Rietveld analysis of the ordering in V_8C_7

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Abstract

The ordered low-temperature phase of vanadium carbide (V_8C_7) was investigated using X-ray diffraction and analysed by the Rietveld method. This confirmed the long-range ordering of carbon atoms at the octahedral positions in the space group $P4_332$, which was accompanied by the ordering of vacancies at the non-metal positions. It was found that the vanadium octahedra surrounding the vacant positions are distorted and that carbon atoms are shifted towards vacancies. Besides the atomic displacement, anisotropic thermal vibrations of atoms near the vacant positions were observed. These effects are assumed to be related to the increase of microhardness and electrical conductivity that were observed recently. © 1998 Elsevier Science S.A.

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1. Introduction

Non-stoichiometric vanadium carbide with the composition of 43.5 at % C is known to occur in two modifications. The high-temperature phase, δ-$VC_{0.87}$ crystallises in the fcc structure (space group *Fm3m*, NaCl type) [1], where the vacancies are randomly distributed among the non-metal sites. Below the transition temperature of $1112\pm8°C$ [2], the carbon atoms tend to create the long-range ordered phase V_8C_7, which can be described using the structure model suggested by Parthé and Yvon [3] and by de Novion et al. [4]. The ordered structure is also cubic (space group $P4_332$) and has an approximately eight times larger elementary cell than the disordered fcc phase.

In a recent study [5], it was established (on polycrystalline material) that this ordering increases the microhardness and the electrical conductivity. The influence of the order–disorder transformation on the electrical conductivity of the vanadium carbide single crystals had been investigated previously by Shacklette and Williams [6]. In our contribution, the structure characteristics of the ordered vanadium carbide are investigated by means of the Rietveld analysis of the diffraction pattern.

2. Experimental

The vanadium carbide, V_8C_7, was prepared from $VC_{0.87}$ powder (Treibacher Powdermet, Austria). The starting material was milled and hot pressed at 1900°C in an Ar atmosphere. The compact specimen was annealed at successively decreasing temperatures: 20 h at 900°C, 20 h at 800°C and, finally, 60 h at 700°C. Details of the sample preparation procedure are given elsewhere [5]. Chemical analysis of the carbon contents, carried out using Dumas gas chromatography (GC) confirmed the expected sample stoichiometry ($VC_{0.87}$). The nitrogen and oxygen contents were 0.21 at % N (Dumas GC) and 0.64 at % O (hot extraction).

X-ray diffraction was performed with a conventional Bragg-Brentano diffractometer, with $CuK\alpha$ radiation. The $CuK\beta$ line was separated by a graphite secondary monochromator. The divergence of the primary beam was 1° and the width of the receiving slit was 0.2 mm. The diffraction pattern was recorded between 14 and 120° in 2Θ in the step scan mode, with a step size of 0.02° (2Θ) and with a counting time of 10 s per step.

3. Results and discussion

According to the suggested structure type [3,4], the

space group *P4₃32* was used for the structure refinement of the long-range ordered phase, in which the 32 vanadium atoms occupy the Wyckoff positions (*8c*) and (*24e*) and the 28 carbon atoms are located at the Wyckoff positions (*4a*), (*12d*) and (*12d*) [7]. The structure refinement was carried out with the computer program DBW3.2s [8] with ten structure and eleven instrumental parameters. The lattice parameter, six atomic positions, the temperature factors of vanadium and carbon, and one parameter for the preferred orientation were refined. Only a weak preferred orientation of crystallites in the crystallographic direction {111} was found in the material. The texture was assumed to be fibre-shaped as the sample was rotated during the measurement. The refined lattice parameter and the atomic fractional coordinates are listed in Table 1.

The line broadening was described by a linear function of the tangent of the diffraction angle; the background was fitted by a polynomial function of the fifth order. The diffraction profiles were approximated by the Pearson VII function, the line shape and the line asymmetry of which were refined. The last refined instrumental parameter was the position of the zero point of the diffractometer.

The good agreement between the measured and calculated intensities is illustrated in Fig. 1. The refined atomic positions (Table 1) show a small distortion of the vanadium octahedra in comparison with the structure model suggested in refs. [3,4], which is illustrated in the structure view given in Fig. 2. The interatomic distances in the metal sublattice are given in Table 2, together with the bonding lengths for V–C as compared with the corresponding parameters calculated for the symmetrical octahedra of the disordered fcc structure. Around the vacant non-metal positions, the vanadium atoms are shifted towards the centre. The displacement is between 0.03 and 0.06 Å. A more significant displacement was observed for carbon, which was shifted towards the vacant positions as well. The displacement was up to 0.5 Å. Including this atomic displacement in the original structure model [3,4]
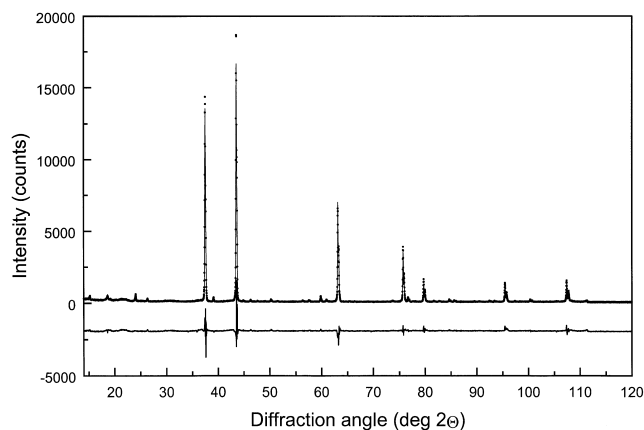

