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Effects of vacancy ordering on structure and properties of vanadium carbide

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Abstract

The microhardnesses, electrical conductivities, specific heats at constant pressure (C_p), lattice parameters and microstructures of ordered and disordered vanadium carbides were investigated. It was found that ordered vanadium carbide has a higher microhardness and electrical conductivity than a disordered carbide of the same composition. In a thermodynamic study the C_p and temperatures of the order→disorder transformations were measured by using differential scanning calorimetry (DSC). The values of latent heats of the disorder–order reactions δ-$VC_{0.87}$→V_8C_7 and δ-$VC_{0.83}$→V_6C_5 were 2354 J/gfw and 2114 J/gfw, respectively. The measured temperatures corresponding to the onset of the transformations were 1095°C for V_8C_7 and 1163°C for V_6C_5. Ordered domains could be made visible in microstructural investigations, which showed that ordering in compact vanadium carbide specimens originates at the grain boundaries of the disordered compound. © 1997 Elsevier Science S.A.

Keywords: Vanadium carbide; Phase transition; Microhardness; Electrical conductivity; Specific heat

1. Introduction

Group IV to VI transition metal carbides, nitrides and carbonitrides attract many researchers' attention because of an unusual combination of physical and chemical properties (high melting temperatures, hardness and high-temperature strength, on the one hand, and good electrical and thermal conductivity, on the other) ensuring their utilisation as high-temperature structural materials and/or as components in wear-resistant hardmetals. An important property of these compounds with the NaCl-type structure is the feature that the octahedral interstitial sites of the metallic fcc sublattice may be only partially filled with carbon or nitrogen atoms, i.e. the presence of structural defects. Under certain conditions their presence may give rise to atomic ordering which results from the redistribution of non-metal atoms and structural vacancies on the interstitial lattice sites. Owing to their high structural vacancy concentration, such non-stoichiometric interstitial compounds are unique materials for the investigation of atomic ordering particularly with respect to the rather high atomic mobility of the interstitial atoms. These compounds display a far greater variety of superstructures than any other alloy. On the basis of crystallographic considerations it has been shown [1] that ordered carbide structures can form, which correspond to the compositions Me_2C; Me_3C_2; Me_8C_5; Me_4C_3; Me_5C_3; Me_5C_4; Me_6C_5 and Me_8C_7 (Me=Ti; Zr; Hf; V; Nb; Ta).

Vanadium monocarbide has a wide region of homogeneity ($VC_{0.65}$–$VC_{0.90}$). Within this region the 'disordered' δ-VC_{1-x} crystallises in the NaCl-type cubic structure. It should be noted that the stoichiometric composition $VC_{1.00}$ cannot be obtained under equilibrium conditions. As with other non-stoichiometric cubic transition metal carbides and nitrides, it is known to have a tendency toward long-range or short-range ordering in the non-metal sublattice. According to [2–5] an ordered cubic phase V_8C_7 was observed near ($0.86 \leq y \leq 0.89$), the carbon-rich limit of δ-VC_{1-x}. This results in a cubic elementary cell with a lattice parameter twice as large as that of a disordered carbide. The superstructure belongs to space group $P4_132$ (or to the enantiomorphic space group $P4_332$). A second ordered phase with a composition V_6C_5 with a trigonal (space group $P3_1$) [6] or monoclinic (space group C2) [7] symmetry was observed in the range $0.66 \leq y \leq 0.88$.

The ordering of non-metal atoms and structural vacancies in these compounds is accompanied by a change in many physical properties as compared to the disordered

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phase. The influence of the order–disorder transformation on the electrical resistivity of single crystals of vanadium carbide was studied by Shacklette and Williams [8]. They found that the electrical resistivity of the disordered vanadium carbide is significantly higher than that of the ordered phase and the temperatures of the order–disorder transitions were found to be 1275±8°C for V_6C_5 and 1124±15°C for V_8C_7. The thermodynamics of order–disorder transformations in δ-VC_{1-x} were studied by Emmons and Williams [9] by use of powdered samples. They concluded from their experiments that both order–disorder transformations were of the first order. According to [9] the temperatures corresponding to the onset of transformations are 1184±12°C for V_6C_5 and 1112±8°C for V_8C_7.

