

Kinetics of interaction of carbon and oxygen in niobium during vacuum levitation melting

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Abstract

The kinetics of the carbon–oxygen interaction in liquid niobium during vacuum high-frequency levitation was studied. The parameters of the relation between mean carbon and oxygen concentrations were determined. A good agreement between calculated and experimental data was found.

1. Introduction

Interaction of carbon and oxygen impurities should be taken into account when obtaining pure metals and investigating their surface and bulk properties. However, the investigation of the behaviour of these impurities in solid and liquid metals has often been qualitative because of the complicated character of the physicochemical processes in the bulk and on the surface of the metal and because of considerable experimental difficulties. A model was proposed in terms of which a closed system of equations has been derived and solved [1–4]. This system of equations enables one to describe the kinetics of interaction of carbon and oxygen impurities in the process of annealing of refractory metals in solid state or keeping them in liquid state in vacuum. It is shown that if carbon and oxygen impurities with initial concentrations $N_o(0)$ and $N_c(0)$ are uniformly dissolved over the metal bulk then, as a result of thermodesorption into the vacuum of CO and MO molecules (at high oxygen concentrations, MO_2), as the mean oxygen concentration $N_o(t)$ infinitely decreases, the mean carbon concentration $N_c(t)$ has to approach a certain threshold level N_c^∞ according to the law

$$N_c(t) = N_c^\infty \left[1 + \frac{\Delta(t)}{N} \frac{1}{S} \right]^S \quad (1)$$

where $\Delta(t) = N_o(t) - N_c(t) + N_c^\infty$ is the actual difference in impurity concentrations, and

$$N_c^\infty = N_c(0) \left[1 + \frac{\Delta(0)}{N_*} \frac{1}{S} \right]^{-S} \quad (2)$$

Here it appears that the relationship between the mean concentrations of oxygen and carbon is unambiguously fixed by the parameters N_* and S . The first of these, $N_* = \omega/\Gamma$, is determined by the ratio of the constant of the metal monoxide desorption rate ω to the effective constant of the carbon monoxide desorption rate Γ , and has a certain critical value that presets a characteristic concentration scale. The influence of one impurity on the other becomes noticeable only when its concentration exceeds this critical value. The second parameter S is a dimensionless index of the relative intensity of diffusional and surface processes. In the case of liquid metals this parameter has the form $S = (1 + q/qp)$, where $q = \omega/\beta_o$; $p = \beta_o/\beta_c$; β_o and β_c are the coefficients of oxygen and carbon mass transfer. S can vary from $S_{\min} = \lim_{q \rightarrow \infty} S = 1/p < 1$ to $S_{\max} = \lim_{q \rightarrow \infty} S = \infty$. For large S when the kinetics is mainly determined by the rate of surface processes, the carbon concentration has to be very sensitive to the Δ value, *i.e.* $N_o/N_c^\infty \leq 1 + \Delta/N_*$.

The relative simplicity of eqn. (1) enables one to verify experimentally from the time behaviour of the mean concentrations of carbon $N_c(t)$ and oxygen $N_o(t)$ how much the model [1–4] corresponds to reality and to determine the N and S parameter values. In fact, from eqn. (1) it follows that

$$\frac{\partial \Delta}{\partial(\ln N_c)} = N_* + \frac{\Delta}{S} \quad (3)$$

So, if the model is valid, then in the coordinates $\partial \Delta / \partial(\ln N_c) - \Delta$ irrespective of the ratio of the initial concentrations $N_c(0)$ and $N_o(0)$ the experimental points must fall on the common straight line with the slope

$$\frac{1}{S} = \frac{\partial}{\partial \Delta} \left[\frac{\partial \Delta}{\partial(\ln N_c)} \right]$$

and initial ordinate

$$N_* = \left. \frac{\partial \Delta}{\partial(\ln N_c)} \right|_{\Delta \rightarrow 0}$$

An analysis of the results and comparison with theory become much simpler if the S values in the experiment are sufficiently large, *i.e.* diffusional processes occur intensively enough as compared with surface processes. In this case, in accordance with eqn. (3), the dependence $\ln N_c = f(\Delta)$ has to be close to linear. Here the points from experiments with different ratios of the initial concentrations $N_o(0)$ and $N_c(0)$ in the coordinates $\ln N_c - \Delta$ must fall on parallel straight lines with the slope $1/N$.

