

Reactivity in Oxygen of a HIPed Zirconium Nitride Material

N. Alexandre & M. Desmison-Brut

Laboratoire de Céramiques Nouvelles C.N.R.S. U.R.A. 320,
123, Avenue Albert Thomas, 87060 Limoges Cédex, France

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Abstract

The oxidation behaviour of hot-isostatically pressed zirconium nitride bodies has been studied in dry oxygen between 550 and 700°C. The kinetic curves are linear but tend to be decelerated in the upper temperature range. A non-protective oxide scale is formed which permits the reacting gas to easily reach the substrate. The influence of temperature, pressure and reaction-product morphology is investigated and the results suggest that the reaction is governed by an interfacial process located at the nitride–oxide phase boundary.

Die Oxidationsbeständigkeit heißisostatisch gepreßter Formkörper aus ZrN in einer trockenen Sauerstoffatmosphäre wurde im Temperaturbereich von 550°C bis 700°C untersucht. Die Reaktionskinetik zeigt ein lineares Verhalten, das jedoch bei höheren Temperaturen eine abnehmende Tendenz aufweist. An der Oberfläche bildet sich eine Oxidschicht aus, die vom reagierenden Gas allerdings leicht durchdrungen wird und somit nicht schützend wirkt. Auf die Einflußgrößen Temperatur, Druck und Morphologie der Reaktionsprodukte wird eingegangen. Die Ergebnisse zeigen, daß der geschwindigkeitsbestimmende Schritt durch eine Reaktion an der Nitrid–Oxid Grenzfläche gegeben ist.

La résistance à l'oxydation dans l'oxygène d'un nitrure de zirconium dense élaboré par compression isostatique à chaud a été étudiée entre 550 et 700°C, à la pression atmosphérique.

Les cinétiques d'oxydation sont linéaires aux basses températures et légèrement décélérées lorsque la température augmente.

La couche d'oxyde formée n'étant pas protectrice permet l'accès direct de l'oxygène à l'interface interne.

L'étude de l'influence de la pression et de la morphologie des échantillons indique que la réaction est gouvernée par un processus d'interface.

1 Introduction

Zirconium nitride, as well as several other types of transition metal nitride, i.e. tantalum, hafnium or titanium nitride, are unstable in oxidizing atmosphere. Zirconium nitride is known to present a very poor oxidation resistance. Indeed, the oxidation behaviour of ZrN powders and plates has been investigated in oxygen, water and carbon dioxide.^{1–4} The kinetic results were interpreted by a Prout and Tompkins type model, the transformation being governed by a phase boundary reaction.

The kinetic aspects of the oxidation of ZrN coatings have been studied between 550 and 700°C, for pressures within the range 0.07–0.7 atm.⁵ The general shape of the kinetic curves changes with temperature: up to about 650°C, they exhibit an upward concavity in their initial stage, followed by an approximately linear stage. At the lowest temperatures, the authors observed a mass diminution of the sample at the beginning of the reaction. The proposed mechanism involves the formation of zirconium–oxygen solutions preceding that of zirconia.

Moreover, sputtered zirconium nitride thin films⁶ which may be an excellent barrier against the diffusion of silicon and aluminum in semiconductors, were treated in an oxygen atmosphere. Surprisingly, the oxide thickness follows a parabolic dependence on time and the diffusion of oxygen through the already-grown oxide was proposed as the limiting process. The present study was aimed to

analyse the oxidation behaviour of a fully dense material prepared by Hot Isostatic Pressing. The influence of the symmetry of the specimens on the kinetics shape is analysed.

2 Materials and Methods

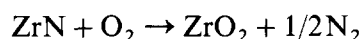
The commercial grade powder was supplied by CERAC (USA). Its particle size distribution, determined by sedigraphy, varies from 1 to 50 μm . A significant amount of the powder consists of large and irregular grains. The average particle size is about 15 μm . This material contains between 2 and 4% of hafnium. The main characteristics of the starting powder are presented in Table 1.