Fig. 1. Diffraction pattern of the ordered V_8C_7 phase. The measured intensities are plotted by points, the calculated intensities by the upper solid line. The difference diffraction pattern is given in the lower part of the figure.

improved the agreement between the measured and the calculated intensities of diffraction lines.

The match in intensities was further improved if anisotropic thermal vibrations of vanadium located at the Wyckoff position (*8c*) and that of carbon located at (*12d*) were taken into account. These carbon atoms are shifted most from their regular positions; the respective vanadium atoms are adjacent to them. The temperature factors of both vanadium and carbon were dominant in the *y* direction, which was characterised by a large value of the β_{22} parameter for both species (Table 1). Thermal vibrations in the remaining directions are negligible.

The anisotropic temperature factors can be interpreted as a deformation of the charge density near the vacant positions, which is probably responsible for the increase in the electrical conductivity confirmed previously [5,6].

Table 1
Structure parameters of the ordered V_8C_7 phase and the Bragg R-factor of the refinement, calculated from the integrated intensities

Space group	P4₃32		
Lattice parameter *a*	8.34027(2) Å		
Fractional coordinates	*x*	*y*	*z*
C (*4a*)	0.1250	0.1250	0.1250
C (*12d*)	0.1250	0.6296(6)	0.6204(6)
C (*12d*)	0.1250	0.3254(8)	0.9246(8)
V (*8c*)	0.3705(4)	0.3705(4)	0.3705(4)
V (*24e*)	0.1216(4)	0.3811(6)	0.1326(4)
β_{22} of V (*8c*)	0.083		
β_{22} of C (*12d*)	0.183		
R (Bragg)	8.1%		

The fractional coordinates given without estimated standard deviations were not refined, as they are fixed by the structure.
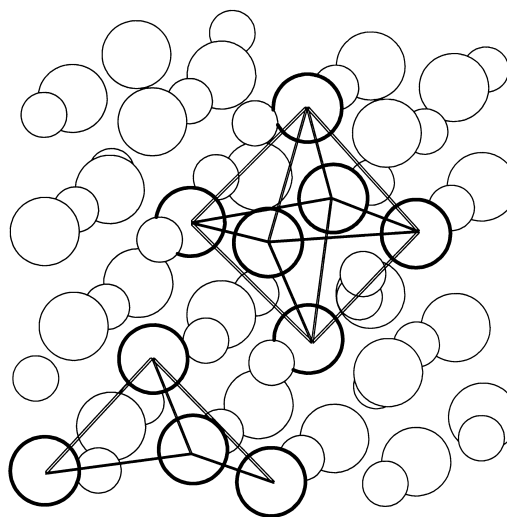

Fig. 2. View of the ordered V_8C_7 phase. The large circles denote the vanadium atoms; the small circles are for carbon. The vacant vanadium octahedra are emphasised.

Table 2
Comparison of the V–V and V–C atomic distances for the disordered and ordered structure of V_8C_7

Distance	Disordered (Å)	Ordered	
		Empty octahedra (Å)	Occupied octahedra (Å)
V–V	2.95	2.82–2.93	2.95–3.11
V–C	2.09	1.80–2.09	2.09–2.58

The atomic distances between vanadium and carbon are as measured between the vanadium atoms creating the respective (empty or occupied) octahedra and the next carbon atoms located outside these octahedra.

Furthermore, it can be considered that the atomic displacement improves the mechanical properties of the ordered phase that was observed in the increase of the microhardness [5].

4. Concluding remarks

Using the Rietveld structure refinement, it was confirmed that carbon atoms and vacancies located at the non-metal positions tend to create long-range ordering in the low-temperature V_8C_7 phase. The observed long-range ordering caused the atomic displacement of both species, i.e. V and C, towards the vacant positions. Additionally, deformation of the charge density was detected, which was recognised as anisotropy of the thermal vibrations of vanadium and carbon near the vacant vanadium octahedra. The correlation between the atomic shift and the deformation of charge density on the one hand, and the increase of the electrical conductivity and the improvement of the microhardness on the other hand, was considered.

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