This study has been extended to experimental verification of the proposed model of carbon and oxygen interaction, their solution in niobium being taken as an example.

2. Experimental details

A method of liquid metal levitation in a high-frequency electromagnetic field that is characterized by high rates of diffusional processes even for massive samples, the absence of contact with the contaminating crucible and the possibility of automatic maintenance of the temperature at a preset level (determined by the metal mass [5]) was used in the experiment (Fig. 1).

Niobium and graphite powders were mixed and pressed under a pressure of 8 t cm^{-2} to pellets of $25 \pm 0.5 \text{ g}$. The difference from preset oxygen and carbon concentrations in the mixture did not exceed 5%. After sintering at $1900 \text{ }^\circ\text{C}$ compact samples with a density about 80% of the theoretical value were obtained. After a careful selection of samples with appropriate carbon and oxygen concentrations using non-destructive fast-neutron-activation analysis we prepared four series of pressed samples with an initial oxygen concentration of 0.93 at.% and carbon concentrations of 0.35, 0.58, 0.81 and 1.09 at.%. The high-frequency levitation set-up comprised a multiposition vacuum chamber with an inductor fed from a 65 kW 220 kHz generator. The sample surface was subjected to preliminary degassing and the sample levitating in an electromagnetic field was melted. The keeping time was counted from the moment of complete melting of the sample and formation of a stable levitated liquid metal droplet. Because of the automatic maintaining of the preset electric regime the majority of the samples melted for $17 \pm 0.5 \text{ s}$, which made it possible to select additionally the samples with respect to their melting time. This is very important because the transition via the solid-liquid state strongly affected the position of the starting concentration reference point from which we took the N_{O} and N_{C} values 1 s after melting (see Table 1).

After keeping the samples for some time in the liquid state the droplet was quenched in a copper water-cooled crystallizer by instantaneously switch-

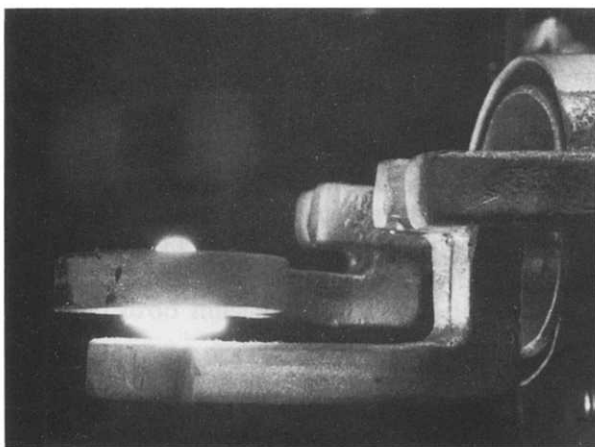
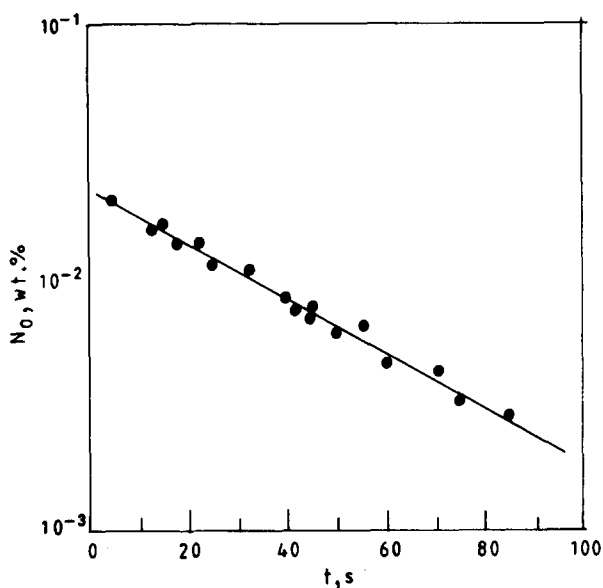


