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The role of water vapour in the oxidation of glass in the YSiAlON system

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Abstract

The effect of water vapour on the oxidation of an oxynitride glass in the system YSiAlON has been studied in the temperature range 1050–1200°C. Three categories of oxidising atmospheres were used; dry oxygen/nitrogen, nitrogen plus water vapour and oxygen plus water vapour. The water vapour pressure was varied within the range 360–2690 Pa. The oxidation kinetics, derived from thermogravimetric data, and the reaction products, examined by XRD and SEM, were analysed in order to understand the reaction mechanisms. The reaction kinetics and product morphology indicate that the rate of oxidation is controlled by the chemical reaction at the internal interface (oxide scale/substrate). The oxidation of the glass is found to be much faster in an atmosphere of nitrogen plus water vapour than in pure oxygen, showing that water vapour is an effective independent oxidant. The oxidation rate for oxygen plus water vapour is greater than the sum of the individual oxidation rates, indicating a synergy. The relationships between the reaction rate and the water vapour pressure and oxidation temperature are determined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Glass-oxynitride; Kinetics; Oxidation; Sialons; Water vapour

1. Introduction

The properties, and in particular the oxidation resistance, of silicon nitride-based ceramics are strongly linked to the composition of the residual grain boundary phase. Mixtures of oxide additives, such as yttria and alumina, are widely used as sintering aids for such ceramics, usually resulting in a residual glassy phase in the system YSiAlON. The rate of the oxidation reaction of LnSiAlON glasses is highly dependant on the glass composition, having been shown to vary with the nitrogen content and the nature and quantity of the cations.[1]

It has been noted that the presence of water vapour in the oxidising atmosphere has a significant effect on the oxidation of silicon nitride based materials,[2–4] but very little quantitative research has been reported on the subject. For the oxidation of silicon containing materials, water vapour reacts with silicon-oxygen bonds in the oxide layer, replacing the oxygen with hydroxyl groups which either lower the glass viscosity and promote the diffusion of oxygen in the substrate or act as effective oxygen carriers themselves.[5] Molecular water can also diffuse through a silica glass, reacting with it to form hydroxyl groups in a local equilibrium:[6–8]

$$H_2O + \equiv \text{Si-O-Si} \equiv \leftrightarrow\ 2 \equiv \text{SiOH}$$

The presence of the molecular water itself has little effect on the silicate network,[9] but the incorporation of hydroxyl groups (the predominant form at high temperature) produces significant structural changes; decreasing the glass viscosity and increasing structural relaxation and crystallisation.

The present work attempts to improve the understanding of the role of water vapour in the oxidation of a YSiAlON glass by examining the oxidation reaction in atmospheres of dry oxygen, water vapour plus nitrogen and, finally, water vapour plus oxygen.

2. Materials and procedure

2.1. Preparation and analysis of glass

The glass was prepared from a mixture of oxide and nitride powders using the melting procedure described

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by Hampshire et al.,[10] having the composition shown in Table 1.

The nitrogen content of the glass was determined by elemental analysis, achieved by the combustion of powder samples using an analyser (Carbo-Erba 1106), and by the complete oxidation of a sample at 1150°C. The elemental analysis was carried out on material from various parts of the supplied glass bar, confirming its homogeneity. Long exposure XRD analysis (Guinier camera) showed that no crystalline phases were present in the starting glass. The density of the glass was found to be 3.40±0.01.

Thermal dilatometry, using a dilatometer (Setaram TMA 92198), under a flow of high purity nitrogen (N50), gave values for the glass transition temperature, softening temperature and thermal expansion coefficient (measured over the temperature range 200–900°C) of $T_g = 962\pm10$°C, $T_s = 1016\pm10$°C and $\alpha = 6.0\pm0.4\ 10^{-6}\ K^{-1}$ respectively. The crystallisation temperature, determined by DTA, is found at 1050°C.

The glass samples used for the oxidation and thermal dilatometry were cut into cubes with sides of around 4 mm and were polished using a succession of silicon carbide and diamond powder-impregnated papers, the final polish being with a 3 μm diamond powder. The cubes were then cleaned in acetone using an ultrasonic bath, dried and weighed.

2.2. Oxidation experiments

Thermogravimetric analysis (Setaram B60) was carried out in an atmosphere-controlled vertical alumina tube furnace with the sample suspended in an alumina crucible connected to a balance by a platinum chain. The sample was lowered into the hot-zone at the required temperature and was removed at the end of the run, ensuring that isothermal conditions were observed. The hot-zone temperature was measured directly by a thermocouple.

