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Hot-pressing kinetics of zirconium carbide

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The hot-pressing kinetics of zirconium carbide were studied between 1700 and 2400° C in argon. The validity of different theoretical models due to Murray, Koval'chenko, Skorokhod, Scholz and Lersmacher was tested. For temperatures exceeding 2200° C, there is reasonably good agreement between kinetics and the whole set of models, but it has not been possible to classify them in order to draw conclusions on the sintering mechanism. The activation energy of ZrC hot-pressing was calculated, starting from the viscosity calculated by Murray's formula, as 41 kcal mol^{-1} (171.7 kJ mol^{-1}).

1. Introduction

Owing to their refractory qualities, their mechanical strength and hardness, the transition-metal carbides of the fourth to sixth group of the periodic table are regarded as future materials for structural applications at very high temperatures [1]. In particular, zirconium carbide is a promising material which, so far, has not been studied as much as WC, TiC or TaC. Moreover ZrC may be used as a thermoionic emitter in the electronic industry [2, 3], or, owing to its low capture section of neutrons [4], as a diffusion barrier for fission metals in the coating of nuclear fuel [5].

It is very difficult to get fully dense specimens of pure zirconium carbide by conventional sintering unless using very fine powders [6, 7]. Hot-pressing is therefore an essential technique for sintering zirconium carbide. The first investigation of ZrC hot-pressing was carried out by Watt *et al.* in 1953 [8], followed by other studies [9–13].

The aim of this work is to study the hot-pressing kinetics of zirconium carbide and to compare the results with theoretical models. A survey of different studies of hot-pressing, plasticity and self-diffusion measurements of zirconium carbide was carried out to correlate all these phenomena.

2. Theoretical models of hot-pressing

There are two kinds of theoretical model for hot-pressing kinetics. The first and the oldest approach is derived from pressureless-sintering models, and is mostly supported by morphological assumptions as reviewed by Pastor in 1972 [14]. More modern theories are based on creep theory and the deformation of dense specimens. Although we used the first category of model we can review all the models as follows.

2.1. Morphological models

We have listed in Table I the integrated formulae of five models. They are derived from different modes of deformation of solids, and different assumptions on the geometrical relation between the pressure and the driving force of the densification. They are due to Murray *et al.* [15] (a historic model and also the simplest one); Koval'chenko and Samsonov [16]; Skorokhod [17]; the second model of Koval'chenko, assuming a grain growth with Nabarro–Herring diffusion [18, 19]; and the last one due to Scholz and Lersmacher [20] which is only empirical. The mathematical formulae (Table I) allow one to compare the models by plotting $Y = f(Q)$, depending only on the porosity Q, against X as the time t or $\ln(1 + bt)$, in order to determine the interval where these curves look linear.

2.2. Non-Newtonian models

Other models, starting from the creep theory of dense specimens, aimed to find the deformation mechanism through the determination of the coefficient n, the power of the stress, appearing in the differential equation

$$\dot{\varepsilon} = K\frac{\sigma^n}{T}\exp\left(-\frac{E}{RT}\right)$$

where K is a constant, σ the stress, T the temperature, E the activation energy and $\dot{\varepsilon}$ the strain rate related to the densification by the relation

$$\dot{\varepsilon} = \frac{1}{\varrho}\frac{d\varrho}{dt}$$

where ϱ is the density.

If $n = 1$ the deformation process is called Newtonian and diffusional mechanisms are prevailing (see Nabarro [18], Herring [19] or Coble [21]). In this case the models derived from pressureless sintering can be related to this process by the viscosity, given by

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{T}{K}\exp\left(\frac{E}{RT}\right)$$

If $n > 1$ the process is called "non-Newtonian", and the creep mechanisms are described by dislocation theory.

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TABLE I Integrated formulae for the theoretical models used in this study

Murray [15]	$\ln Q = \ln Q_0 - \frac{3P}{4\eta} t$
Koval'chenko I [16]	$\ln (3 - Q)^{5/3} Q^{1/3} = \ln (3 - Q_0)^{5/3} Q_0^{1/3} - \frac{P}{4\eta} t$
Skorokhod [17]	$\ln Q - Q = \ln Q_0 - Q_0 - \frac{3P}{4\eta} t$
Koval'chenko II [16]	$\ln (3 - Q)^{5/3} Q^{1/3} = \ln (3 - Q_0)^{5/3} Q_0^{1/3} - \frac{P}{4B\eta} \ln (1 + Bt)$
Scholz [20]	$\ln Q = \ln Q_0 - N \ln (1 + \varepsilon t)$
Linear regression	$Y = B - AX$

3. Experimental procedure

3.1. Starting material

An industrial powder of zirconium carbide, prepared by the carbothermic reduction of zirconia and produced by H. C. Stark, Berlin, Germany (vacuum quality, low hafnium content) was used. We determined both the free and total contents of carbon, and the amounts of the main impurities iron, oxygen and nitrogen (Table II). Thereafter the content of ZrC was calculated by difference from the total weight.