The purpose of the present study is to investigate in detail under which conditions ordered phases in non-stoichiometric vanadium carbide are formed and how non-stoichiometry and ordering affects some physical properties of these compounds.

2. Experimental

Cylindrical specimens of δ-VC_{1-x} of 15 mm in diameter and 4 mm height and various carbon contents (y=0.66; 0.79; 0.83; 0.87) were synthesised by hot-pressing of powder mixtures of metallic vanadium and vanadium carbide $VC_{0.87}$ (supplied by Treibacher Powdermet, Austria). Starting powders were intensively mixed in a planetary ball mill with methanol as milling aid, dried and hot pressed in a graphite die at temperatures up to about 1900°C at a pressure of 35 MPa in an Ar atmosphere with a ramp time of 30 min. Layers of graphite foil and Zr foil were placed between the powder and the graphite die. The graphite foil prevented sticking between the die and the sample, which otherwise led to cracking of the samples. The Zr foil was carburized during the hot-pressing cycle and served as a getter as well as a diffusion barrier. The hot-pressed compacts were slowly cooled to room temperature within about 1 h.

In order to obtain fully ordered vanadium carbide specimens, the compact specimens were annealed at a temperature of 900°C for 20 h, then at 800°C for 20 h and finally at 700°C for 60 h, whereupon they were cooled down to 25°C. In order to obtain (disordered) δ-$VC_{0.87}$, closely corresponding in composition to V_8C_7, a sample was annealed at a temperature of 1150°C for 10 min in a silica tube and then water quenched. The formation of δ-$VC_{0.87}$ was proved by the absence of superstructure reflections in the XRD pattern.

The phases present in the δ-VC_{1-x} specimens before and after annealing and quenching were investigated by XRD with Cu Kα radiation. XRD was performed in a step-scanning mode with steps of $\Delta 2\Theta$=0.02° and an exposure time of 10 s at each point within the region 2Θ=14–120°.

Chemical analysis for nitrogen and carbon was carried out by use of Dumas gas chromatography (GC) on a Carlo Erba CHN 1108 analyser [10]. The finely powdered sample was placed in a Sn crucible, mixed with V_2O_5 and combusted in a He–O_2 atmosphere (Table 1). The oxygen contents of the starting powder and of the samples with the carbon contents VC111 and VC112 were measured by a vacuum hot extraction equipment Balzers exhalograph EAO-201.

Metallographic analysis was performed by grinding the samples first with a diamond disc, then by polishing with a 3-μm diamond paste and finally with a 1-μm diamond suspension. For etching an aqueous solution 10% KOH+ 10% $K_3[Fe(CN)_6]$ was used.

The microhardness of disordered and ordered vanadium carbides was measured with a Reichert microhardness tester applying a load of 0.98 N and a loading time of 10 s.

Electrical conductivity measurements at room temperature were performed by means of a device Sigmatest (Förster, Germany) using an inductive eddy current principle. The device was calibrated against standards of alloys with defined electrical conductivities. Polished, as well as ground, samples were used.

C_p was determined with a differential scanning calorimeter (Netzsch 404, Germany) between 50°C and 1300°C in inert gas atmosphere. Measurements were done at a heating and cooling rate of 20°C/min. The samples were cylindrical plates 5-mm in diameter and 1-mm thick.