The effect of water vapour on the oxidation process was studied quantitatively by the introduction of known partial pressures of water vapour in the inlet gas. This was achieved by passing the inlet gas first through distilled water and then up a glass column cooled or heated by water (circulated from a separate tank and kept at a known temperature). This allowed the water vapour pressure to be controlled in the range 360–2690 Pa.[11] Calculations show that the standard gas flow of 60 cl.min^{-1} used for the oxidation provides water vapour molecules in excess of the number required for the reaction rates observed. In these runs in which H_2O was the only oxidant, high purity nitrogen (N50) gas was used, and the furnace was evacuated then flushed with nitrogen plus water vapour for around 10 h to ensure the elimination of oxygen.

Table 1
Composition of starting glass

	Y	Si	Al	O	N
Equivalent %	18	47	35	80	20
Atomic %	7.89	15.44	15.33	52.57	8.76
Weight %	28.16	17.16	16.43	33.38	4.87

Analysis of the oxide layers and substrates was carried out by XRD using a diffractometer, or Guinier camera in certain cases where the quantity of powder was small, and by SEM (Philips X.L. 30). Phase analysis was then carried out by reference to I.C.D.D. data.

3. Results

During the oxidation of a YSiAlON glass, the nitrogen is replaced by oxygen to produce an oxide layer according to an overall reaction such as:

$$\mathrm{YSiAlON_{glass}} + \mathrm{aO_2} \rightarrow \mathrm{bY_2Si_2O_7} + \mathrm{cAl_6Si_2O_7} + \mathrm{dN_2}$$

where $3O^{2-}$ replaces $2N^{3-}$. The loss of nitrogen and gain of oxygen produces a net weight gain in the sample. This is used to define the degree of advancement of the reaction at any given time as:

$$\alpha = \frac{\Delta m_t}{\Delta m_\infty}$$

where Δm_t is the weight gain at time t and Δm_∞ is the weight gain after an infinite time, calculated for the glass considered in the present work as 3.48 wt.% using the nitrogen content of 4.87 wt.% obtained by elemental analysis.

Isothermal oxidations were carried out in the temperature range 1050–1200°C, corresponding to the temperature domain producing coherent oxidation kinetics for the current glass in air.[12] Above 1200°C, the crystallisation of the glass is too fast as it is shown later.

3.1. Oxygen/nitrogen atmosphere

Oxidising atmospheres corresponding to nitrogen plus 60% oxygen or nitrogen plus 20% oxygen were used, each having a total pressure of one atmosphere. The advancement of the reaction is plotted versus time in Fig. 1. It is seen that the oxidation reaction is very limited at 1050°C, as it would be expected at a temperature less than 100°C in excess of T_g. At higher temperatures, however, the reaction is still slow, producing an advancement of only $\alpha = 0.3$ after 20 h at 1100°C. At 1125, 1150 and 1200°C, the fractional weight gain increases rapidly at the beginning of the reaction. Then it becomes very slow after around 10, 3 and 1 h respectively.

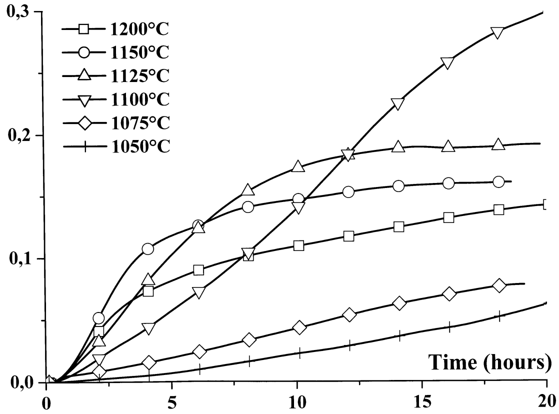


Fig. 1. Oxidation kinetics under dry O_2/N_2 (20/80) mixture.

SEM observations of these samples show that the behaviour results from microstructural changes of the substrate. In the temperature range studied, the scale is relatively porous with large pores mainly located at the internal interface (Fig. 2a,b). At high temperatures an extensive crystallisation of the substrate (Fig. 3) explains the decrease of the oxidation's rate.

The reaction products identified by XRD analysis do not follow a simple progression with reaction time, temperature or oxygen partial pressure (Table 2).

