

Study of the Oxidation Kinetics of Vanadium Carbide

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The oxidation of an oxycarbide of vanadium, $VO_{0.6}C_{0.7}$, and of a vanadium carbide, $VC_{0.98}$, was studied athermally up to temperatures of 800°C and isothermally between 400 and 580°C at oxygen pressures ranging from 10^{-2} to 1 atm. The oxycarbide followed the parabolic rate law below 450°C with V_2O_5 forming as the only reaction product. The activation energy was 49 kcal/mole. $VC_{0.98}$ did not form an oxide in this temperature range, but rather dissolved oxygen, the activation energy being 26.6 kcal/mole. No oxygen pressure dependence on the kinetics was found for either sample in this temperature range. Both samples followed the cubic rate law during oxidation in the range of 500–580°C during which V_2O_5 formed. There was a $P^{1/3}$ dependence and the activation energy was the same for both materials, 51 kcal/mole. The cubic rate law and the positive pressure dependency (rather than an anticipated negative dependency) were attributed to an electric field associated with oxygen ions chemisorbed on a thin layer of V_2O_5 .

KEY WORDS: vanadium carbide; vanadium oxycarbide; oxidation; parabolic rate law; cubic rate law; chemisorption.

INTRODUCTION

The carbides of refractory materials such as TiC, VC, WC, etc., have become very important in metallurgy in recent years, because of their intrinsic properties and because of the characteristics they are capable of bestowing on the materials in which they are incorporated. Such carbides are used in cements and in materials resistant to fatigue (automotive parts, wheels,

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chains, etc.) and to thermal shock (with a WC and TiC base), as well as in cutting materials (with a Co, TiC, and VC base).

However, these carbides, especially that of vanadium, have a great affinity for oxygen. Thus the amount of VC incorporated in composite materials must be carefully proportioned to avoid disastrous oxidation. In view of this particular sensitivity to oxidation, it was considered important to study the oxidation kinetics of VC and to identify the mechanism of the oxidation reactions.

EXPERIMENTAL RESULTS

The kinetics study was performed by means of a Mettler thermogravimetric unit, using samples of vanadium carbide (minus 350 mesh) supplied by Kek of Hollywood, California.

One sample, of which only a limited quantity was available, was found to be an oxycarbide of vanadium ($\text{VO}_{0.6}\text{C}_{0.7}$), with a face-centred cubic

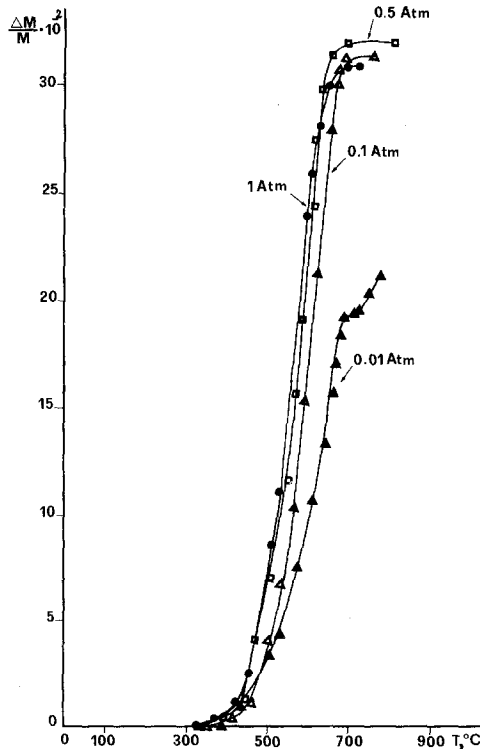


Fig. 1. Effect of oxygen pressure on the athermal oxidation of $\text{VO}_{0.6}\text{C}_{0.7}$ heated at $2^\circ\text{C}/\text{min}$.