Table 1
Chemical composition and properties of the investigated vanadium carbide specimens

Sample	Composition				Lattice parameter (nm)		Microhardness (GPa)		Electrical conductivity ($10^4\ \Omega^{-1}\ cm^{-1}$)	
	[C]/[V]	At% C	At% N	At% O	Ordered	Disordered	Ordered	Disordered	Ordered	Disordered
VC110	0.87	46.1	0.21	0.64	0.41660	0.41638	30.5	25.9	2.36	1.44
VC111	0.83	45.2	0.16	0.27	0.41651	n.m.[a]	29.5	29.0	1.49	1.22
VC112	0.79	43.9	0.11	0.50	0.41607	n.m.	26.7	25.5	1.19	1.10
VC113	0.66	39.7	0.12	n.m.	0.41305	n.m.	24.7	24.1	0.57	0.57

[a] n.m.=not measured.

Sapphire and gold standards were used as reference materials.

3. Results and discussion

Upon annealing of samples with the composition $VC_{0.79}$, $VC_{0.83}$ and $VC_{0.87}$ the occurrence of XRD superstructure lines could be observed. $VC_{0.66}$ did not show any significant indications of ordering upon low temperature annealing. The ordered phase has cubic symmetry (space group $P4_332$) and the resulting unit cell has double the lattice parameter of the disordered cell. An XRD pattern is shown in Fig. 1. The superstructure lines are stronger than calculated on the basis of the structure model of de Novion et al. [2]. Therefore a refinement of the structure seems appropriate which will be published elsewhere.

The annealed $VC_{0.83}$ specimen apparently contains an ordered V_6C_5 phase with trigonal symmetry (space group $P3_1$) and the V_8C_7 phase. The specimen with composition $VC_{0.79}$ contains the V_6C_5 phase with trigonal symmetry together with δ-VC_{1-x} after annealing.

The function lattice parameter vs. composition of δ-VC_{1-x} ($0.66 \leq y \leq 0.87$) showed a slight deviation from linearity (Fig. 2). Apparently, the ordered sample V_8C_7 has a lattice parameter of about 0.002 Å greater than the cubic subcell of δ-$VC_{0.87}$. Similar effects were observed previously upon ordering in non-stoichiometric carbides of niobium [11–13], vanadium [14] and tantalum [13,15]. This is opposed to what is generally observed in metallic ordered alloys where ordering is usually accompanied by a decrease of the lattice parameter.

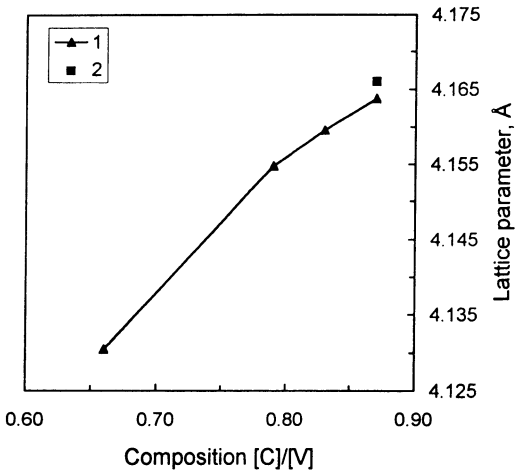

Fig. 2. The fcc lattice parameter versus the composition of δ-VC_{1-x} (1) and for the subcell of V_8C_7 (2).

Fig. 3 presents the temperature dependence of the heat capacity C_p of V_8C_7 (carbon content corresponding to $VC_{0.87}$, sample no. VC110) from 50–1300°C. The phase transformation $V_8C_7 \rightarrow \delta$-$VC_{0.87}$ occurs in this sample at $T_c = 1095$°C where C_p vs. T features a marked peak arising from the heat of transformation. This effect is typical of phase transitions of the first order, where the long-range order parameter drops to zero discontinuously. The specific heat of the disordered carbide in the region above T_c apparently is larger than the extrapolated value of the ordered carbide. Our own measurements agree fairly well with previous data tabulated in Barin [16] below the transition temperature (see Table 2). The C_p as well as H_T