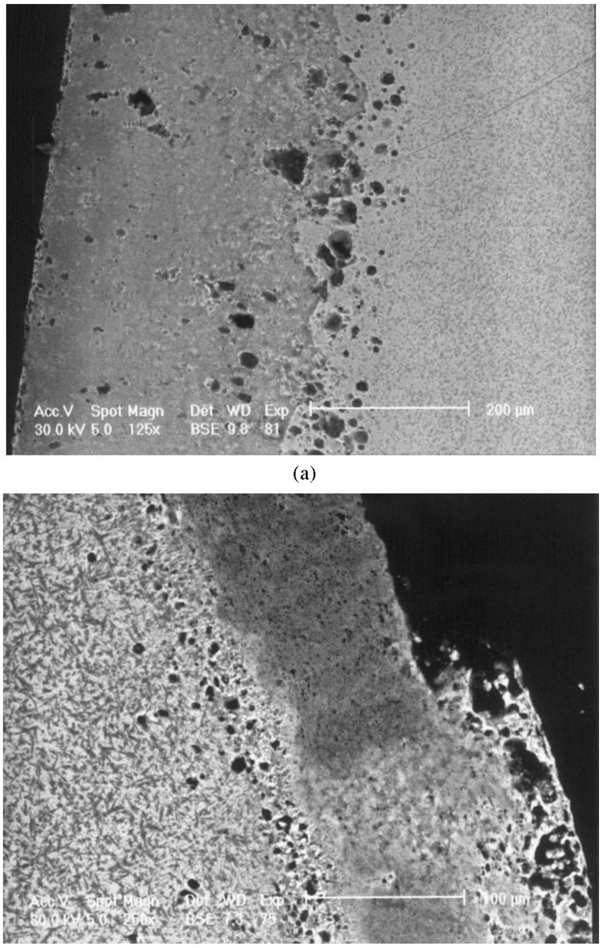
Several new phases (Q1, Q2, Q3), which have been observed in the oxidation of the current glass in air[12] but are not found in I.C.D.D. data, are seen in the scale along with yttrium disilicates (α, β, y) and mullite (mull). Another phase having a pattern similar to that of SiO_2 from the silica-rich end of the silica O series (I.C.D.D. card 12-708), possibly stabilised by Y, Al or N, is also seen.

3.2. Water vapour/nitrogen atmospheres

Oxidation by water vapour mixed with high purity nitrogen shows it to be an effective independent oxidant (Fig. 4). For the same range of temperature the rate of oxidation is faster in water vapour than in oxygen/nitrogen mixture (Fig. 1) and the kinetic curves exhibit a sigmoidal shape.

At 1150°C, even for the lowest pressure of 360 Pa, water vapour produces a weight gain greater than that observed with 100 kPa of dry oxygen (Fig. 5). Reaction products analysed for various temperatures and durations (Table 3) are similar to those observed after oxidation in air. The oxide scale comprises mostly α, y and β yttrium disilicate and mullite. Observations of oxidised samples with SEM show that, for the temperature range studied, the oxide layer is porous and more expanded than in dry oxygen (Fig. 6)

The scale thickness is higher for the same fractional weight gain. The oxidation being very fast at 2120 Pa, the substrate's crystallisation advancement remains limited.



(a)

(b)

Fig. 2. SEM observations O_2/N_2 (20/80): (a) $T = 1100°C$; (b) $T = 1100°C$.

3.3. Oxygen/water vapour atmospheres

The advancements of the reactions in O_2 plus 2120 Pa of water vapour are plotted versus time (Fig. 7). A rapid degradation of the sample is observed and complete oxidation is detected at 1150°C after 3 h. The same behaviour was observed when the reaction was followed for various water vapour pressures.

The reaction products were analysed for the temperature range and for the various water vapour pressures studied. Results are summarised in Table 4. The crystallised compounds are very similar to those observed in nitrogen plus water vapour.

SEM observations of cross-sections show that the oxide layer is highly expanded at all advancements of the reaction (Fig. 8).

Due to the brittleness of the scale, the pore diameter distribution was not determined but, as it is shown on

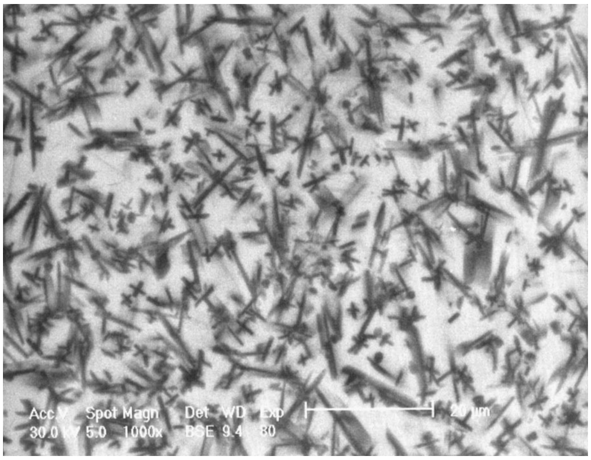


Fig. 3. SEM observations: crystallization of the substrate ($T = 1200°C$).

