The Composition of the Phases in the Vanadium-Carbon System

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The intermediate phases V_5C , V_2C , V_4C_3 , VC , and V_2C_3 have been reported to exist. Because of the difficulty in avoiding contamination by oxygen and nitrogen, the methods of preparation in many cases cast doubt on the validity of the results. X-ray diffraction and microscopical studies have established the existence of two intermediate phases, although the data about the compositions given by the different authors differ essentially. They are of the common "interstitial" types with the metal atoms arranged in hexagonal and cubic close-packing respectively. Analogous carbides exist in, for instance, the Nb—Ta—C system, with the ideal formulas $(Nb,Ta)_2C$ and $(Nb,Ta)C$.

A brief summary of earlier investigations has been given by — among other authors — Schwarzkopf and Kieffer (34 references)¹, Rostoker and Yamamoto (15 references)².

EXPERIMENTAL

Finely powdered vanadium metal (Vanadium Corporation of America, 99.7 % Grade) and carbon (soot) were carefully mixed in different amounts and moulded into briquettes weighing 1–5 g. The sintering (melting) of the specimens was performed in graphite crucibles, in some cases in a high frequency vacuum induction furnace³ and others in a graphite tube vacuum resistance furnace⁴ (1 900° C). The samples were then cooled to room temperature during a time of about twenty minutes.

X-ray powder photographs of the samples taken in a Guinier focussing camera with monochromatized Cr-K α radiation revealed the existence of three phases *viz.* vanadium, the V_5C phase with the metal atoms in the hexagonal close-packed arrangement, and the VC phase with the sodium chloride structure. The amount of "total" carbon in the samples was determined by combustion and the amount of "free" carbon after dissolving the carbide phase in a mixture of dilute hydrochloric and hydrofluoric acid. The vanadium content of some samples was controlled by potentiometric titration with ceric sulphate⁵.

The homogeneity limits of the phases were determined from Fig. 1, where the lattice constants of the three phases have been plotted against the composition.

THE COMPOSITION OF THE PHASES

V-phase. For the pure metal (99.7 %) the cubic axial length was found to be $a = 3.026 \text{ \AA}$ ($V = 27.71 \text{ \AA}^3$), and for the vanadium phase in equilibrium with the V_2C phase the value obtained was $a = 3.037 \text{ \AA}$ ($V = 28.00 \text{ \AA}^3$).

Fig. 1. The lattice constants of the phases in the V-C system v s. the composition.

The latter value of the parameter was also obtained for a sample containing 0.33 weight-% (1.4 atom-%) of C. Accordingly the solubility of carbon in vanadium is assumed to be as low as about 0.2 weight-% (1 atom-%) at a temperature of about 1 000° C.

Tammann and Schönert⁶ found that carbon does not diffuse into vanadium at 800° to 900° C. This suggests that the solubility of carbon in vanadium is very small.

V_2C -phase. The hexagonal unit cell dimensions were found to vary continuously between $a = 2.881$ Å, $c = 4.547$ Å, $c/a = 1.578$ ($V = 32.68$ Å³) at the composition $VC_{0.37}$ (8.0 weight-% = 27 atom-% of C) and $a = 2.906$ Å, $c = 4.597$ Å, $c/a = 1.576$ ($V = 33.50$ Å³) at the composition $VC_{0.50}$ (10.5 weight-% = 33 atom-% of C). It is seen that the c/a value remains practically constant, although the homogeneity range is comparatively broad.

The mean interatomic distances are: V—6V = 2.83 Å, V—6V = 2.89 Å, C—6V = 2.02 Å, as compared with the intermetallic distances in pure vanadium: 2.62 Å (8-coordination).

VC-phase. The formula of this carbide has been disputed in the literature. Some authors have given it as V_4C_3 and others as VC. From the present investigation it is evident that these two formulas closely correspond to the lower and upper homogeneity limits of the phase. By analogy with the great number of related carbide and nitride phases, the ideal formula VC seems preferable (compare V_2C).

At the lower phase limit, with the composition $VC_{0.75}$ (15.1 weight-% = 43 atom-% of C), the lattice constant is $a = 4.136$ Å ($V = 70.75$ Å³). Samples

with a carbon content up to the approximate composition $VC_{0.8}$ could be prepared. But on increasing the amount of total carbon, this did not in its entirety react with the vanadium. As a consequence, a small fraction of free carbon was always obtained in the samples. The theoretical carbon content for the composition VC is 19.08 weight-%. Even with a great excess of carbon — up to 40 weight-% — it was not possible to introduce more carbon into the phase than corresponding to the composition $VC_{0.96}$ (18.5 weight-% = 49 atom-% of C). The corresponding lattice constant is $a = 4.182 \text{ \AA}$ ($V = 73.14 \text{ \AA}^3$). If a homogeneous phase with the composition VC exist, it is at least difficult to prepare it in this state.

The mean interatomic distances are: $V-12V = 2.94 \text{ \AA}$ and $C-6V = 2.08 \text{ \AA}$.

SUMMARY

The compositions of the phases in the V—C system have been determined by X-ray methods.

The solubility of carbon in vanadium is about 0.2 weight-% (1 atom-%) at about 1000°C .

The V_2C phase of the L'3 type is homogeneous between the limits $VC_{0.37}$ (8.0 weight-% = 27 atom-% of C) and $VC_{0.50}$ (10.5 weight-% = 33 atom-% of C).

The VC phase of the B1 type is homogeneous between the limits $VC_{0.75}$ (15.1 weight-% = 43 atom-% of C) and $VC_{0.96}$ (18.5 weight-% = 49 atom-% of C). The fact that the formula VC could not be attained may be due to low reaction velocities.

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