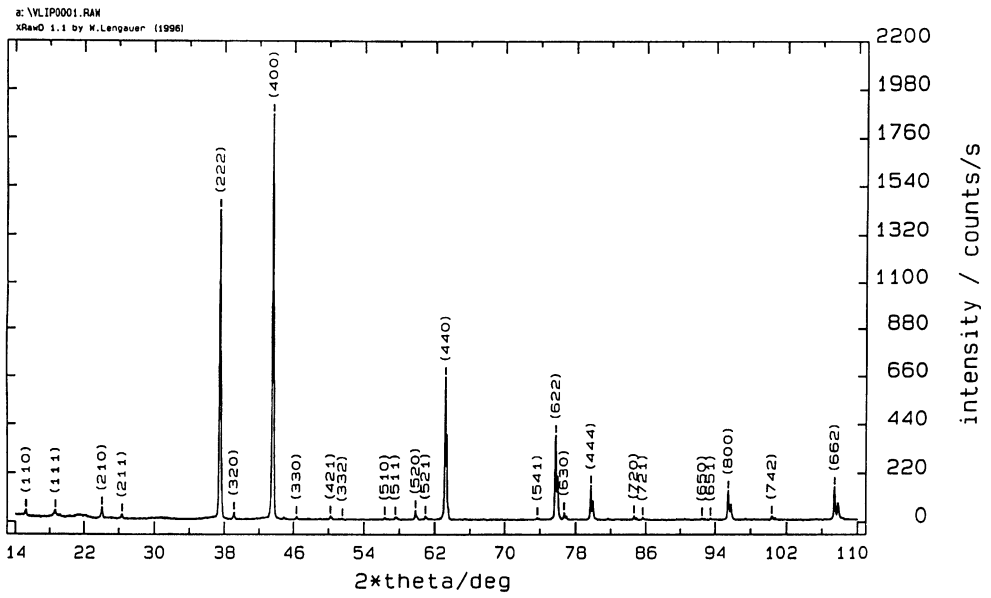

Fig. 1. X-ray diffractogram of the ordered vanadium carbide V_8C_7 (Cu Kα radiation).

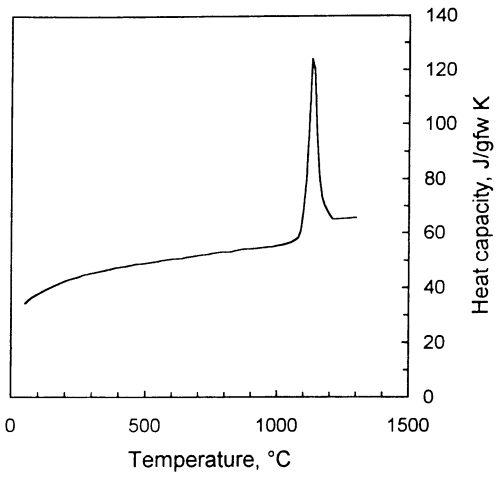

Fig. 3. Temperature dependency of heat capacity of the sample no. VC110 ($VC_{0.87}$). The DSC measurement was started at room temperature with an ordered sample (V_xC_{1-x}) so that C_p on the left of the peak belongs to this phase. A large peak of transition ordered→disordered state can be observed. Right of the peak: disordered δ-$VC_{0.87}$.

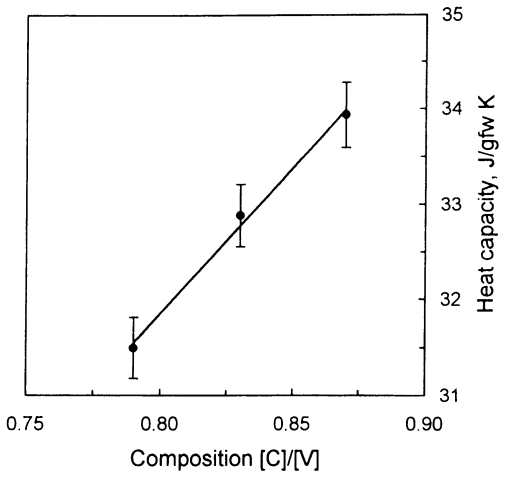

Fig. 4. Heat capacity vs. composition of δ-VC_{1-x} at 50°C (323 K).