Fig. 1. A sample of liquid niobium levitated in vacuum.

TABLE 1

Concentration of oxygen and carbon in initial samples of niobium and after their melting

Series	N_o (at.%) ^a	N_c (at.%)	
		Before melting	After melting
1	0.77	0.35	0.09
2	0.64	0.58	0.27
3	0.48	0.81	0.40
4	0.33	1.09	0.55

^a1 s after melting; concentration before melting is 0.93 at.%. Fig. 2. Kinetics of changing mean oxygen concentration in niobium with carbon concentration $N_c(0) < 10^{-3}$ wt.%.

ing off the electromagnetic field. The metal temperature was measured by an optical micropyrometer. With account taken of the measurement error, the metal temperature amounted to 2850 ± 50 K. The mean oxygen concentration was determined by the fast-neutron-activation method with sensitivity about 10^{-5} wt.% [6], and the carbon concentration by coulometry with sensitivity about 10^{-3} wt.%.

3. Results and discussion

Figure 2 shows the experimental points for the change in the mean oxygen concentrations in niobium samples with low carbon concentration

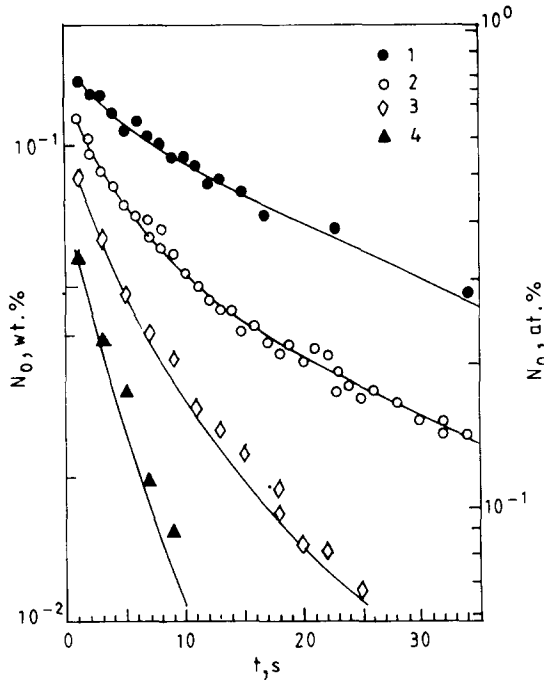


Fig. 3. Kinetics of changing beam oxygen concentration in niobium: ●, series 1; ○, series 2; ◇, series 3; ▲, series 4; —, calculated data from eqn. (7).

during vacuum levitation melting. Figures 3 and 4 demonstrate the data for the time behaviour of the mean oxygen and carbon concentrations, obtained for four series of samples in which the initial ratio of oxygen and carbon contents was varied from unity in series 1 to 0.6 in series 4. It can be clearly seen that the transition from series 1 to series 4 leads to a drastic change of the slope of the curves in both plots; *i.e.* in the concentration range studied the mutual influence of impurities is strongly manifested. Here in series 4 where the initial value of Δ is about 0.035 at.% the fixed value of the ultimate concentration of carbon is lower by a factor of 2 than its initial level, and in series 1, where the initial value of Δ is about 0.7 at.%, the ultimate carbon concentration is beyond the sensitivity of the employed method of analysis. It should be emphasized that under levitation conditions even in comparatively massive samples (about 25 g) the carbon content may be decreased by one order of magnitude in several seconds.