Table 1. Chemical analysis of starting powder

Impurities	Hf	C	O	Al	Fe	Ti
wt%	2-4	0.5	2.1	0.04	0.04	0.03

The ceramic material is sintered by hot isostatic pressing up to 1950°C and 195 MPa. Zirconium nitride density measurements, using Archimedes' Principle, show that more than 99% of the theoretical density is achieved. The grain size can be evaluated by SEM observations on chemically etched samples (etching medium: HF/HNO₃). The average grain size is 18 μm . Cubic samples (4 mm side) are polished, washed in alcohol with ultrasonic assistance and dried. The oxidation resistance is tested in a dynamic flow of pure oxygen (20 litres/h) at atmospheric pressure using a SETARAM micro-balance.

The procedure is as follows: First, the furnace is evacuated (10^{-1} atm) and then, a stream of argon is introduced. As the temperature is increased, the specimen is kept out of the hot zone with a magnetic device and lowered, 15 min after the introduction of oxygen. The zero time is taken when the platinum crucible containing the sample reaches the hot zone. The kinetic curves are obtained by plotting the fractional weight change ($\alpha = \Delta m / \Delta m_{\infty}$) versus time. The weight gain Δm_{∞} corresponds to the complete oxidation evaluated by considering that ZrN is transformed into ZrO₂ according to the reaction:



3 Results

3.1 Effect of temperature

The oxidation of zirconium nitride (ZrN) begins around 640°C but the reaction becomes really rapid

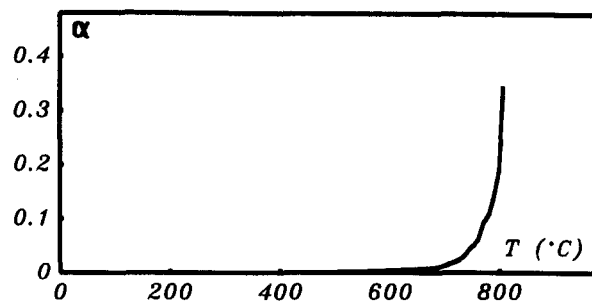


Fig. 1. Oxidation curve for cubic sample exposed to flowing oxygen at 1 atm.

above 700°C (Fig. 1). Isothermal curves have been recorded between 550°C and 700°C, at atmospheric pressure. Their shape is linear at low temperatures but is showing some deceleration in the upper temperature range (Fig. 2). After 15 h at 700°C, the specimen is totally oxidized. Each curve can be superimposed onto any other by an affinity relationship with time (Fig. 3). A master run roughly in the middle of the series was chosen and a factor A was calculated for each curve such that multiplication of the time scale of the run by A would superimpose onto the master run curve.^{1,2,7} Log A was found to be a linear function of $1/T$. This implies that the

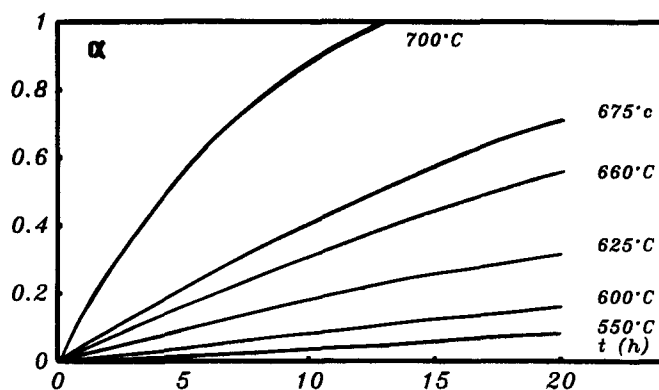


Fig. 2. Isothermal curves recorded at 1 atm in the temperature range 550–700°C.

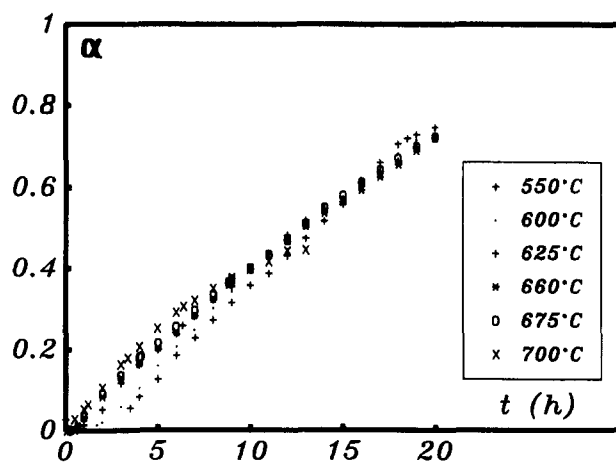


Fig. 3. Superimposed isothermal curves.