and S_T (heat and entropy of transformation) of δ-VC_{1-x} need to be corrected for the heat of the order–disorder transition and for the higher level of heat capacity above the transition temperature. By heat capacity measurements order–disorder transformations were also detected in the samples $VC_{0.79}$ and $VC_{0.83}$ which is consistent with XRD results. The $C_p(T)$ curves for the samples of composition $VC_{0.83}$ and $VC_{0.79}$ feature two peaks. Apparently these samples contain more than one ordered phase.

Upon cooling the DSC peaks were shifted towards slightly lower temperatures, which is a further indication that the phase transformation is of the first order. The temperature interval of the transformation hysteresis represents a region of metastability which is not unusual in first-order transformations. This result agrees with the theoretical conclusion [17] that the MeC_y–Me_6C_5 and MeC_y–Me_8C_7 disorder–order transformations must be of the first-order.

There are no studies on the heat contents and heat capacities of fcc vanadium carbide with varying carbon contents. Emmons and Williams [9] have measured the latent heat of transformation of 1538±619 J/gfw for $VC_{0.875}$ at 1112°C and of 1454±713 J/gfw for $VC_{0.833}$ at 1184°C by DTA. Volkova et al. [18] also reported a value of ΔH=2778 J/gfw at 1120°C for $VC_{0.89}$. According to our results the latent heat of the transformation $VC_{0.87}\rightarrow V_8C_7$ is 2354 J/gfw and of the transformation $VC_{0.83}\rightarrow V_6C_5$ 2114 J/gfw. Our results have been arrived at by numerical integration of the area of the $C_p(T)$ curve near the transformation interval. The difference between the data of Emmons and Williams [9] and our data could be due to the fact that these authors used powdered samples whereas we used compact samples which provide better heat transfer. Within the accuracy of the results the present findings indicate a linear increase of C_p with increasing carbon content (Fig. 4).

Table 2
Heat capacity of δ-VC_{1-x} with different carbon content

Present data							Ref. [16]
Temperature	$VC_{0.79}$		$VC_{0.83}$		$VC_{0.87}$		$VC_{0.88}$
(K)	(J/g K)	(J/gfw K)	(J/g K)	(J/gfw K)	(J/g K)	(J/gfw K)	J/gfw K
298.15	–	–	–	–	–	–	31.966
300	–	–	–	–	–	–	32.148
323	0.5212	31.496	0.5398	32.879	0.5528	33.937	–
400	0.5960	36.016	0.6230	37.947	0.6379	39.161	39.078
500	0.6556	39.618	0.6876	41.881	0.7049	43.274	43.034
600	0.6952	42.011	0.7298	44.452	0.7457	45.779	45.777
700	0.7242	43.763	0.7618	46.401	0.7769	47.694	47.913
800	0.7480	45.201	0.7865	47.906	0.8045	49.389	49.697
900	0.7678	46.398	0.8081	49.221	0.8245	50.617	51.249
1000	0.7866	47.534	0.8286	50.470	0.8455	51.906	52.536
1100	0.8141	49.196	0.8541	52.023	0.8702	53.422	53.890
1200	0.8252	49.867	0.8774	53.443	0.8825	54.177	55.037
1300	0.8511	51.432	0.9165	55.824	0.9123	56.007	56.089

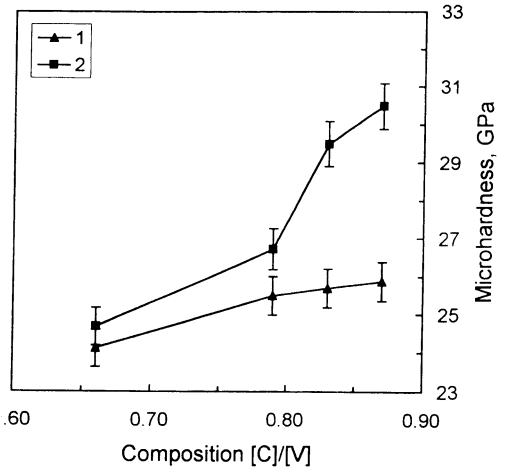

Fig. 5. Composition dependency of the microhardness of vanadium carbide: (1) disordered state; (2) ordered state.