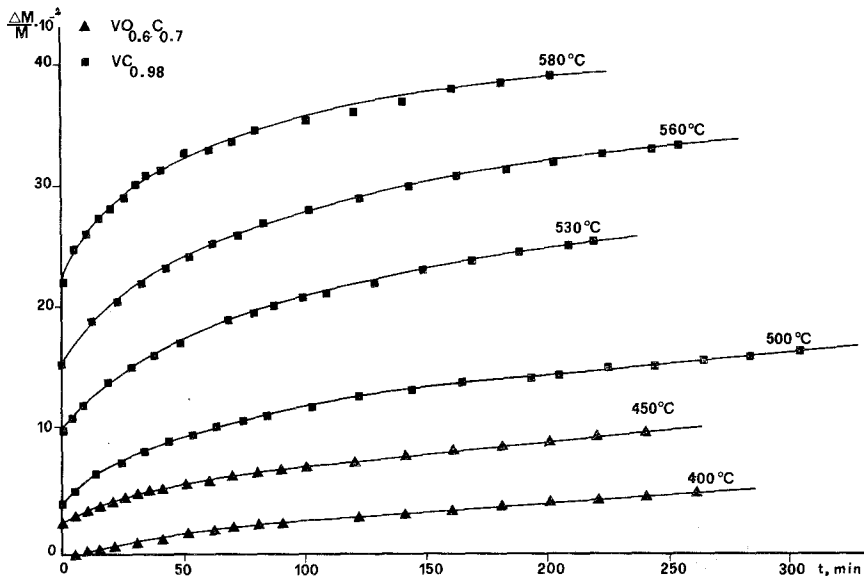


Fig. 2. Effect of temperature on the oxidation kinetics of $\text{VO}_{0.6}\text{C}_{0.7}$ and $\text{VC}_{0.98}$ at 1 atm oxygen pressure.

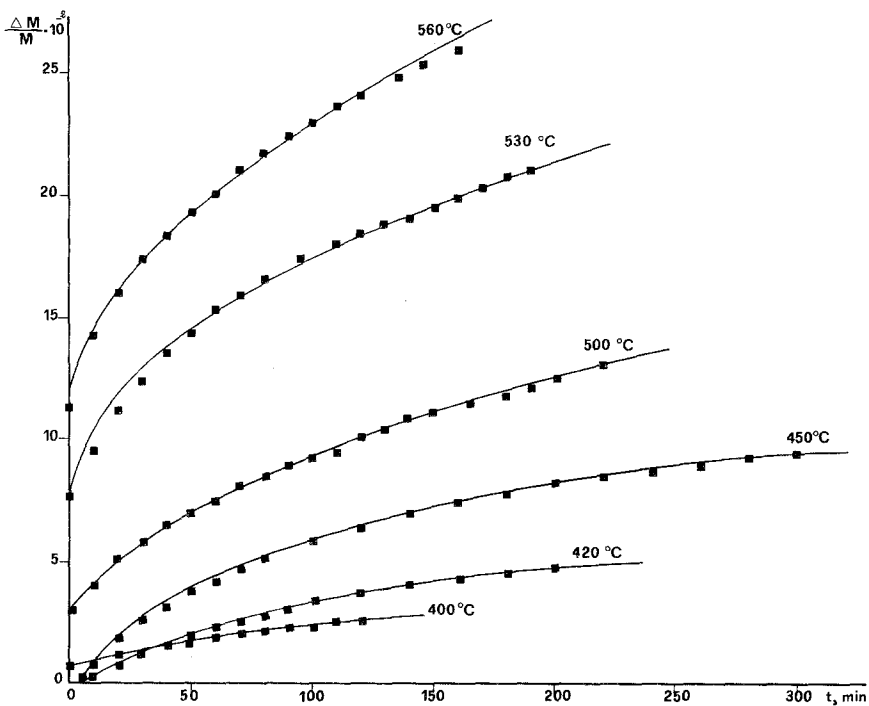


Fig. 3. Effect of temperature on the oxidation kinetics of $\text{VC}_{0.98}$ at 0.5 atm oxygen pressure.