As regards the oxygen behaviour we shall note the following. In terms of the model [1–4] the kinetics of mean oxygen concentration alteration in a liquid drop must obey the equation

$$\frac{d(\ln N_O)}{dt} = - \frac{\mathcal{H}(1 + N_C^{(s)}/N_*)}{1 + q(1 + N_C^{(s)}/N_*)} \quad (4)$$

where $N_C^{(s)}$ is the surface concentration of carbon, $\mathcal{H} = V_a \omega \alpha$, V_a is the atomic volume of the metal, and α is the specific surface of the droplet. At small

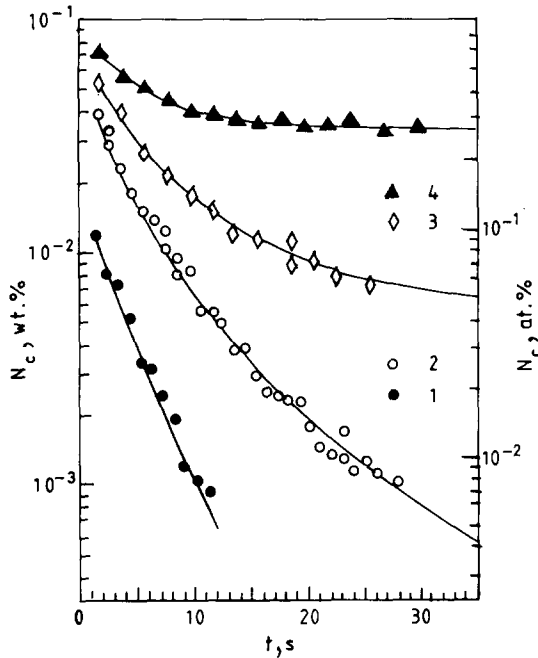


Fig. 4. Kinetics of changing mean carbon concentration in niobium: ●, series 1; ○, series 2; ◇, series 3; ▲, series 4; —, calculated data from eqn. (7).

S ($q \gg 1$) eqn. (4) degenerates to the equation

$$\frac{d(\ln N_o)}{dt} = \frac{\mathcal{H}}{q}$$

At large S ($q \ll 1$) eqn. (4) degenerates to the equation

$$\frac{d(\ln N_o)}{dt} = -\mathcal{H} \frac{1 + N_c^{(s)}}{N_*}$$

So, if the S value is small, then the slope in the coordinates $\ln N_o - t$ must be constant irrespective of changes in the surface concentration of carbon $N_c^{(s)}$. If the S value is sufficiently large, the slope in the coordinates $\ln N_o - t$ is strongly dependent on $N_c^{(s)}$ down to $N_c^{(s)} \ll N_*$ and decreases rapidly, approaching some constant. Precisely this picture is observed in Fig. 3. All these confirm the assumption about a high rate of diffusional processes in levitating metal and indicates that the experiment occurred in the overcritical concentration range.

The results obtained were analysed in terms of eqn. (3), using the data for series 1 and 2, since in series 3 and 4 the Δ values appeared comparable with systematic error in the determination of the oxygen and carbon concentrations themselves. In accord with eqn. (3) at large S the dependence of $\ln N_c$ on Δ must be close to linear. In this case the points belonging to

series with different ratios of the concentrations $N_o(0)$ and $N_c(0)$ in the coordinates $\ln N_c - \Delta$ must fall on parallel straight lines with slope $1/N_*$. Figure 5 shows $\ln N_c$ vs. Δ , plotted for series 1 and 2 on the basis of the data of Figs. 3 and 4. It can be seen that for both series the data are really close to linear and a variation of Δ by a factor of approximately 5 leads to an insignificant difference in the slope from $1/0.55$ for series 2 to $1/0.67$ for series 1. So, using eqn. (3), one can easily find that in our experiments $S > 50$, i.e. S is really very large.