Table 2
Oxidation products under dry O_2

Temp. (°C)	%O_2	Time (h)	α Final	XRD of the scale
1050	100	21	0.06	Q1, Q2, Q3
1075	100	19	0.09	α,y, mull, Q2, Q3
1100	100	21	0.31	Q2, Q3, α, mull
1150	100	20	0.16	Q2, Q3, α,y, mull
1150	100	1.3	0.03	α, y, mull, Q2
1150	100	1.6	0.05	α, y, mull, Q2
1200	100	20	0.16	β, α, mull, Q2
1150	60	18	0.12	β, α, y, mull, Q3
1100	20	21	0.15	Q2, Q3, α, y mull
1150	20	22	0.11	β, y, mull, Q3
1200	20	19	0.16	β, α, mull, Q2, Q3, Q1

Fig. 8, the size of some pores exceeds 100 μm in diameter.

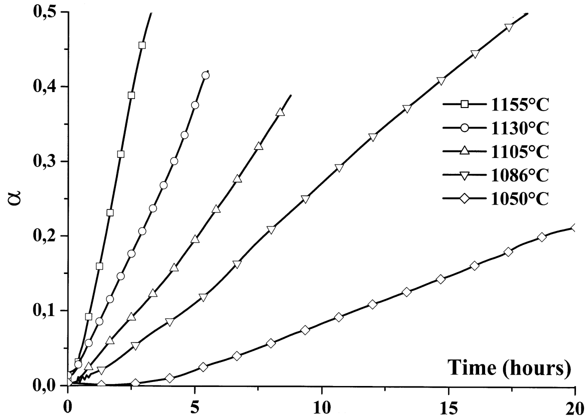


Fig. 4. Oxidation under 2110 Pa of water vapour pressure.

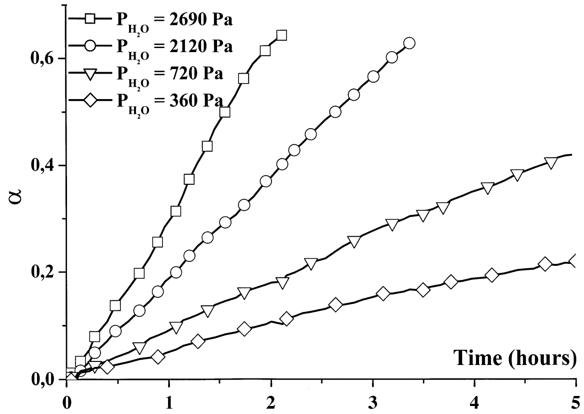


Fig. 5. Oxidation under water vapour $T = 1150°C$.

Table 3
Oxidation products under N_2/H_2O

Temp. (°C)	P_{H_2O} (pa)	Time (h)	XRD of the scale
1050	2120	24	α, y, mull, Q1, Q2
1100	2120	9	α, y, β mull, Q1
1150	360	5	α, y, β, mull, Q1
1150	720	5	α, y, β, mull, Q1
1150	1220	5	α, y, β, mull, Q1
1150	2690	10	α, y, β, mull, Q1

4. Discussion

The reactions between silicon based materials and oxygen, air or water vapour have been studied extensively,[13] but in fact quantitative results show that the role of water vapour is still controversial.[14,15] During oxidation in wet air of silicon nitride ceramics containing a glassy YSiAlON phase, the devitrification of the glassy phase and of the amorphous oxide products has been suggested as the mechanism by which water vapour promotes the reactions.[2] The acceleration of the crystallisation induces porosity in the oxide layer, allowing improved access for the oxidants to the reaction area. It is known that water vapour can react with silica, dismuting the silica network by the formation of non-bridging Si–OH groups. The atomic scale structure of silica or silicates is modified which enhances oxygen diffusion, but water vapour can also act as an additional oxidant. In the case of YSiAlON glasses, the experiments evidence a direct reaction with pure water vapour by replacing M–N bonds with M–OH which subsequently decompose to M–O. XRD results show that the oxides formed are not exactly identical with oxide products in dry oxygen. Some phases are transformed more rapidly into allotropic structures or stabilised by OH groups.

