_3$ is mentioned throughout the paper. Moreover, these authors pointed out the experimental evidence of unknown extra-spots in an electron diffraction pattern: these extra-spots are indeed fully consistent with superlattice reflections due to the $V_6C_5$ phase, unknown at that time!

In fact the composition $M_4C_3$ refers to the $M_4C_3$ or $\zeta$-MC$_{1-x}$ structure, as identified in the transition metal carbides of the Vth group (VC, NbC and TaC), at the phase boundary between the cubic monocarbide MC$_{1-x}$ and the hexagonal hemicarbide M$_2$C [34]. However, an obsolete ‘deleted’ JCPDS file (01-1159) describes $V_4C_3$ as a simple fcc, B1-type structure (space group Fm3m) with $a=0.416$ nm, which can account for indexing errors (i.e. $V_4C_3$ instead of the Na–Cl monocarbide VC$_{1-x}$ – see for example [35]). It is worth noting that in a previous study on carbides in cast iron [19], the authors mention the same statement, that is, no evidence is reported in the literature of the $\zeta$–MC$_{1-x}$ phase in the carbides labelled VC$_{0.75}$ or $V_4C_3$ in multi-components alloys.

According to the detailed crystallographic analysis of the $M_4C_3$ phase reported in the appendix, it can be concluded that: (i) the ordered $V_6C_5$ phase unambiguously identified here cannot be confused with the $V_4C_3$ phase; (ii) since we are not aware of any positive identification of $V_4C_3$ through an unambiguous electron diffraction experiment in the previously mentioned literature, the hypothesis that $V_4C_3$ has been invoked instead of the $V_6C_5$ phase, or simply a fcc VC$_{1-x}$ phase, is indeed very probable.

Obviously, Electron Energy Loss Spectroscopy (EELS) would allow the chemical composition of precipitates to be ascertained (but not directly their crystallography). Such experiments require a delicate calibration procedure, using normalized reference spectra for the vanadium-L and carbon-K edges, as was recently done in the case of niobium carbonitrides [9]. Moreover, EELS analysis obviously requires us to get rid of any spurious carbon signal: this appears to be very delicate to achieve in the case of thin foils (due to carbon contamination and poor signal to noise ratio) and, a fortiori in the case of carbon extraction replicas [36]. Nevertheless, the basic crystallographic analysis in TEM remains an elegant way to evaluate the chemical composition of sub-stoichiometric metal carbides, which is associated to different long- and short-range ordered states (among them, the $V_6C_5$ and $V_4C_3$ forms), easily identified in diffraction and HRTEM modes [14, 16].

6. Conclusions

(i) After a specific two-step heat treatment (10 hours at 700°C and 10 days at 800°C) designed to get coarse vanadium precipitates, different reversion treatments (from 870°C to 920°C) led to precipitates ranging from 10 to
200 nm in size. All analyzed precipitates have been positively identified as monoclinic ordered V$_6$C$_5$ carbides, and no evidence has been obtained for the V$_4$C$_3$ structure.

(ii) Due to knock-on damages arising from incident primary electrons, disordering of the carbon-vacancy distribution within precipitates occurred in a few seconds with the intense beam of the FEG-TEM.

(iii) Precipitates resulting from the 10 hours at 700°C treatment were too thin to be unambiguously identified as monoclinic ordered V$_6$C$_5$ carbides.

(iv) Many authors report the presence of ordered V$_4$C$_3$ structure for vanadium carbide precipitates, often referring to the famous paper by Backer and Nutting. However, the description of the diffraction pattern made by Backer and Nutting corresponds surprisingly well with the monoclinic ordered V$_6$C$_5$ structure, that was unknown at that time.

(v) To our knowledge, no unambiguous diffraction experiment has been performed in the literature, which positively identifies the V$_4$C$_3$ structure within precipitates. It thus seems that the often reported V$_4$C$_3$ precipitates structure could be V$_6$C$_5$ instead.

Acknowledgements

The authors are grateful to the CLYME (Consortium Lyonnais de Microscopie Electronique) for access to the JEOL 2010F microscope. This work was financially supported by Ascometal and thanks are due to P. Dierickx (CREAS) for fruitful discussion.