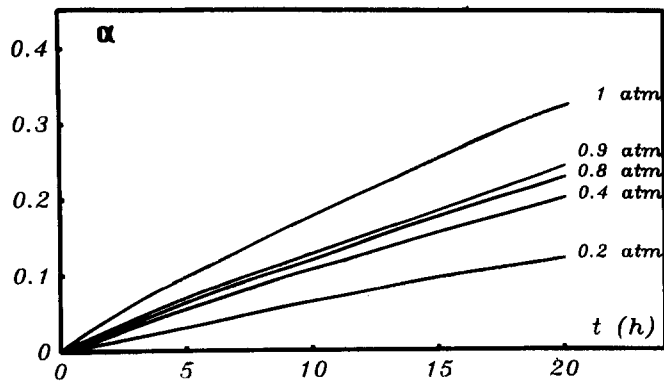


Fig. 4. Isobaric curves recorded at 630°C in the pressure range 0.2–1 atm.

activation energy is unique over the whole temperature range ($E = 140$ kJ/mole).

3.2 Effect of pressure

To assess the effective contribution of the oxygen partial pressure on the reaction rate, isobaric curves have been recorded at 630°C, in the pressure range 0.2–1 atm and plotted as a function of time (Fig. 4). The general shape of the kinetics is conserved and the curves can be superimposed.

3.3 Reaction products and morphological observations

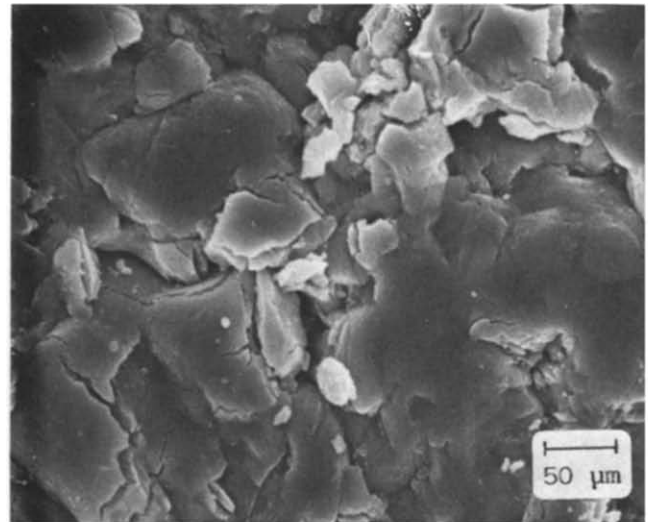
X-ray analysis shows the presence of monoclinic zirconia, independent of pressure and temperature. However, depending on the temperature, the morphological aspect of the oxide may be quite different. At lower temperatures, a powdered oxide is formed. With increasing temperature, the sintering of the oxide scale occurs and the outer layer becomes more compact (Fig. 5). For the same temperature but different oxidation time, we have measured the ZrN core thickness and a linear law is obtained (Fig. 6).

4 Interpretation

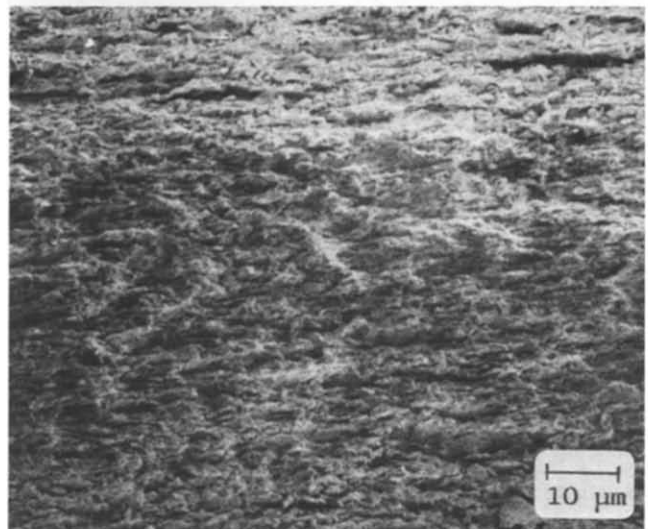
The characteristic features of the experimental results allow confirmation that the reaction rate V is a function of pressure and temperature. As both isothermal and isobaric curves are in a close affinity relationship with time, the equation can be written as a function of separated variables:

$$V = \frac{d\alpha}{dt} = f(\alpha)g(T)h(P) = Cte f(\alpha)h(P) \exp - \frac{E}{RT} \quad (1)$$