In order to compare the reactivity of oxygen or water vapour, experiments were carried out in dry oxygen, water vapour or in an oxygen/water vapour mixture (Fig. 9).

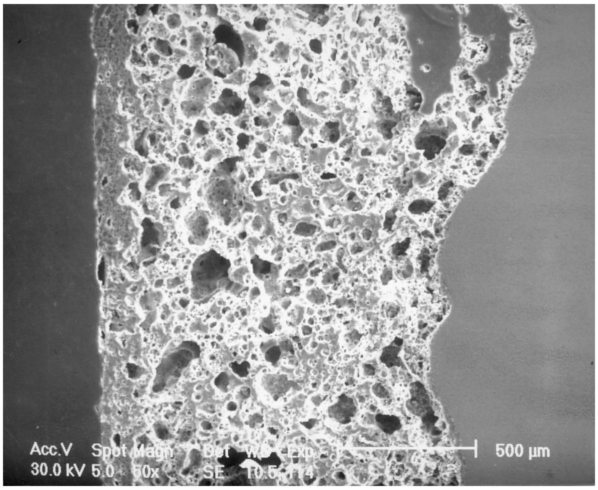


Fig. 6. SEM observation: $T=1100°C$; $P_{H_2O}=2110$ Pa.

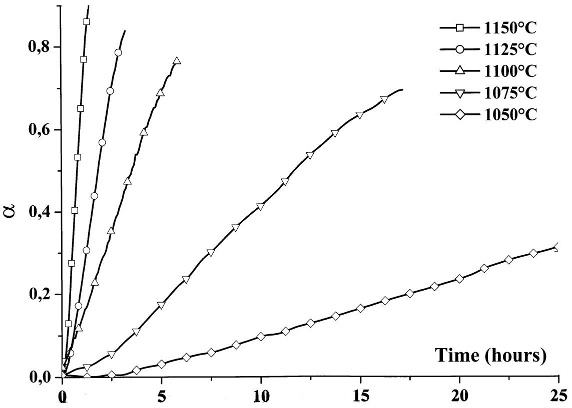


Fig. 7. Oxidation under O_2 plus water vapour $P_{H2O}=2120$ Pa.

Table 4
Oxidation products under O_2/H_2O mixture

Temp. (°C)	P_{H_2O} (Pa)	Time (h)	XRD of the scale
1150	0	20	Q1, Q2, α
1150	400	5	α, y, β, mull, Q1
1150	580	5	α, y, β, mull, Q1
1150	860	5	α, y, β, mull, Q1
1150	1200	5	α, y, β, mull
1150	1960	5	α, y, β, mull, Q1
1150	2570	15	α, y, β, mull
1150	3870	5	α, y, β, mull, Q1

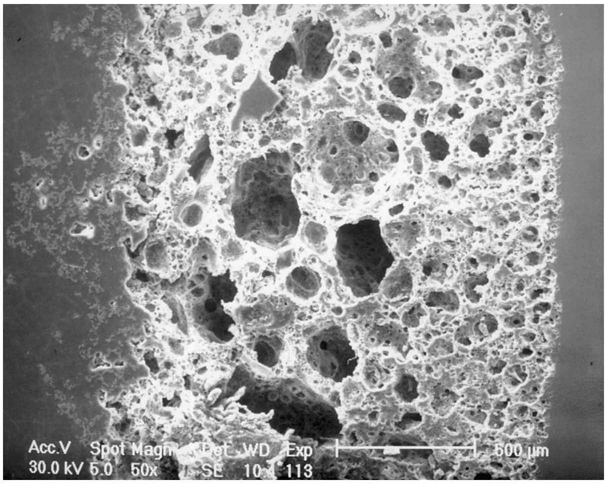


Fig. 8. SEM observation: oxidation under O_2 plus water vapour ($T=1100°C$, $P_{H_2O}=2110$ Pa).

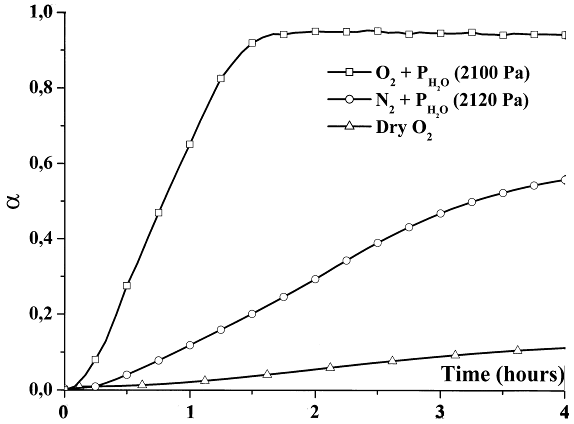


Fig. 9. Oxidation kinetics for various atmospheres ($T=1150°C$).

