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Simultaneous carburisation and oxidation of niobium in the presence of carbon monoxide

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Abstract

During reaction with CO, niobium was observed to carburise and oxidise simultaneously, with Nb_2C, NbO and NbO_2 forming as intermediate products before complete conversion to NbC. It was shown that the reason for such a complex reaction path was the fact that during the carburising reactions enough CO_2 is produced to oxidise the metal. Oxidation takes place by the inward diffusion of CO_2 through cracks and pores to the metal surface. After depletion of Nb, Nb_2C and NbO, the monocarbide continues to grow on NbO_2. The reaction $NbO_2+4CO=NbC+3CO_2$ is extremely slow and is controlled by chemical kinetics.

1. Introduction

During an investigation involving the development of new carbide production processes, niobium in the presence of CO was observed to carburise and oxidise simultaneously at temperatures between 900 °C to 1300 °C. Alyamovksi *et al.* [1] had previously reported the formation of oxycarbides by heating niobium powder in CO between 1300 °C to 1700 °C at varying pressures. The existence of a cubic oxycarbide Nb(CO) analogous with NbC and a hexagonal phase $Nb_2(CO)$ analogous with Nb_2C was claimed. In contrast to this, the products observed during the present study were the oxides and carbides of niobium. The reasons for this unusual reaction path were further explored and explained.

2. Experimental details

An apparatus was used consisting of a platinum resistance furnace with a silica reaction tube achieving a hot zone of 30 mm in length.

Niobium powder of an average grain size of 20 μm was pelletised into discs 6 mm in diameter by pressing in a steel die. Samples were placed on a platinum pan and introduced into the reaction tube by suspending from the extension lead to a load cell. Having flushed the tube with CO at 500 ml min^{-1}, the reaction tube was introduced into the hot furnace. Weight changes were determined with time using the load cell whose output was fed to a chart recorder.

Samples were analysed by an X-ray diffraction technique using a Guinier focusing camera with monochromatic Co Kα_1, radiation to determine the phases that had formed during the reaction period.

3. Results

Niobium powder was reacted with flowing CO gas at a rate of 500 ml min^{-1} at temperatures in the range 900 °C and 1300 °C. The expected weight gain for complete carburisation was 12.9%, but surprisingly the metal exhibited weight increases well above this change. Figure 1 shows a plot of the weight gain for the reaction

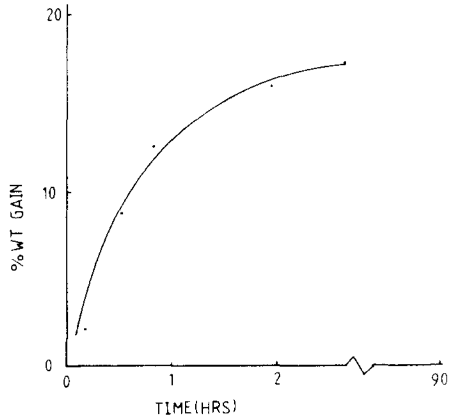

Fig. 1. Kinetic curve for the reaction between Nb and CO at 1100 °C.

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against time at 1100 °C where a maximum weight increase of 17.5% after 160 min was recorded followed by an extremely slow weight decrease to about 12.9%, the weight change expected for conversion to NbC. When samples obtained from the early stages of reaction were analysed by means of X-ray diffraction Nb, Nb_2C and NbC were detected as well as NbO and NbO_2. Such an observation was most surprising.

The reaction at 1100 °C was further studied by quenching samples after appropriate reaction times and analysing the products by X-ray diffraction. The initial product was Nb_2C (after 0.5 min) followed by the observation of NbO. After 1.5 min (equivalent to a weight increase of 1.3%), NbC was observed to be nucleated and soon after evidence of the NbO_2 phase appeared on the X-ray diffraction patterns. While the amounts of NbC and NbO_2 increased with longer reaction times, the presence of Nb_2C and NbO was depleted. After 30 min of reaction (8% weight gain) Nb_2C disappeared completely from the diffraction patterns. The intensity of the NbC and NbO_2 diffraction patterns continued to increase whilst first Nb and then NbO were consumed. At this stage, the sample had gained 17.5% which corresponds to a product of approximately 85% NbC and 15% NbO_2 from mass balance calculations. A slow weight loss then followed as the reaction

$$NbO_2+4CO=NbC+3CO_2$$

takes place until reaction is complete. It eventually took approximately 90 h for this reaction to reach completion. Table 1 shows the phases present at a particular time and weight change for the reaction at 1100 °C and Fig. 1 demonstrates the weight change with time. The observed lattice parameters of Nb_2C and NbC lie well within the accepted range as compiled from previous data by Storms [2] without any variation. For example, the lattice parameter of NbC formed at 1100 °C was determined to be 4.432 Å with no variation from the start to the completion of the reaction. This indicated that the products of this work were indeed carbides and not the oxycarbides which were reported by Alyamovski *et al.* [1].