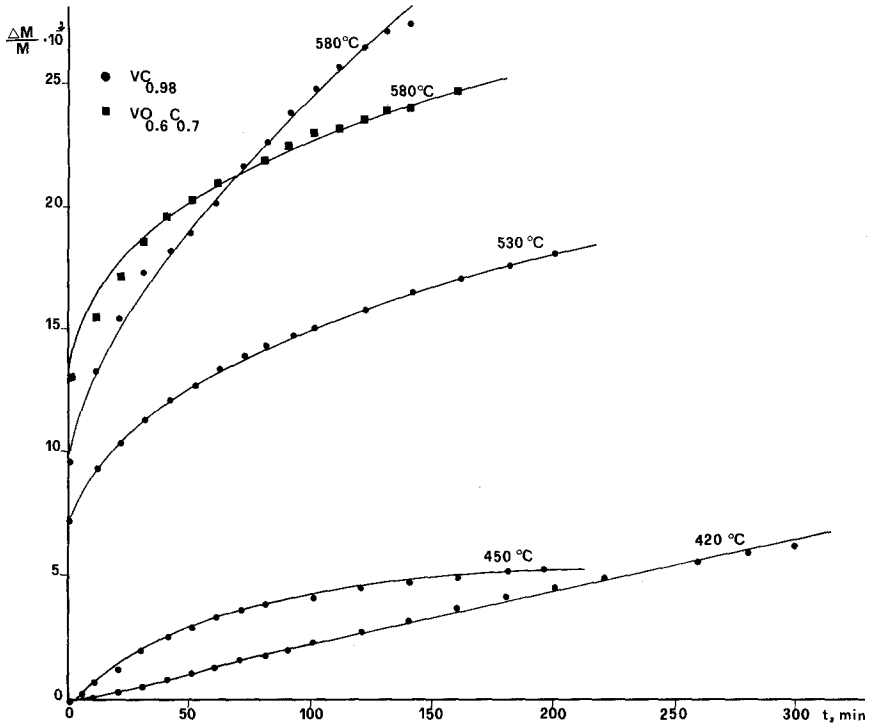


Fig. 4. Effect of temperature on the oxidation kinetics of $\text{VO}_{0.6}\text{C}_{0.7}$ and $\text{VC}_{0.98}$ at 0.1 atm oxygen pressure.

structure ($a = 0.4169 \pm 0.0005$ nm). This is referred to as sample 1 [VC(1)]. A second sample was vanadium carbide ($\text{VC}_{0.98}$) with a face-centred cubic structure ($a = 0.4164 \pm 0.0005$ nm). This is referred to as sample 2 [VC(2)].

Oxidation kinetics tests were run on both samples. The temperature was raised to 800°C at a heating rate of $2^\circ\text{C}/\text{min}$ —preliminary tests having revealed that higher rates caused marked thermal effects, which affected the kinetics of reaction—and four different oxygen pressures were used (1 atm, 0.5 atm, 0.1 atm, and 0.01 atm). Isothermal tests were run at temperatures from 400 to 580°C , in an atmosphere of oxygen, the isothermal temperature being reached at a heating rate of $2^\circ\text{C}/\text{min}$ (Figs. 1–5).

X-ray analysis of the oxidized samples indicated that the oxidation product was V_2O_5 in all cases except for sample 2 in the 400 – 450°C range, when only the presence of the VC phase was noted.

At temperatures below 450°C the oxidation kinetics follow the parabolic rate law (Figs. 6a and 6b show some typical examples), while at temperatures above 500°C the cubic rate law describes the kinetics (Fig. 7).