The comparison of the degree of advancement of the reaction points out that the reaction rate in wet oxygen exceeds the sum of the rates for the independent oxidation by water vapour and dry oxygen. Thus, a synergy must take between the two oxidizing species. As mentioned for the oxidation of silicon nitride materials, water vapour modifies the oxide glass viscosity and the crystallisation kinetics during the formation of the reaction products. Moreover, the pore size distribution is higher when water vapour is added which facilitates the access of the molecules to the substrate. It appears that the rate of the reaction between the oxynitride glass and water is higher than with oxygen.

When a mixture (O_2/H_2O) reacts simultaneously with a substrate with different mechanisms and activation energies, a global exploitation of the results is impossible. Moreover, experimental results show that the rate of oxidation under oxygen is influenced after a short period by microstructural changes of the oxide layer. Therefore, only the experiments with water vapour are discussed by using two different approaches.

To model the oxidation behaviour, the kinetics curves are treated first according to the affine transformation method,[16] corresponding to an analytical treatment of these experimental results without any assumption about the reaction mechanisms. It consists in a transformation of an oxidation curve to another in calculating the ratio:

$$\left.\frac{t_{T,P(\mathrm{ref})}}{t_{T,P}}\right|_{\alpha} = \mathcal{A}$$

where $\mathcal{A}$ is the average coefficient of affinity, $t_{T,P(\mathrm{ref})}$ is the time for a specific advancement at a reference temperature or pressure, and $t_{T,P}$ is the time for an isothermal or isobaric curve for a specific advancement. At a given temperature and water vapour pressure, the time scale is then reduced with a constant ratio $\mathcal{A}$. The apparent activation energy and the pressure exponent are respectively found by plotting, the curves $\ln\mathcal{A} = f\left(\frac{1}{T}\right)$ and $\ln\mathcal{A} = f(\ln P)$. The plotted curves (Figs. 10 and 11) are affine versus the reduced time, whatever the reference curve, for the initial period of oxidation prior to the crystallisation of the glassy substrate. The interest of this approach is to ensure that there is one reaction mechanism in the temperature range, the water vapour pressure or the progress of the reaction under $\alpha < 0.6$. From the affine transformation results, the apparent activation energy and the pressure exponent are calculated (Figs. 12 and 13). The results are shown in the Table 5.

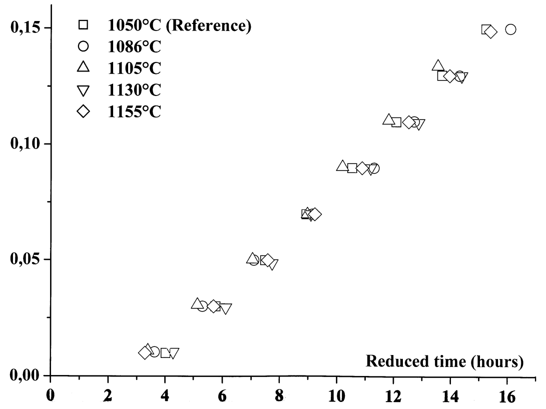


Fig. 10. Affine transformations: temperature influence; $P_{H_2O} = 2110$ Pa.

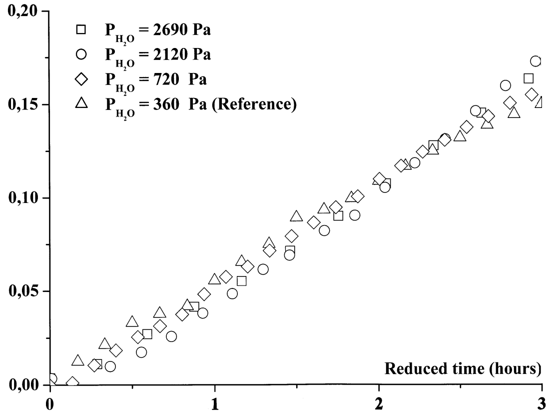


Fig. 11. Affine transformations: water vapour pressure influence; $T = 1150$°C.