TABLE 1. Observation of phases present with time for the reaction of Nb+CO at 1100 °C

Time (min)	% Weight gain	Phases present
0	–	Nb(vs)
1	0.83	Nb(vs), Nb_2C(vw), NbO(vw)
1.5	1.30	Nb(vs), Nb_2C(vw), NbC(vw), NbO(vw)
12	4.51	Nb(s), Nb_2C(w), NbC(w), NbO(w), NbO_2(vw)
32	8.48	Nb(m), Nb_2C(vw), NbC(m), NbO(w), NbO_2(w)
50	13.00	Nb(w), NbC(s), NbO(vw), NbO_2(w)
120	16.02	NbC(vs), Nb_2C(vw), NbO_2(w)
160	17.48	NbC(vs), NbO_2(w)
2640	14.84	NbC(vs), NbO_2(vw)
5400	12.91	NbC(vs)

Key to Table 1 (X-ray intensities)
vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

4. Discussion

This simultaneous carburisation and oxidation of niobium powder can be understood from a knowledge of the equilibrium gas compositions for the various reactions that occur. The equilibrium gas compositions for one bar total pressure at 1100 °C calculated from thermodynamic data compiled by Turkdogan [3] are as follows:

Reaction 1

$$2Nb+2CO=Nb_2C+CO_2 \quad K=1.38\times10^4$$
$$pCO=8.49\times10^{-3}$$
$$pCO_2=0.992$$

Reaction 2

$$Nb_2C+2CO=2NbC+CO_2 \quad K=6.11$$
$$pCO=0.331$$
$$pCO_2=0.669$$

Reaction 3

$$NbO_2+4CO=NbC+3CO_2 \quad K=6.10\times10^{-7}$$
$$pCO=0.992$$
$$pCO_2=8.4\times10^{-3}$$

Reaction 4

$$Nb+CO_2=NbO+CO \quad K=1.06\times10^5$$
$$pCO=0.9999$$
$$pCO_2=10^{-5}$$

Reaction 5

$$NbO+CO_2=NbO_2+CO \quad K=4.485\times10^3$$
$$pCO=0.9978$$
$$pCO_2=2.23\times10^{-4}$$

The equilibrium carbon dioxide pressure for the carburising reactions 1, 2 and 3 is sufficiently high for the oxidation reactions 4 and 5 to take place. In other words more than enough CO_2 is generated by the carburising reactions to initially oxidise niobium and to further oxidise NbO. From the X-ray diffraction results, it has been established that reaction 1 occurs first, followed by reaction 4, with NbO forming between niobium and Nb_2C as observed by metallographic examination. Later, NbC forms adjacent to the layer of Nb_2C (by reaction 2) with CO_2 diffusing inwards so that reaction 5 commences and NbO_2 begins to form adjacent to NbO. After nucleation it is observed that NbC grows at the expense of Nb_2C. Once the Nb_2C has been completely converted to the monocarbide, NbC continues to grow on NbO_2 (by reaction 3) with CO_2 continuing to diffuse inwards to further oxidise Nb and NbO. Nb finally disappears and NbO continues to be converted to NbO_2. This sequence of events is to be expected as it is thermodynamically impossible for Nb and NbO_2 to co-exist (that is a layer of NbO must always be present between the two). At that stage the sample at 1100 °C is estimated to consist of about 85% NbC and 15% NbO_2 from mass balance calculations. The inward diffusion of CO_2 to oxidise Nb takes place through cracks and pores that are evident from microscopic studies, an example of which is shown in Fig. 2. Eventually, carburisation proceeds *via* reaction 3 which is very slow, taking about 90 h for completion. The reasons for the tardiness of this reaction were investigated by studying the kinetics of the reduction–carburisation of fine-grained NbO_2 (0.5 μm) in CO at temperatures between 1000 °C and 1200 °C.

Gas solid reactions can be divided into a number of intermediate steps [4]:

(1) Gaseous diffusion of reactants from the bulk of the gas phase to the surface of the reacting solid particle.

(2) Diffusion of gaseous reactants through a solid reaction product *via* pores.

(3) Adsorption of the gaseous reactants on the surface of the solid reactant.

(4) The chemical reaction between the adsorbed gas and the solid.

(5) The desorption of the reaction products from the reaction surface.

(6) Diffusion of gaseous products through a solid reaction product.

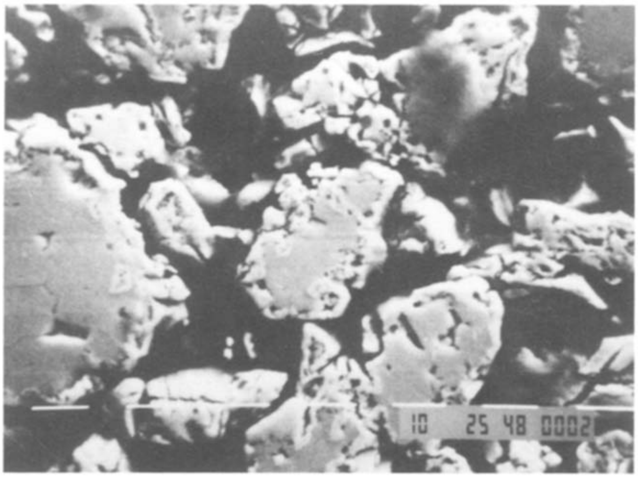

Fig. 2. Micrograph showing cracks and pores during reaction between Nb and CO.