Appendix: Additional comments on the M$_6$C$_5$ and M$_4$C$_3$ phases in the V–C system

A.1. The V$_6$C$_5$ ordered structure and crystallographic analysis of figure 3

Basically, the fcc-based, Na–Cl or B1-type structure of the transition metal carbides such as VC$_{1-x}$ and NbC$_{1-x}$ accommodates the departure from stoichiometry (x) by the presence of constitutional vacancies within the carbon sublattice. Ordering at the M$_6$C$_5$ (MC$_{0.833}$) composition is due to the regular succession of full and vacancy-containing interstitial carbon close-packed planes in a given [111]$_{fcc}$ direction, which determines the longest repeat distance of the ordered phase. In the case of the monoclinic structure (M), the periodicity is established by the stacking of four such ‘basal’ planes, and the complete sequence of both metal and carbon (111)$_{fcc}$ planes can be written as:

\[ \alpha \square \ C \beta A \gamma \square \ B \alpha C \beta \square \]

where Greek and Roman letters represent respectively the metalloid and metal layers, while the ‘\( \square \)’ subscript indicates the vacancy-containing interstitial planes.

In this sequence, it clearly appears that the starting and ending (carbon + vacancy) planes are not of the same type (\( \alpha \square \) and \( \beta \square \)), which explains why the \( b_M \) parameter defined by the sequence is not along the [111]$_{fcc}$ direction, leading
to a monoclinic cell (the angle $\gamma$ between the $b_M$ axis and the $a_M$ axis lying in the (111)$_{\text{fcc}}$ ‘basal’ plane is 109.47°). The parameters of this monoclinic superlattice are ideally related to the parameter of the fcc disordered carbide ($a_{\text{fcc}} \approx 0.416$ nm for VC$_{0.833}$) through the analytical relations:

$$a_M = \frac{1}{2}[11\bar{2}]_{\text{fcc}} \quad \left( a_M = \frac{\sqrt{3}}{2} a_{\text{fcc}} \right)$$

$$b_M = [112]_{\text{fcc}} \quad \left( b_M = \sqrt{6} a_{\text{fcc}} \right)$$

$$c_M = \frac{3}{2}[1\bar{1}0]_{\text{fcc}} \quad \left( c_M = \frac{3}{\sqrt{2}} a_{\text{fcc}} \right).$$

Similarly, the hexagonal superlattice ($H$) shown in figure 3(f) is based on a repeat sequence of six interstitial planes:

$$\alpha \square C \beta \square A \gamma \square B \alpha C \beta \square A \gamma B \alpha \square.$$

In this case, the $c_H$ axis defined by this sequence is parallel to the [111]$_{\text{fcc}}$ direction. As for the monoclinic structure, the parameters of this hexagonal superlattice are simply related to the parameter $a_{\text{fcc}}$ ($a_{\text{fcc}} \approx 0.446$ nm for NbC$_{0.833}$):

$$a_H = \frac{1}{2}[11\bar{2}]_{\text{fcc}} \quad \left( a_H = \frac{\sqrt{3}}{2} a_{\text{fcc}} \right)$$

$$c_H = 2[111]_{\text{fcc}} \quad \left( c_H = 2\sqrt{3} a_{\text{fcc}} \right).$$

From these descriptions, it can easily be understood that the $h$112$^i_{\text{fcc}}$ azimuths are of special interest for identifying which ordered form occurs in $V_6C_5$: one of these axes (i.e. [112]$_{\text{fcc}}$) is strictly the [100] direction of both structures, with the ‘basal’ planes in zone. Then, in the case of the monoclinic phase, the reciprocal lattice vector $(111)_{\text{fcc}} = (040)_M$ is possibly divided into 4, as for parallel rows (see figure 3c), while a division by 6 of the $(0006)_H = (111)_{\text{fcc}}$ vector is expected in the hexagonal structure (figure 3d).

The experimental pattern in figure 3b exhibits a division by 4, and does unambiguously correspond to the monoclinic form of $V_6C_5$. This agrees well with previous work on ‘bulk’ materials, which has shown that the monoclinic form is much more frequent than the hexagonal one in the case of vanadium carbide [14].