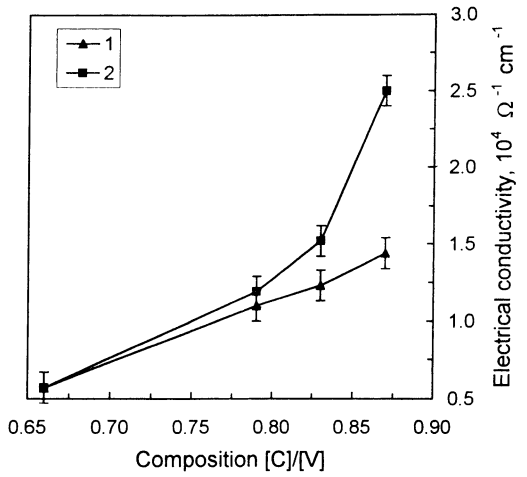

Fig. 6. Electrical conductivity of vanadium carbide at room temperature as a function of carbon content in the disordered (1) and ordered (2) states.

The microhardness data for vanadium carbide specimens before and after annealing are shown in Fig. 5. It can be seen that the microhardness increases upon ordering. For example, the microhardness for vanadium carbide $VC_{0.87}$ in the disordered state is 25.9 GPa, and in the ordered state 30.5 GPa, a value amongst the highest of any transition metal carbide and nitride.

Microstructural investigations have shown that the disorder–order transformation starts at the grain boundaries of the crystallites of the disordered specimen. Unfortunately a black-and-white reproduction cannot show these microstructural features so we refer to our internet pages under: http://info.tuwien.ac.at/physmet/vc.html. The more or less straight and well defined polygonal grain boundaries acquire a somewhat flurry appearance and the resulting microstructure appears to successively eat up the remaining grain area. When the highly polished and etched surfaces of ordered vanadium carbide samples $VC_{0.79}$, $VC_{0.83}$ and $VC_{0.87}$ are examined a domain type substructure is observed. Typical microstructures observed with reflected polarised white light for a sample containing the trigonal ordered phase contain blue and yellow regions corresponding to ordered domains. The trigonal sub-structure is visible because each domain develops a colour in polarised light, according to the specific orientation of the superlattice within the nominally cubic vanadium carbide lattice. Also in a recent diffusion-couple study the ordered domains could be observed (see colour reproduction in [19]).

Measurements of the electrical conductivities at room temperature of vanadium carbide specimens in the ordered and disordered states have shown that the electrical conductivity increases with the increase of carbon content from $0.57 \cdot 10^4$ Ω^{-1} cm^{-1} to $1.44 \cdot 10^4$ Ω^{-1} cm^{-1} at room temperature (Fig. 6). The electrical conductivity of ordered vanadium carbide is higher than that of the disordered of the same composition. Such a change in the electrical conductivity as a result of the ordering process can be easily explained on the basis of the quantum mechanical model of electrical conductivity. According to that model the variation of the electrical conductivity during ordering is associated with a decrease in the scattering of conduction electrons on structural defects in the ordered state.

4. Conclusion

It was established that ordering of carbon atoms and structural vacancies in vanadium carbide is accompanied by an increase in the microhardness and electrical conductivity. The disorder–order transitions in δ-VC_{1-x} are reflected in the microstructures of vanadium carbide and can be made observable by optical microscopy. By DSC it was established that at the temperature of the order–disorder transformation the heat capacity C_p undergoes a finite discontinuity typical of an order–disorder phase transition of the first order.

Acknowledgments

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