The formula of zirconium carbide determined by the chemical analysis is $ZrC_{0.963}$. It shows a face-centred cubic crystallographic structure (NaCl type). The lattice parameter (0.4698 nm) is calculated from the X-ray powder diffraction patterns. The theoretical density calculated from these data is 6.58 $g\,cm^{-3}$.

The powder granulometry stated by the supplier (3 to 5 μm) is confirmed by scanning electron microscope (SEM) examination. The specific surface area, as determined by BET measurements, is 0.5 $m^2\,g^{-1}$.

3.2. Apparatus

The hot press used has already been widely described in previous papers [22–24]. A graphite die and punches are used to give cylindrical specimens of 12.5 mm diameter and 10 to 15 mm height after firing. The temperature is controlled by means of an infrared radiation pyrometer, and pressure with a strain gauge. The movement of the punches is measured by an inductive displacement controller.

3.3. Computer processing of hot-pressing data

The four parameters (time, temperature, pressure and linear shrinkage) recorded during hot-pressing are manually typed into the computer. Data are taken every minute or more if a parameter changes very much with time. In order to calculate the density $D(t)$ during the whole compression, that is with temperature and pressure change, we must take in consideration the dilatation and the creep of the graphite punches. Therefore we used a set of blank experiments to calculate the relation between the movement of the outer punches and the actual linear shrinkage of the sample $R(t)$. The final density D_f measured by Archimedes' method, the final height of the sample L_f and the final shrinkage R_f, are used in the following formula to calculate the density $D(t)$:

$$D(t) = \frac{D_f L_f}{L_f + R_f - R(t)}$$

This relation assumes constant mass and diameter for the sample. Exploitation of the data [22, 23, 25] is performed in the interpreted A.P.L. language, whose interactivity and graphical outputs fit our objective of comparing theoretical models while keeping in touch with the real physical facts. Actually a real dilatometric study is carried out, which has also given, for other phases, informations about physical changes of the sample during the whole hot-pressing process [26].

TABLE II Chemical analysis of zirconium carbide

Element	C_{total}	C_{free}	Fe	O_2	N_2	Zr
wt %	11.47	0.28	0.012	0.106	0.253	88.159

4. Results and discussion

4.1. Experimental results

Isothermal hot-pressing of zirconium carbide was studied between 1700 and 2400° C under a pressure of 40 MPa. The temperature was raised linearly with time at 30° C min^{-1} with a low pressure of 8 MPa, under a vacuum up to 1000° C and under argon at higher temperatures. When the maximum temperature was reached it was held constant for one or two hours, as a pressure of 40 MPa was applied.

Experimental results are summarized in Table III. Fig. 1 shows the density evolution of samples hot-pressed at different final temperatures. The star on each curve marks the moment when final pressure is applied. The discrepancy between the curves against time before that moment comes from the limited precision of the density calculation; the temperature programming is also far from accurate below 900° C.

TABLE III Experimental results for the hot-pressing of zirconium carbide

Specimen reference	Hot-pressing temperature (° C)	Sintering time at 40 MPa (min)	Final density	
			$g\,cm^{-3}$	% d_{th}
CZ 57	1700	120	4.92	(74.7)
CZ 11	1800	60	5.26	(79.9)
CZ 35	1800	120	5.47	(83.2)
CZ 07	1900	60	6.07	(92.2)
CZ 32	1900	120	6.29	(95.5)
CZ 14	2000	60	6.35	(96.5)
CZ 29	2000	120	6.40	(97.2)
CZ 58	2100	60	6.38	(96.9)
CZ 10	2200	60	6.40	(97.3)
CZ 09	2300	60	6.45	(98.1)
CZ 59	2400	60	6.43	(97.8)