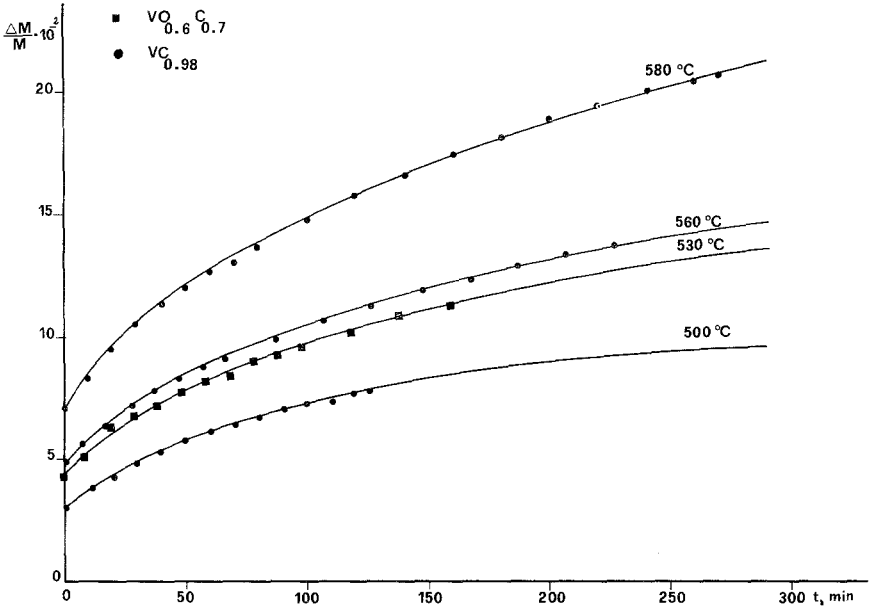


Fig. 5. Effect of temperature on the oxidation kinetics of $VO_{0.6}C_{0.7}$ and $VC_{0.98}$ at 0.01 atm oxygen pressure.

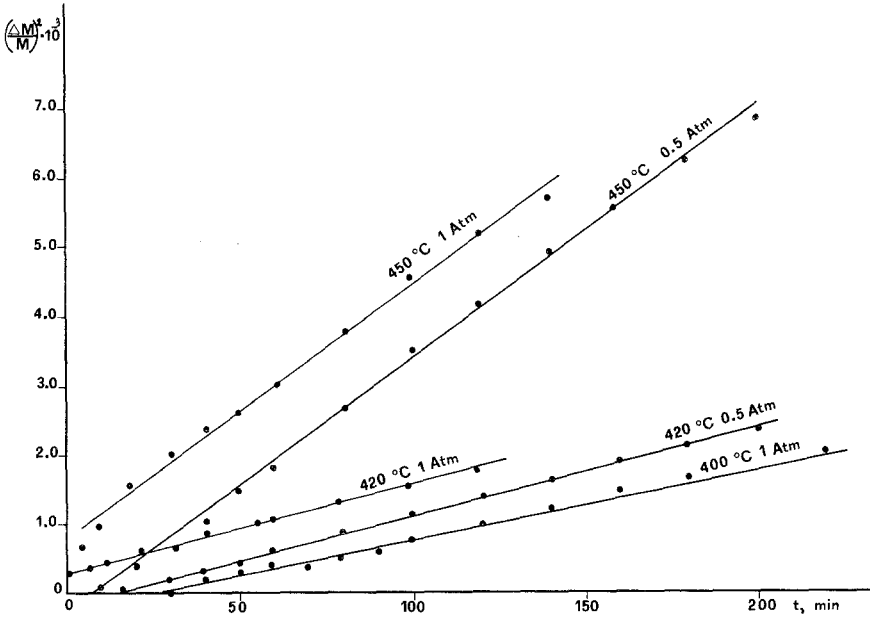


Fig. 6a. Parabolic plot of $VC_{0.98}$ oxidation kinetics.

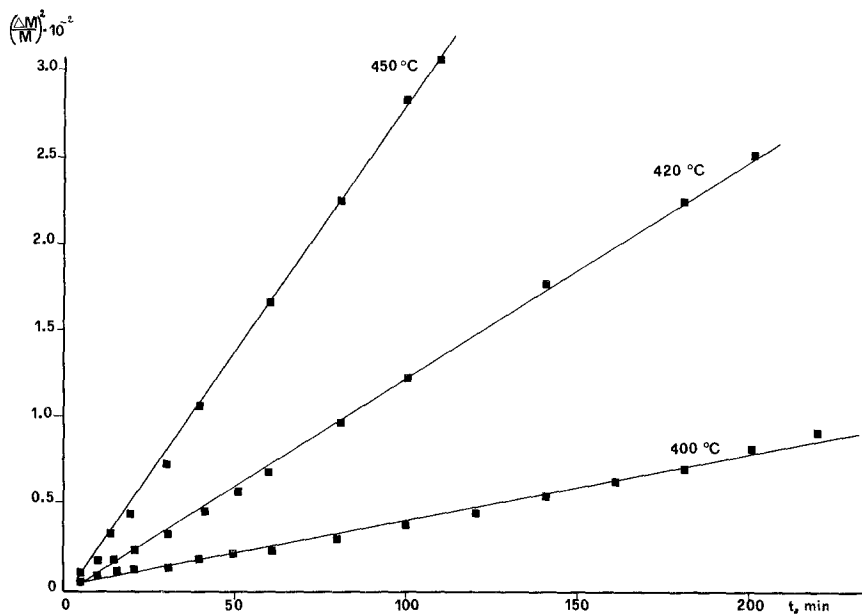


Fig. 6b. Parabolic plot of VC_{0.98} oxidation kinetics at 1 atm oxygen pressure.