Taking this circumstance into consideration, one may estimate the influence of NbO_2 desorption on the course of the dependence $\ln N_c = f(\Delta)$ that we ignored so far, assuming it to be small, and determine the N_* value more precisely. According to refs. 1-4, at large S the dependence $\ln N_c = f(\Delta)$ with account taken of the desorption of NbO_2 must have the form

$$\ln N_c = \ln N_c^\infty + \frac{N'}{N_*} \ln \left(1 + \frac{\Delta}{N'} \right) \quad (5)$$

where N' is the characteristic oxygen content at which the rates of its desorption as NbO and NbO_2 become equal. Hence we find

$$\frac{\partial \Delta}{\partial (\ln N_c)} = N_* \left(1 + \frac{\Delta}{N'} \right) \quad (6)$$

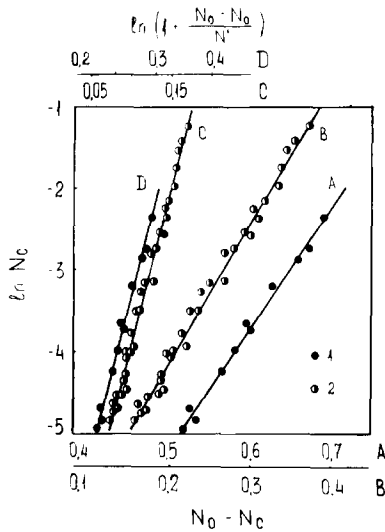


Fig. 5. Mean carbon concentration as a function of the value $\Delta = N_o - N_c + N_c^\infty$, plotted in coordinates $\ln N_c - \Delta$ (lines A and D) and $\ln N_c - \ln(1 + \Delta/N')$ (lines C and B) on the basis of the data of Figs. 3 and 4 (in these series $N_c^\infty \ll N_o - N_c$; therefore $\Delta = N_o - N_c$ (at.%)): ●, series 1; ○, series 2.

The value of N' which weakly depends on temperature, according to the data in ref. 7, reaches about 2 at.% at 2850 ± 50 K for niobium.

So in series 1 the ratio Δ/N' changes from 0.25 to 0.35, *i.e.* $\bar{\Delta}/N' \approx 0.3$, and in series 2 from 0.07 to 0.17, *i.e.* $\bar{\Delta}/N' \approx 0.1$. Hence it is clear that the observed difference in the slope of the straight lines for series 1 and 2 is to a large extent due to the contribution of desorption of NbO_2 molecules. In fact, as can be seen from Fig. 4, the straight lines A and B replotted in accordance with eqn. (6) in coordinates $\ln N_c - \ln(1 + \Delta/N')$ are practically parallel. The value of N_* , obtained from the slope of the straight lines D and C, turned out equal to 0.05 ± 0.01 at.%.

After we had made sure that the relationship in eqn. (2) actually holds in a wide range of Δ and had determined the values of N_* and S , it became possible to compare directly the behaviour of the contents of carbon $N_c(t)$ and oxygen $N_o(t)$, obtained from solution of the starting system of kinetic equations [1-4], with the experimental results. In view of the fact that at $S > 50$ the kinetics becomes slightly sensitive to the S value, we put $S \rightarrow \infty$ ($q \rightarrow 0$) and numerically solved the non-linear system

$$\begin{aligned} \frac{dN_o}{dt} &= -\mathcal{K}N_o \left(1 + \frac{N_c}{N_*} + \frac{N_o}{N'} \right) \\ \frac{dN_c}{dt} &= -\mathcal{K}N_o \frac{N_c}{N_*} \end{aligned} \quad (7)$$

for values $N_* = 0.05$ at.% and $N' = 2$ at.%. From preliminary experiments with niobium doped solely with oxygen ($N_o < 10^{-3}$ wt.%), the value $\mathcal{K} = 0.023 \text{ s}^{-1}$ was determined from the slope in the coordinates $\ln N_o(0) - t$ (Fig. 2) for the four series, and the results of the numerical calculation were compared with the experimental points. The results of such comparison are shown by the curves in Figs. 3 and 4. It can be seen that for all four series the calculation agrees well with experiment. So the data of this study prove experimentally the validity of the model [1-4] in the investigated range of impurity concentrations.