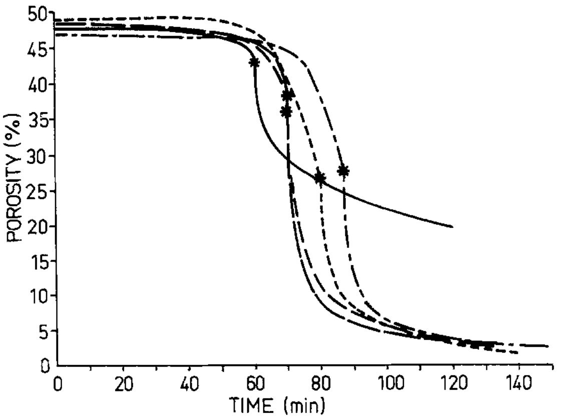

Figure 1 Hot-pressing kinetics at different temperatures plotted by the computer: (—) 1800, (— —) 2000, (———) 2100, (-·-) 2200, (- - - -) 2300° C.

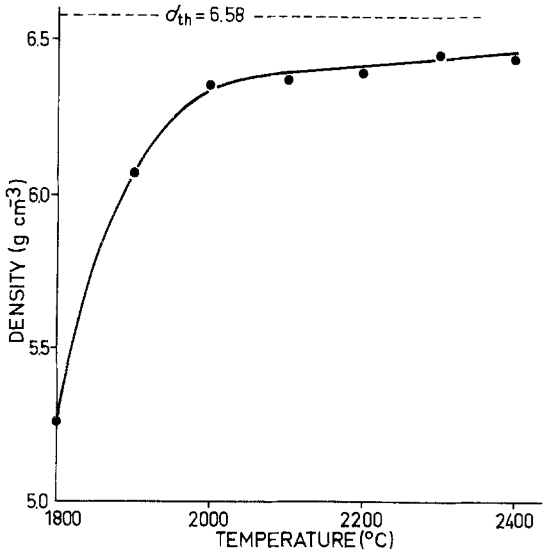

Figure 2 Density against hot-pressing temperature (time = 60 min).

Variations of final density plotted against temperature (Fig. 2) show that it is possible to reach high densities, up to 95% of 6.58 theoretical at 1900 to 2000° C.

4.2. Application of theoretical models

4.2.1. Experimental limitations

Although the theoretical approach of Section 2.2 is more satisfactory the models explained could not be tested. The results are too scattered when different pressures are used. This can be explained by the difficulty of applying precise and constant pressure on the sample, as verified by the measurements we made with the strain gauge. On the other hand, if the same pressure is applied for a batch of experiments, the transient effects and the pressure changes are relatively reproducible. In this way we were able to compare the five models listed in Table I.

4.2.2. Validity of Murray's model

The validity of Murray's model [15] was tested at each sintering temperature. Figs 3a, c and e show some of the transformed curves used to fit the models to experimental data. They give the actual results compared to the regression lines. Figs 3b, d and f show the difference between the regression line, i.e. the theoretical behaviour, and the real data, in addition to the confidence interval which is the interval where the experimental results should lie with a probability of 95%. All the numerical results are given in Table IV.

According to the theoretical hypothesis, Murray's model should be valid only during the final sintering stage. Experimental results show a good fit between this model and the hot pressing of zirconium carbide between 2300 and 2400° C. The higher the sintering temperature, the wider is the interval where this model is valid.

4.2.3. Comparison between different models

The validity of the five models investigated was compared. To give an example, Table V shows the results of the examination at 2300° C, a temperature at which the validity of the previous model is satisfactory. Fig. 4 demonstrates the way this comparison was made.

According to these results, it can be affirmed that the validity of the five models is reasonably good at this temperature. The fact that the regression coefficients are very similar and that the intervals of validity are almost identical makes it impossible to prefer one of the five models. Hence, for the temperature and pressure examined, it can be concluded that all of the equations drawn from the models fit more or less to the last stage of the hot-pressing process of zirconium carbide, the best fit being at higher temperatures. The differences between the models are less important than the error introduced by the evaluation of the parameters used for calculating the density. The results obtained do not allow us to decide which of the models is the best, and therefore it is not possible to draw any conclusion concerning the sintering mechanism on the basis of hot-pressing kinetics data alone.