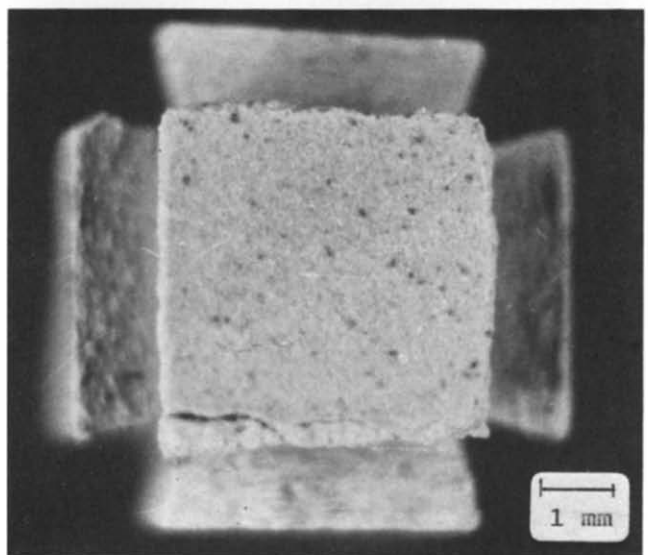
where $f(\alpha)$ is a morphological term characteristic of the reaction area. This means that the controlling process is unique and identical to itself over the whole reaction range.^{1,2,7} At constant temperature



(a)



(b)



(c)

Fig. 5. Morphological observations: (a) surface of a 1 h oxidized specimen at 600°C; (b) oxide scale at $T = 675^\circ\text{C}$; (c) maltse cross obtained at 630°C after 20 h oxidation ($P = 0.8$ atm).

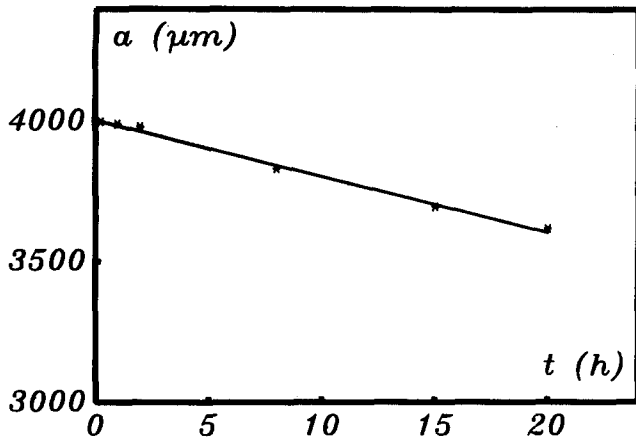


Fig. 6. Time dependence of zirconium nitride core thickness at 630°C.

and pressure, the shape of the curves is determined only by geometrical factors.

SEM observations show that the oxide porosity and the opening of the cube edges at the beginning of the reaction, permit direct access of oxygen at the nitride-oxide interface. On the other hand, the nitrogen release from the core is easy. All these remarks suggest a reaction regime at this inner interface. Therefore, the reaction rate V is directly proportional to the surface area of the non-oxidized cubic nitride core of edge a at time t .

$$V = \frac{d\alpha}{dt} = K(T, P)S(\alpha) \quad (2)$$

$S(\alpha) = 6a^2$ being related to the conversion degree α through a .⁸

Indeed

$$\alpha = 1 - v/v_0$$

with v the volume of the residual substrate and v_0 the volume of the initial cube of edge a_0 . By extension:

$$\alpha = 1 - \frac{a^3}{a_0^3} \quad (3)$$

or

$$a = a_0(1 - \alpha)^{1/3} \quad (4)$$

The rate law² becomes:

$$\frac{d\alpha}{dt} = 6K(T, P)a_0^2(1 - \alpha)^{2/3} \quad (5)$$

Integration of expression (5) leads to:

$$F(\alpha) = 1 - (1 - \alpha)^{1/3} = kt \quad (6)$$

with $k = 2a_0^2 K(T, P)$.