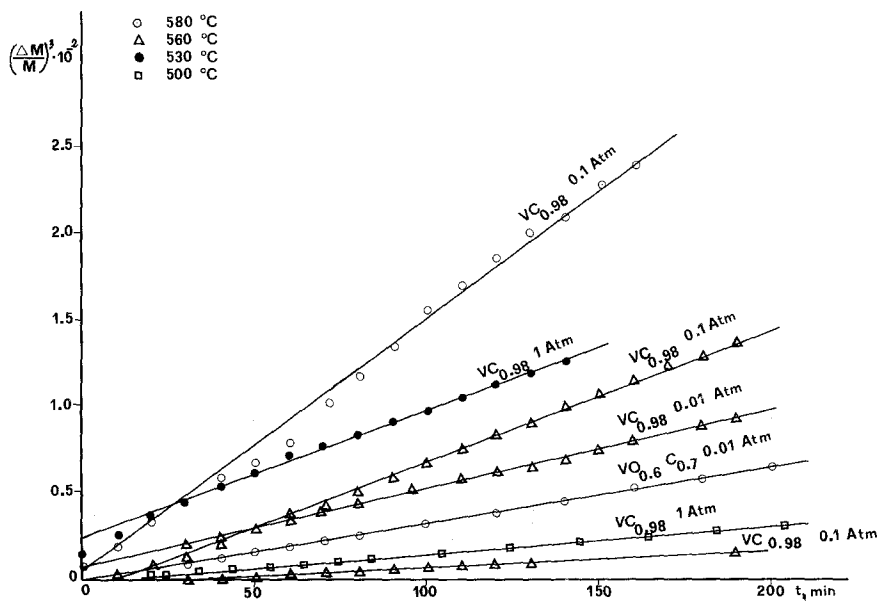


Fig. 7. Cubic plot of oxidation kinetics of VO_{0.6}C_{0.7} and VC_{0.98}.

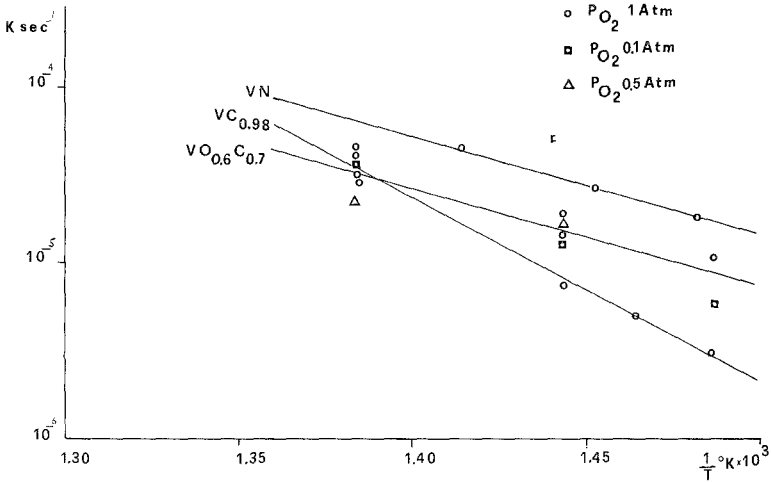


Fig. 8. Arrhenius plot of parabolic rate constants.

Figures 8 and 9 give the specific reaction rates as a function of reciprocal temperature at constant pressure and as a function of pressure at constant temperature.