**A.2. The V$_4$C$_3$ structure**

The $M_4C_3$ structure was initially suggested in the region VC$_{0.50}$–VC$_{0.74}$ below 1344°C [37]. It was refined by X-ray diffraction (JCPDS file 35-0786 in the case of V$_4$C$_3$) in the V-C, Nb-C and Ta-C systems [34], and further confirmed by TEM in the V–C [38] and Ta–C [39, 40] systems.
According to the notation given in section A1, the repeat sequence of the M₄C₃ structure can be written as a stacking of 12 metallic close-packed planes [34]:

\[
A \gamma B \gamma A \gamma B \alpha C \beta A \beta C \beta A \gamma B \alpha C \alpha B \alpha C \beta A.
\]

Consequently, the structure appears to be of trigonal (T) symmetry (space group R3m), with \(a_T = 0.2917\) and \(c_T = 2.783\) nm. In the original X-ray diffraction work by [34], the question of possible ordering of constitutional carbon vacancies could not be addressed. TEM work shows that short-range ordering exists in the case of V₄C₃ [38], whereas periodic removal of complete carbon layers is supposed in the case of Ta₄C₃ [39, 40]. However, the exact distribution of carbon atoms within the interstitial \(\alpha, \beta\) and \(\gamma\) planes remains questionable; hence, the Greek letters in the sequence written above designate carbon planes with averaged \(\frac{3}{4}\) occupancies. But what is essential to note here is that this structure differs from the fcc-based MC₁₋ₓ structure, since the stacking of the close-packed metallic planes (e.g. A B A B A C A B C B C) is a mixture of hcp and fcc layers. As for the M₆C₅ structures, the parameters of this trigonal superlattice are simply related to the parameter \(a_{\text{fcc}}\):

\[
a_T = \frac{1}{2}[11\bar{2}]_{\text{fcc}} \quad \left( a_T = \sqrt{\frac{3}{2}} a_{\text{fcc}} \right) \\
c_T = 4[111]_{\text{fcc}} \quad \left( c_T = 4\sqrt{3} a_{\text{fcc}} \right).
\]

A.3. Comparing both V₄C₃ and V₆C₅ structures

At first sight, the V₄C₃ and V₆C₅ phases exhibit strong similarities in both imaging and diffraction modes: on the one hand, faulted microstructures are observed for both phases in bright or dark field micrographs (see [38–40]); on the other hand, faint ‘superlattice-type’ reflections occur in diffraction patterns, as shown in figure A1†. However, these similarities are due to very different origins: in V₄C₃, such features arise from stacking faults within the metallic sublattice, whereas they are caused by ordering of carbon vacancies in V₆C₅.

A detailed examination of the most significant diffraction patterns allows both structures to be discerned. Let us, for example, compare the \(h_{110}\) reciprocal lattice sections of both the V₆C₅ and V₄C₃ structures in figure A1. In the T-V₄C₃ phase, superlattice reflections occur at \(\frac{1}{4}(111)_{\text{fcc}}, \frac{1}{2}(111)_{\text{fcc}}\) and \(\frac{3}{4}(111)_{\text{fcc}}\) (that is, \((0003)_T\), \((0006)_T\) and \((0009)_T\)), while only one authorized additional spot occurs at \(\frac{1}{2}(111)_{\text{fcc}}\) for the M-V₆C₅ form ((020)ₘ in the \([001]_M\) zone axis), and equivalently for the H-V₆C₅ form (in the \([1\bar{1}00]_H\) zone axis). Moreover, kinematical calculations

†This montage summarizes some of the \(h_{110}\) and \(h_{112}\) reciprocal lattice sections of the various forms of V₆C₅ as indexed in the disordered cubic structure. For the sake of brevity, only the most significant zone axes are shown. In the case of the monoclinic phase, it must be emphasized that the \([032]_M\) and \([032]_M\) diffraction patterns (respectively \([101]_{\text{fcc}}\) and \([011]_{\text{fcc}}\)) do not exhibit any superlattice reflections, which may correspond to what is observed in figure 2 (as discussed in section 5).
show that no multi-diffraction effect could cause the appearance of \( \frac{1}{4}(111)_{\text{fcc}} \)-type diffraction spots in V\(_6\)C\(_5\). Regarding the \( h112i \) fcc reciprocal lattice sections, the presence of diffractions rows at \( \frac{1}{3}(220)_{\text{fcc}} \) and \( \frac{2}{3}(220)_{\text{fcc}} \) proves unambiguously the existence of the V\(_6\)C\(_5\) structure.

According to the above analysis, the present experimental results (e.g. figure 4) lead to the following conclusions: (i) the V\(_6\)C\(_5\) structure is positively identified in the \( h112i \) fcc zone axes (furthermore in the monoclinic form – see main text for details); (ii) the V\(_4\)C\(_3\) structure is incompatible with the \( h110i \) fcc diffraction patterns.

Surprisingly, none of these significant and unambiguous V\(_4\)C\(_3\) diffraction patterns are reported in any of the numerous works that refer to the V\(_4\)C\(_3\) phase in studies of vanadium carbide precipitation in ferrite (see the references cited in the main text, section 5).
References