The effect of water vapour pressure (H_2O/N_2 mixtures) on the oxidation's rate ($\mathcal{V}$) was determined by using the following equation $\mathcal{V} = f\left(P^{n}_{H_2O}\right)$.[16] As shown in Fig 13, the reaction rate follows a simple relationship with water vapour pressure: $\mathcal{V} = \left(P^{0.64}_{H_2O}\right)$ in the pressure range studied.

Another method was used to determine the oxidation mechanism. The sigmoidal shape of the curves and the microstructural observations show that the oxide scale does not form a gas-tight barrier for the migration of water vapour molecules to the internal interface (oxide scale/oxynitride glass). When the rate of the oxidation is controlled by the reaction of water vapour with the oxynitride glass, the degradation depends on the surface

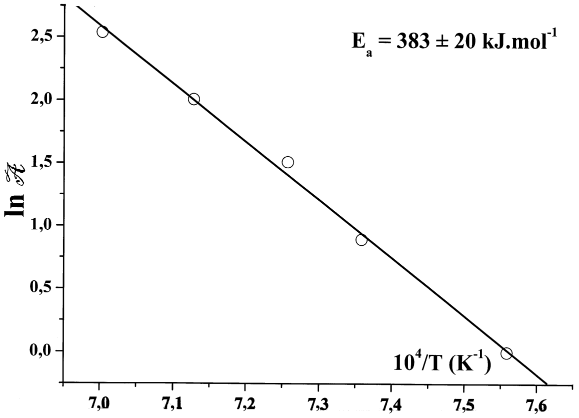


Fig. 12. Determination of the apparent activation energy by the affine method.

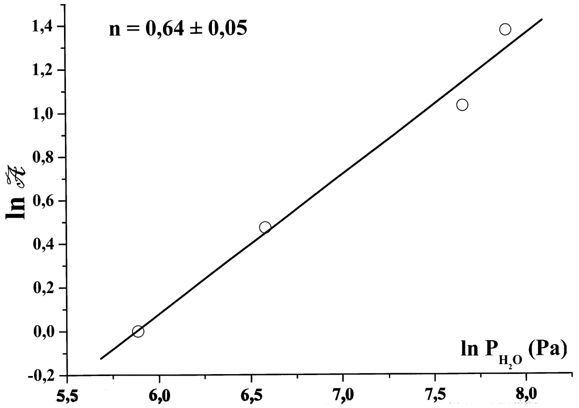


Fig. 13. Determination of the pressure exponent by the affine method.

Table 5
Different values of the apparent activation energy and pressure exponent

	Method of the limiting stage	Affine transformation
n	0,67±0.03	0,64±0.05
E_a(kJ mol^{-1})	409±30	383±20

area of the internal interface.[1] For a cubic symmetry, the kinetic equation is:

$$F(\alpha) = 1 - (1-\alpha)^{\frac{1}{3}} = \frac{2k.t}{a_0}$$

where α represents the fractional weight gain, a_0 the initial length of the cube edge, k the rate constant of the reaction ($k = k_0 \exp\left(-\frac{E_a}{RT}\right)$). By applying this equation to the isotherms or isobars, linear curves are obtained which verify the assumption of a reaction regime of oxidation at the oxide/oxynitride glass interface as the limiting step (Figs. 14 and 15). Then, the apparent activation energy can be determined (Fig. 16) by plotting $\ln k = \left(\frac{1}{T}\right)$ and is equal to 409 kJ mol^{-1}.

The rate constant for a fixed temperature changes with water vapour pressure. The pressure exponent obtained from the graph of the Fig. 17 ($\ln k = f(\ln P_{H_2O})$) is equal to 0.67 ($n = 0.67$).

In order to compare the results from the affine transformations method and the kinetic law, the different values are summarised in the Table 5.

The results given by the different approaches are consistent with the model, which confirms that the limiting step of the oxidation, for the temperature range (1050–1200°C) and pressure interval (360–2690 Pa) studied, is the reaction regime of water vapour with the oxynitride glass at the internal interface.

Because of the affinity of the oxidation reaction, the rate of the oxidation can be expressed by an equation, with separated variables, as follows:

$$\mathcal{V} = S(\alpha).B(P).C(T)$$

where, $S(\alpha)$ represents the reaction area for a cubic specimen and is a function of the fractional weight gain, $B(P)$ and $C(T)$ the influences of the temperature and the pressure respectively.