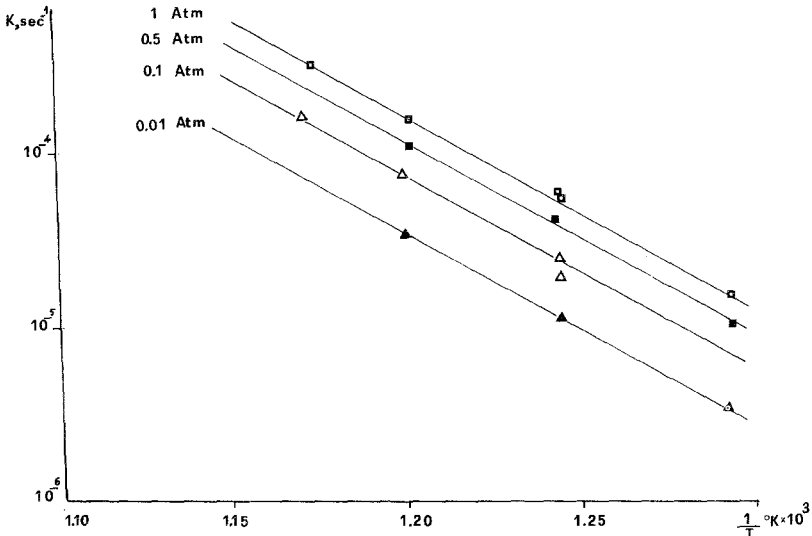


Fig. 9. Arrhenius plot of cubic rate constants for $\text{VC}_{0.98}$ oxidation at various pressures.

DISCUSSION

From examination of the data, it is evident that the temperature interval over which oxidation of the vanadium oxycarbide, VC(1), and of the vanadium carbide, VC(2), was studied can be considered as two separate parts: 400–450°C and 500–580°C.

400–450°C

As is quite apparent from the results, VC(1) behaves differently from VC(2) in the 400–450°C range. Indeed, x-ray examination of the former revealed the presence of V_2O_5 . On the other hand, although the weight increase during oxidation was sufficient to reveal any V_2O_5 that may have been present, no trace of this oxide was observed on the latter.

Moreover, the activation energy calculated for sample VC(1) is 49 ± 5.1 kcal/mole, while that for VC(2) is 26.6 ± 7.2 kcal/mole; the pre-exponential term A is 0.383 sec^{-1} for VC(1) and $0.9 \times 10^{-3} \text{ sec}^{-1}$ for VC(2).

In the case of the first sample, the oxygen that reacted was capable of nucleating the V_2O_5 phase, probably because the original sample already had sufficient oxygen to be considered as an oxycarbide of the V(O, C) type. In the case of the second sample, however, which was virtually oxygen-free, the initial presence of a phase of the V(O, C) type is to be excluded; thus the initial oxidation involved the formation of the oxycarbide rather than of V_2O_5 .

The possibility that the VC(2) sample changed to an oxycarbide between 400 and 450°C by the dissolution of oxygen in vacant carbon positions is also supported by the fact that—within the limits of experimental error—the kinetics data are the same as those derived for the first stage of the vanadium nitride oxidation process ($A = 2.0 \times 10^{-3} \text{ sec}^{-1}$; $E_{VN} = 28.8 \pm 4.2$ kcal/mole), which starts with oxygen occupying the vacant nitrogen sites.¹

As further evidence of this, the chemical analysis of VC(2), oxidized for 120 min at 420°C, indicates an empirical formula of the type $VO_{0.15}C_{0.85}$. Compared with $VC_{0.98}$, this gives a weight increase that corresponds to the one found by thermogravimetric analysis, allowing for experimental error. Additional confirmation is provided by chromatographic analysis of the gas leaving the thermogravimetric unit. This shows the presence of CO_2 in the gas only at temperatures above 465°C.

The oxygen pressure dependence could not be investigated in the case of the first sample because of a shortage of material, while for the second it appears that oxygen pressure has no influence on the kinetics. It is likely