The value of the critical concentration N_* in liquid niobium turned out to be rather low; therefore even at comparatively small values $\Delta \approx 0.1 - 1$ at.%, keeping the drop of niobium in the conditions described provided a practically full 'burning out' of carbon from the sample. So for series 2, according to eqn. (2), we have $N_c^\infty \approx 6 \times 10^{-4} N_c(0) \approx 10^{-4}$ at.%, and for series 1 $N_c^\infty \approx 1.2 \times 10^{-6} N_c(0) \approx 10^{-7}$ at.%. These results relate still more to high-vacuum annealing of niobium foils or wires with $R < 1$ mm, since with decreasing temperature the value of N_* must drop.

Using the above value of \mathcal{K} one can easily determine the desorption rate of niobium monoxide $\omega = \mathcal{K}/V_a \alpha$. Inasmuch as $\mathcal{K} = 0.023 \text{ s}^{-1}$, $\alpha = 3.5 \pm 0.5 \text{ cm}^{-1}$ and $V_a = 11.4 \text{ cm}^3 (\text{g at.})^{-1}$, then $\omega = (5 \pm 1) \times 10^{-6} \text{ g mol cm}^{-2} \text{ s}^{-1} (\text{at.})^{-1}$. Knowing N_* and ω [1-4], one can calculate the effective constant of desorption rate Γ and sticking coefficient b of CO molecules on niobium by means of the equations

$$\Gamma = \omega/N$$

$$b = \Gamma K_p (2\pi MRT_g)^{1/2}$$

where K_p is the equilibrium constant of the reaction $C_s + O_s \rightarrow CO_{\text{gas}}$. Inasmuch as $N_* = 0.05 \pm 0.01$ at.%, and $K_p = 2.1 \times 10^{-1}$ (at.%)² Torr⁻¹, we have $\Gamma = (1 \pm 0.3) \times 10^{-4}$ mol⁻¹ cm⁻² s⁻¹ (at.%)⁻² and $b = 0.04$.

The obtained value of the sticking coefficient at 2850 ± 50 K nearly coincides with its value at 300 K, equal to about 0.06 [8] and measured on niobium at room temperature. This value is lower than the high-temperature sticking coefficients of carbon monoxide: on molybdenum $b \approx 0.4$ at 1700 K or more and on tungsten $b \approx 1$ at 2000 K or more [9].

Let us take the relationship $S = (1 + q)/qp > 50$ that makes it possible to evaluate the mass transfer coefficients of oxygen β_o and carbon β_c in the levitated drop of niobium. Taking into account that in niobium at 2850 K $p = \beta_o/\beta_c \approx (D_o/D_c)^{1/2} \approx 2/3$ [1-4] we have $q = V_a \omega/\beta_o < 10^{-2}$ whence $\beta_o > 0.6$ cm s⁻¹. This indicates the high intensity of mass transfer in the high-frequency levitation melting.

4. Conclusion

The interaction kinetics of carbon and oxygen has been studied in a wide range of ratios of their initial concentrations for the levitation of niobium in vacuum. It was shown that the temporal relation between the mean concentrations of carbon and oxygen in a wide range of Δ obeys the simple law; the parameters of this relation were determined. The kinetics of the mean concentration behaviour of carbon and oxygen was numerically calculated; a good agreement between calculation and experiment was found for all the investigated series by direct comparison. The effective constant of desorption rate of CO and the high-temperature sticking coefficient of CO on niobium were determined.

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