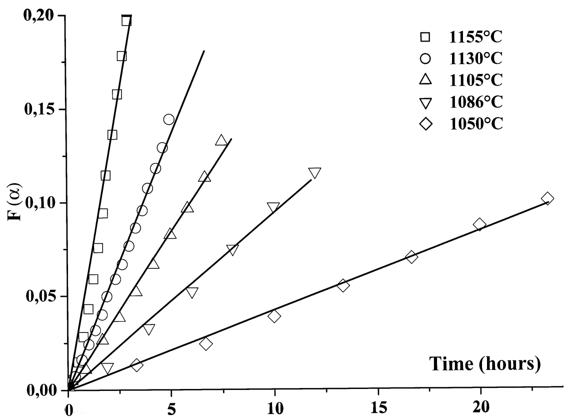


Fig. 14. $F(\alpha)$ for N_2 plus water vapour $P_{H_2O} = 2110$ Pa.

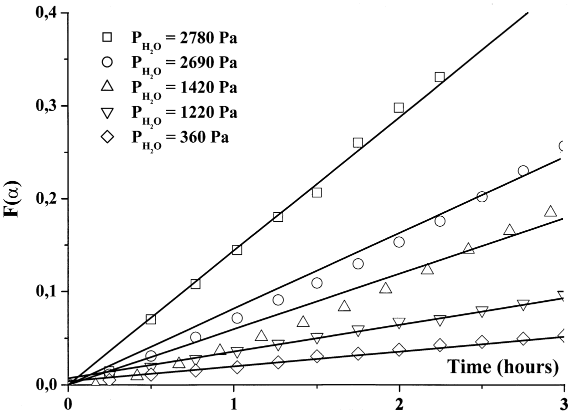


Fig. 15. $F(\alpha)$ for N_2 plus water vapour $T = 1150$°C.

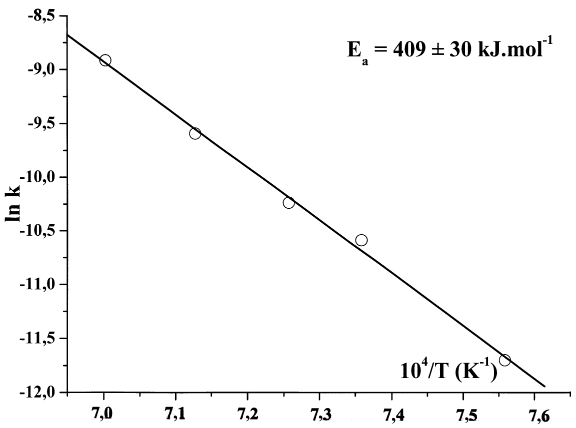


Fig. 16. Apparent activation energy under water vapour ($P_{H_2O} = 2110$ Pa).

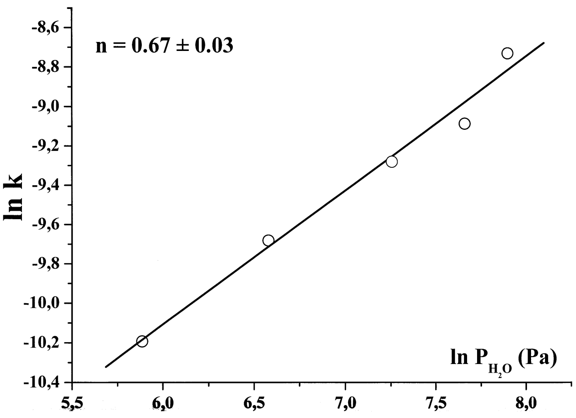


Fig. 17. Pressure exponent ($T = 1150$°C).

Thus, the kinetic equation for the oxidation rate by water vapour of the oxynitride glass is:

$$\mathcal{V} = K(1-\alpha)^{2/3}.P_{H_2O}{}^{0.65}.\exp\left(-\frac{398.10^3}{RT}\right)$$

5. Conclusion

The role of water vapour on the oxidation of a YSiAlON glass has been studied. In the temperature range 1050–1200°C, experiments carried out under O_2/N_2, N_2/H_2O or O_2/H_2O mixtures show that water vapour acts as an effective independent oxidant. At a low partial pressure ($P_{H_2O} = 2120$ Pa), water vapour in nitrogen gives a significantly higher degree of advancement of reaction than an atmosphere of pure dry oxygen. A mixture of oxygen plus water vapour produces an oxidation rate greater than the sum of the rates of the individual oxidants which points out synergy between the action of the two gases.

The exploitation of the results, according to different methods (affine transformation, kinetics law), shows that the slowest mechanism or the limiting step for the oxidation by water vapour of a YSiAlON glass is the reaction at the internal interface (oxide scale/oxynitride glass).

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