This confirms the results of previous studies on

TABLE IV Results obtained by using Murray's model

Specimen reference	Temperature (° C)	Viscosity (Pa sec)	Validity interval		Regression coefficient
			Time (min)	Porosity (%)	
CZ 57	1700	8.3×10^{11}	130–173	27.7–25.3	0.9993
CZ 35	1800	4.6×10^{11}	130–174	19.9–16.8	0.9976
CZ 32	1900	2.0×10^{11}	145–178	5.9–4.5	0.9991
CZ 29	2000	1.5×10^{11}	140–181	3.6–2.7	0.9959
CZ 58	2100	5.5×10^{11}	110–130	3.9–3	0.9957
CZ 10	2200	1.4×10^{11}	125–147.2	3.5–2.6	0.9989
CZ 09	2300	7×10^{10}	110–140.4	4.15–1.9	0.9995
CZ 59	2400	5.9×10^{10}	95–132	6.8–2.2	0.9995

TABLE V Comparison of the different models' validity at $T = 2300°C$

Model	Viscosity (Pa sec)	Validity interval		Regression coefficient
		Time (min)	Porosity (%)	
Murray	7×10^{10}	110 to 140.4	4.2 to 1.9	0.999 57
Koval'chenko I	7.3×10^{10}	110 to 140.4	4.2 to 1.9	0.999 54
Shorokhod	7.2×10^{10}	110 to 140.4	4.2 to 1.9	0.999 56
Koval'chenko II	8.5×10^{8}	105 to 140.4	4.8 to 1.9	0.999 54
Scholz	5×10^{10}	105 to 140.4	4.8 to 1.9	0.999 56

borides [22–24]. Possibly, a higher precision in the measurement of the hot-pressing parameters (especially of the pressure) would allow one to classify the models and hence the deformation mechanism. Independently of the theoretical hypothesis, the models are giving a phenomenological description of hot-pressing. This is the reason why Murray's model [15] will be retained because of its simpler formulation.

4.2.4. Comparison of viscosity

The adjustment coefficient called "viscosity" in the different models (Table V) is in good correspondence for all, except for the "viscosity" found with the second model of Koval'chenko. The value calculated for the "viscosity" in Murray's equation provides a good criterion for estimating the powder "sinterability". The theory predicts that this coefficient is