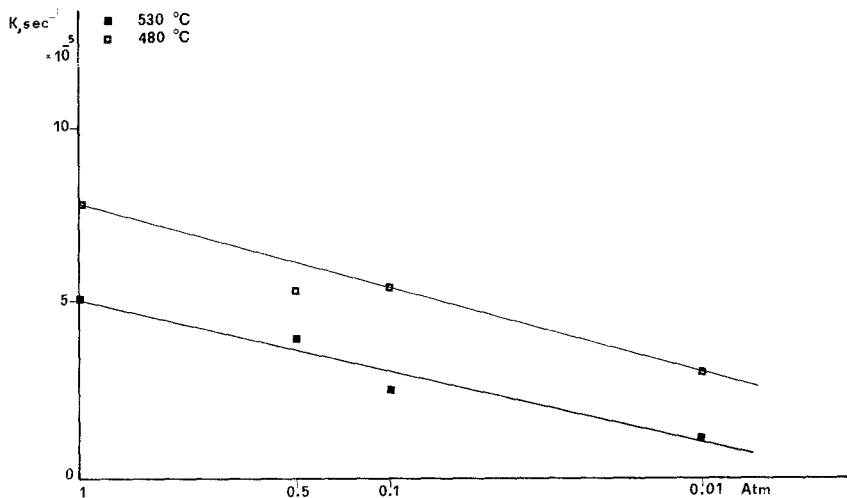


Fig. 10. Oxygen pressure dependence of cubic rate constants for $VC_{0.98}$ oxidation.

with this sample that the reaction is controlled by diffusion of oxygen, because the oxidation process over the temperature range concerned is parabolic. Thus a pressure dependence would be of a low exponential power, e.g., $P_{O_2}^{1/6}$, which is difficult to measure.

During the oxidation of sample 2, the V_2O_5 phase was observed in experiments run at 480°C. At this temperature, a parabolic time dependence, similar to that of sample 1, was also noted. A pressure effect was observed as noted in Fig. 10. It is apparent from the foregoing that the reaction mechanism is similar to that which occurs over the 500–580°C range, which is discussed below.

500–580°C

In the 500–580°C range the reaction kinetics of the two samples are of the same type, i.e., following the cubic rate law, and within the limits of experimental error, the activation energy is equal for both samples (51 ± 5.1 kcal/mole). In both cases, x-ray analysis showed V_2O_5 to be the predominant phase, and the pressure dependence of the reaction was about $P_{O_2}^{1/3}$.

The activation energy value and that of the preexponential term found for the cubic process were the same—allowing for experimental error—as that obtained in the second VN oxidation process,¹ for which a parabolic time dependence controlled by oxygen diffusion through a V_2O_5 layer was observed.

Regarding the pressure dependence of the reaction rate, noting that V_2O_5 is an *n*-type semiconductor, it might have been expected that the

specific reaction rate would be independent of pressure.² However, since it is apparent that pressure dependence is of the $P^{1/n}$ type, it could well be that the force which causes diffusion does not come from a vacancy gradient, as theory would require, but from the electrical field formed by the oxygen ions chemisorbed on the surface of the V_2O_5 . Calculation of the thickness of V_2O_5 on the VC particle shows this to be of the order of 100 Å; thus it is a very thin layer, through which the influence of the electric field can make itself felt.

A similar situation—pressure dependence of the $P^{1/n}$ type for an n -type semiconductor—has been observed by Moore and Lee³ for the oxidation of Zn. Engell and Hauff,⁴ starting from the assumption that the electric field is the force which determines the kinetics, use thermodynamic reasoning to demonstrate that in this case the reaction-rate dependence on oxygen pressure is

$$K = C \log_{10} P_{O_2}$$

This is what happens in our case, too, thus bearing out the assumption made (Fig. 10).

A similar oxidation model also explains why, in our case, the time dependence of the reaction rate is parabolic at 480°C, but becomes cubic above 500°C. Engell and Hauff showed that in this case it is possible to derive both a parabolic and a cubic equation.

SUMMARY

It may be concluded that the reaction of vanadium carbide with oxygen is as follows:

- (a) In the 400–450°C temperature range, the process is independent of oxygen pressure; the time dependence is parabolic and hence the kinetics are governed by a process of diffusion and formation of a phase of the V(O, C) type.
- (b) At 480°C the process is still parabolic, but there is an oxygen pressure dependence of the $P_{O_2}^{1/4}$ type and the formation of V_2O_5 .
- (c) In the 500–580°C range, the process behavior becomes cubic and the oxygen pressure dependence is of the $P_{O_2}^{1/3}$ type, still with formation of V_2O_5 .

In both (b) and (c) there is a diffusion process which may be governed by the electrical field which forms through chemisorption of the oxygen on the surface of the sample.

- (d) In the case of the sample which contains so much oxygen that it can be considered as an oxycarbide (sample 1), V_2O_5 is formed in the 400–450°C range, too, and the behavior of the kinetics is parabolic.

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