(7) Gaseous diffusion of products away from the surface of the reacting solid particle into the bulk of the gas phase.

When one step is much slower than the rest, a limiting condition is reached and this step determines the overall reaction rate. Mathematical formulations were used to assist in determining the rate-controlling step.

When the overall rate is controlled by chemical kinetics, the rate of reaction of a spherical particle is given by the equation [3]:

$$1-(1-F)^{1/3}=\frac{\nu k}{\rho r}(C_0-C_e)t$$

where F = fraction of reaction completed, k = reaction rate constant in cm h^{-1}, ν = number of moles of reduced solid, ρ = density of product in g cm^{-3}, r = reacting particle radius in cm, C_0 = reactant gas concentration in g cm^{-3}, C_e = equilibrium gas concentration in g cm^{-3}, t = time in hours.

Values of $1-(1-F)^{1/3}$ calculated from the experimental data for the reaction $NbO_2+4CO=NbC+3CO_2$ were plotted against time as shown in Fig. 3. A linear relationship was obtained, the slope being equal to $\nu k/\rho r(C_0-C_e)$. From this, the reaction rate constant k, was calculated at the various temperatures. It should be noted that incubation periods where some other rate constrains are controlling, occur in the early stages of reaction. The incubation period is determined by the nucleation of NbC on NbO_2 and the growth of a porous layer of NbC until the surface of the NbO_2 particles is completely covered. The value of k is related to the activation energy by the Arrhenius equation:

$$k=A\exp-\Delta H/RT$$

where A = constant, ΔH = activation energy for the reaction in cal mol^{-1}, R = gas constant in cal mol^{-1} K, T = temperature in K. A plot of ln k against $1/T$, Fig. 4, was a straight line yielding an activation energy of

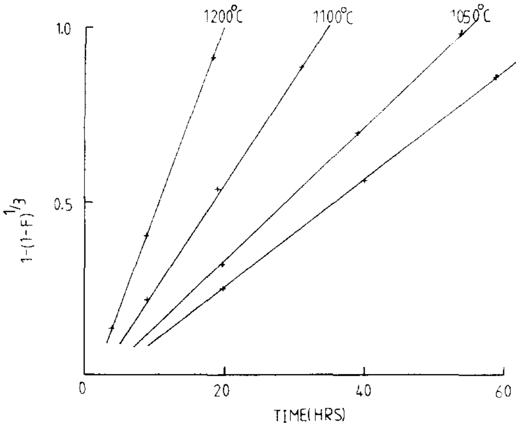

Fig. 3. Plot of $1-(1-F)^{1/3}$ against time for the production of NbC from NbO_2 in flowing CO at a variety of temperatures.

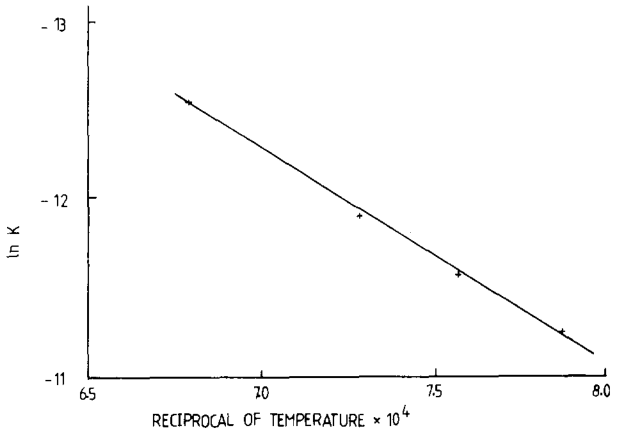

Fig. 4. Plot of ln k against $1/T$ for the carburisation of NbO_2 to NbC in flowing carbon monoxide.

24.5 kcal mol^{-1}, which is in accordance with a value expected for chemical reaction control. It was therefore concluded that the rate determining step was the chemical reaction between the adsorbed CO and NbO_2.

5. Conclusions

(1) During reaction with CO, niobium carburises and oxidises simultaneously.

(2) The simultaneous carburisation and oxidation of niobium takes place because during the carburising reactions enough CO_2 is produced to oxidise niobium.

(3) Oxidation takes place by the inward diffusion of CO_2 through cracks and pores to the metal surface.

(4) The kinetics for the reaction

$NbO_2 + 4CO = NbC + 3CO_2$

are extremely slow. The overall reaction rate is controlled by chemical kinetics. The activation energy for the reaction is 24.5 kcal mol^{-1}.

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