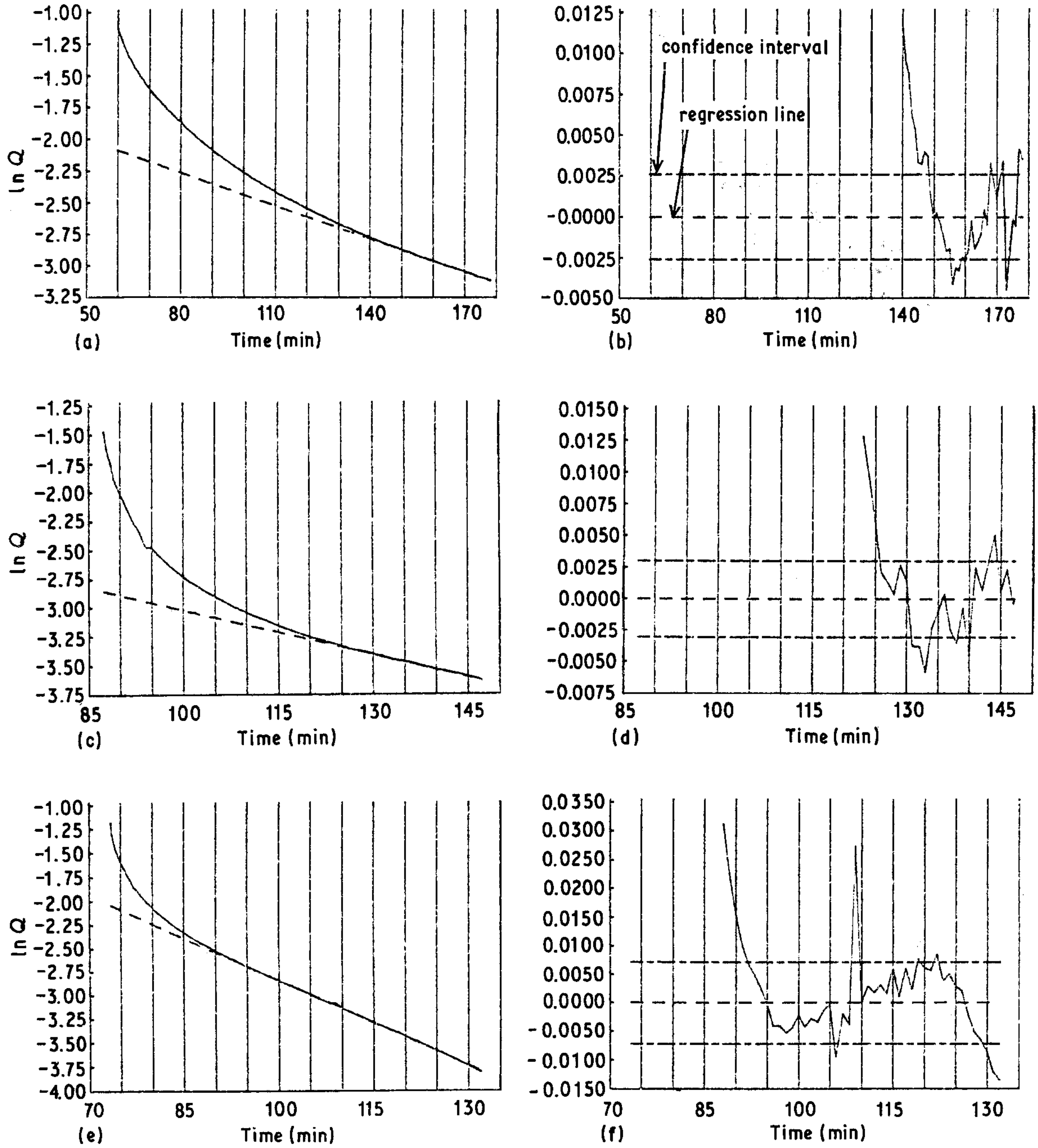

Figure 3 Testing of Murray's model at different temperatures: (a, b) 1900; (c, d) 2200; (e, f) 2400° C. (a), (c) and (e) show the porosity logarithm against time and the regression straight line plotted by the computer; (b), (d) and (f) show the divergence between the regression straight line and the experimental curve (the experimental points are at the tops of the broken lines).