Also, by taking into account (4), eqn (6) may be written:

$$a = a_0 - a_0 kt \quad (7)$$

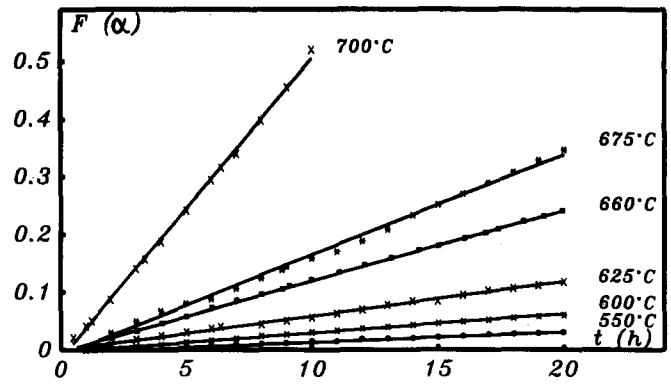


Fig. 7. Oxidation curves plotted against time in the cubic form at various temperatures.

Therefore, the assessment of the validity of our kinetic model may be found either by plotting a versus t or $F(\alpha)$ versus t . Figure 6 shows the linear dependency of a on time at 630°C.

$F(\alpha)$ versus t plots have been reported in Fig. 7. As can be seen, linear plots are obtained for all temperatures up to 675°C.

By plotting $\log k$ versus reciprocal temperature (Fig. 8), a value of 140 kJ/mole is obtained. This value is in good agreement with those already calculated for zirconium nitride plates and oxidized powders. In the same way, a linearization is obtained by plotting, at various pressure, $F(\alpha)$ versus time (Fig. 9). The pressure constant k is influenced by a change in the oxygen pressure.

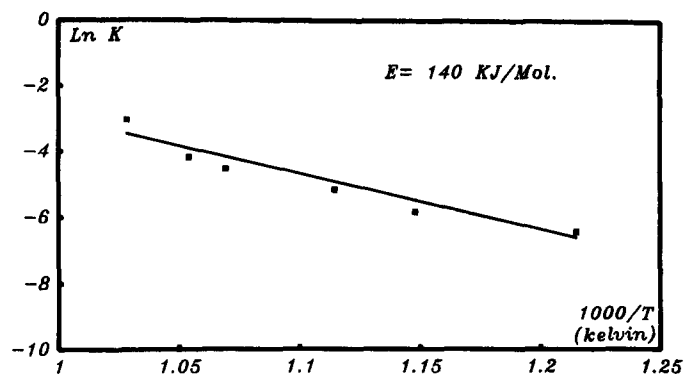


Fig. 8. Influence of temperature on the rate constant K at 1 atm.

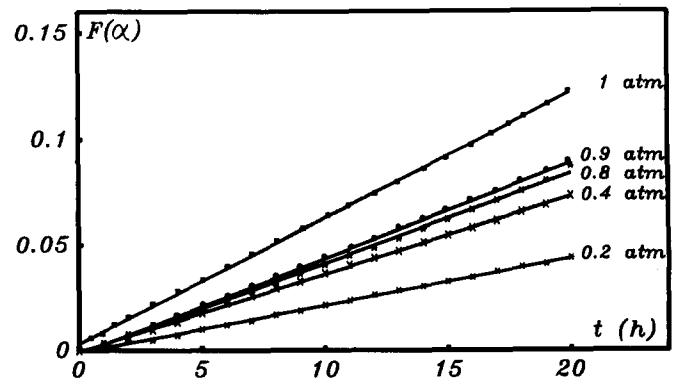


Fig. 9. Oxidation curves plotted against time in the cubic form at various pressures.