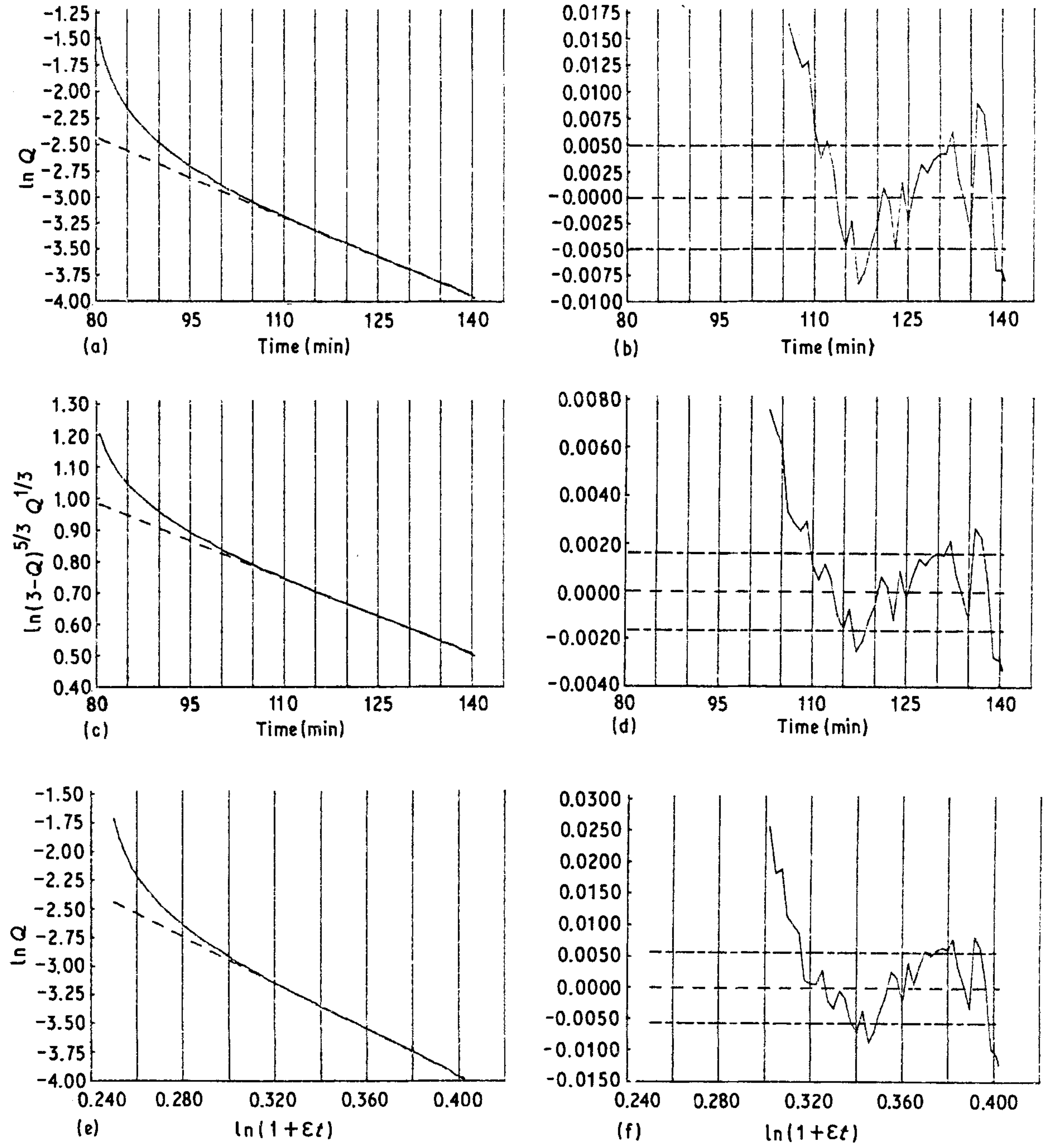

Figure 4 Comparison of different models at $T = 2300°\,C$: (a, b) Murray, (c, d) Koval'chenko I; (e, f) Scholz.

independent of the pressure, but in our case it is not. It may be noticed that this "viscosity", η, at 40 MPa follows approximately the Arrhenius law. The regression straight line drawn by least-squares fit is described by the equation

$$\ln\left(\frac{\eta(\text{Pa sec})}{T\,(\text{K})}\right) = 9.109 + \frac{2.082 \times 10^4}{T\,(\text{K})}$$

The activation energy E_a can be determined by the slope of the line

$$\eta = KT \exp\left(\frac{E_a}{RT}\right)$$

to give $E_a = 41$ kcal mol^{-1} (171.7 kJ mol^{-1}).

Values for the activation energy of hot pressing given in the literature [9, 12. 13] are very scattered and range between 46 and 128 kcal mol^{-1} (192 and 536 kJ mol^{-1}). Our activation energy is close to the lowest value of 46 kcal mol^{-1} (192 kJ mol^{-1}) given by Samsonov and Petrikina [12]. Consequently, it is difficult to correlate hot-pressing activation energy with the self-diffusion activation energy of the material, which could be done according to the formula

$$\eta = kT\sigma D \qquad D = D_0 \exp\,(-E/RT)$$

where D = self-diffusion coefficient and k is a constant.

The activation energy of carbon diffusion in ZrC lies between 106 and 114 kcal mol^{-1} (444 and 477 kJ mol^{-1}) [27–30] using ^{14}C radioactive tracers, or between 78.5 and 78.7 kcal mol^{-1} (329 and 330 kJ mol^{-1}) [31, 32] using less satisfactory methods. The activation energy of zirconium diffusion in ZrC (172 kcal mol^{-1} or 720 kJ mol^{-1}) has been measured [29, 30] using ^{95}Zr radioactive tracers. It seems that the values we found for hot-pressing activation energy are in better agreement with the activation energy of carbon diffusion, but it is hardly possible to draw any further conclusion.

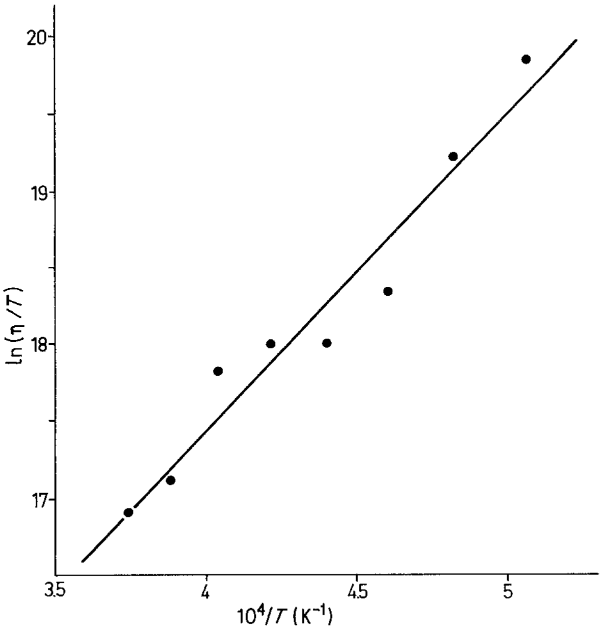

Figure 5 Arrhenius plot of the viscosity calculated from Murray's model.

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