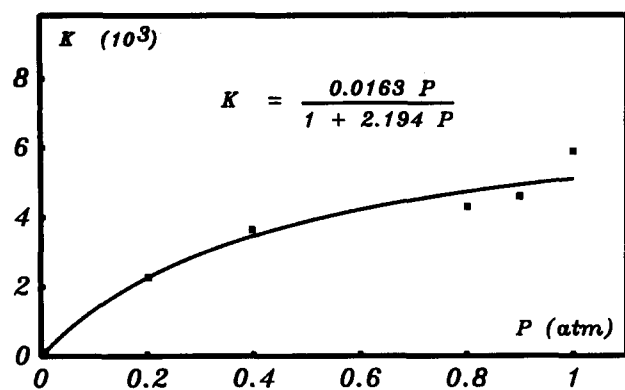


Fig. 10. Effect of oxygen pressure on the rate constant K at 630°C .

The constant dependence with pressure may be represented by a relation of the form:

$$k = aP/(1 + bP) \quad (8)$$

where

$$a = 0.0163 \quad \text{and} \quad b = 2.194 \quad (\text{Fig. 10})$$

Finally, a parametric kinetic law of type (1) may represent the oxidation rate:

$$V = Cte(1 - \alpha)^{2/3} 0.0163P / (1 + 2.194P) \times \exp - 140000/RT \quad (9)$$

The limiting step has to be one in the sequence of the interfacial reaction, i.e. the oxygen adsorption or nitrogen desorption, the nitrogen substitution by oxygen and the reorganization of the crystalline network. In fact, the Langmuir type pressure dependence (8) suggests that the rate-determining step in the oxidation is the subsequent reaction of the adsorbed oxygen molecules.⁹

5 Discussion and Conclusion

This study confirms the importance of morphological data in the kinetic study of the oxidation of transition elements nitrides of groups IV and Va.^{1,2,10,11} Indeed, the high value of the Pilling–Bedworth ratio,⁹ ($\Delta = 1.8$) of zirconium oxide ZrO_2 , with respect to ZrN generates compressive stresses in the scale. The low plasticity of the material below 700°C , very far from the Tammann critical temperature delimiting the plastic deformation region of an oxide¹² (≈ 0.5 the melting point $T_{\text{Tammann}} \approx 1400^{\circ}\text{C}$), and the good oxide adherence on the nitride core do not allow stress relaxation. The direct consequence is the failure of the oxide which takes place at the edges of the cubes. A concave deformation of the outer oxide surfaces is

observed, and the final shape of the sample is a maltese cross.

If platelets (with planar symmetry) rather than cubes had been tested, traditional linear reaction kinetics, reflecting that a phase boundary reaction (with constant reaction area) is rate determining, would have been observed. However, previous studies have shown that thin plates ($125\text{--}250\ \mu\text{m}$ thick) or spheres ($60\ \mu\text{m}$ diameter) exhibit a particular kinetics behaviour.^{1,2} In fact, a cooperative rupture of the scale and substrate leads to a progressive cracking which spreads to the whole specimen. A chain fragmentation takes place after a thin adherent oxide film has been formed. It proceeds inwards according to an autocatalytic type phenomenon which explains the sigmoidal shape of the kinetics.^{1,2,10–12}

With the more voluminous sample used in the present work, relaxation of stresses is only occurring by cracking of the oxide layer, in particular, in the regions where stress intensity is a maximum, i.e. at edges or corners. No significative internal cracking was shown by SEM observations of cross-sections.

To close this comparison with previous work, it is necessary to notice the tendency of the oxide scale to sinter in the higher temperature range. Indeed, this phenomenon, which is almost nonexistent in the case of purer materials,^{1,2} has to be associated with the presence of impurities (Table 1). But the densification of the oxide was never sufficient to lead to a restricted access of oxygen to the ZrN surface, implying the existence of a gaseous diffusion limiting step. Such a mechanistic change towards diffusional behaviour would provoke a modification of the kinetics shape. The affinity relationship of Fig. 3 clearly excludes such an hypothesis.

In conclusion, the oxidation of zirconium nitride is characterized, whatever is the symmetry (plates or cubes), by the formation of a non-protective oxide scale. The global reaction rate is modulated by morphological parameters, i.e. surface cracks, porous and lamellar oxide, opening of the cube edges. The results clearly demonstrated that this cannot be a diffusional process.

The reaction is governed by an external type interfacial process, located at the nitride–oxide interface, this being confirmed by the oxygen pressure dependence of the rate law.

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