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Thermochemical stability of the Y_2O_3–SiO_2 system

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Abstract

A thermodynamic study was carried out in order to quantify the stability of yttrium silicates under different atmospheres (argon, air, moisture), and to predict their behaviour as an EBC. For this purpose, the partial pressures of gaseous species formed during the reactive vaporization in equilibrium with yttrium silicates were evaluated and compared to those over each oxide taken separately. The partial pressures of silicon and rare earth hydroxides at the equilibrium over rare earth silicates are lower than those over each single oxide. Thus yttrium silicates appear to be sufficiently stable to be promising materials to be used as environmental barrier coatings.

Keywords: Corrosion; Chemical properties; Silicate; Structural applications; Thermodynamics

1. Introduction

Because of their mechanical strength at high temperatures and their thermal shock resistance in combination with their low specific weight, thermostructural composites are promising materials for high temperature structural applications. However, in corrosive environments, protective coatings are required because of the degradation of the composite at high temperatures. The coating has to be resistant against corrosion and has to prevent oxygen and water diffusion inwards. Moreover, it must possess low volatility rate to prevent excessive surface recession. To provide adequate adhesion between the coating and the substrate and mechanical stability of the system, the coefficient of thermal expansion of both has to be as similar as possible.[1] Nowadays, yttrium silicates appear to have the potential to be used as a protective layer.[2,3] Several qualitative studies on their stability were made under a moist environment.[4,5] However, in a lot of studies, interaction with the tube furnace ($Al(OH)_3$ or $Si(OH)_4$) often occurs, that leads to aluminates or silicates formation. In this work, thermodynamic calculations are realized at high temperatures (between 1000 and 1400 °C) in order to quantify the stability of yttrium silicates under different atmospheres (argon, air and moisture).

2. Available thermodynamic data

Before any thermodynamic calculations, all phases with Y, Si, O or H, have to be identified and their Gibbs free energy of formation has to be known.

2.1. *The Y_2O_3–SiO_2 system*

In the Y_2O_3–SiO_2 system (Fig. 1), two compounds, Y_2SiO_5 and $Y_2Si_2O_7$ are found, with two (A and B) and four (α, β, γ and δ) polymorphs respectively. The first has a congruent melting, whereas the second has an incongruent one. The thermodynamic parameters of this system have already been assessed, by taking into account experimental results.[6,7] In this work, the more recent evaluation of the system Y_2O_3–SiO_2 established by Mao is considered.[8] Particularly, this assessment takes into account the update of the thermodynamic description of yttrium (recommended by SGTE). The considered phases are the following: liquid, Y_2O_3(R), Y_2O_3(H), B-Y_2SiO_5, α-$Y_2Si_2O_7$, β-$Y_2Si_2O_7$, γ-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$, SiO_2 (cristobalite), SiO_2 (quartz), SiO_2 (tridymite). It can be noticed that the A-Y_2SiO_5 is not considered in the calculations because of the lack of data. We keep

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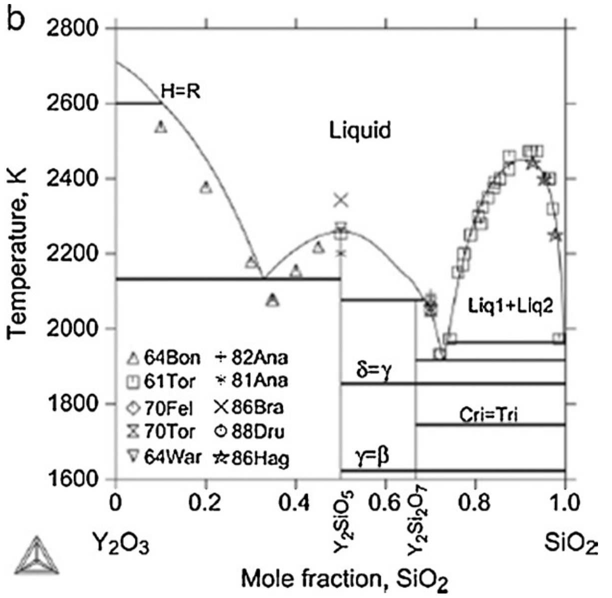

Fig. 1. Y_2O_3–SiO_2 phase diagram[7].

in mind that the apatite phase ($Y_4Si_3O_{12}$ or $Y_{4.67}(SiO_4)_3O$), which is formed by impurities is not introduced in the thermodynamic database. In fact, since this compound is stable from 1650 °C, its presence at lower temperatures (between 1000 °C and 1400 °C).[9]

2.2. *Other condensed phases*

The other condensed phases considered in the calculations are Si (s), Si_2H_6 (s), Y (s), YH_2 (s), YH_3 (s), H_2O (liq) and H_2O_2 (liq). Their thermodynamic data are given by the database COACH.[10]

2.3. *Gaseous species*

The thermodynamic data of oxide and non-oxide gaseous species are also available in the database COACH.[10] With regard to the vaporization of materials under a moist environment, hydroxide species are formed. For silicon hydroxides, their free energies of formation come from the database of Sandia National Laboratory[11] and the Gibbs free energy of yttrium hydroxides has recently been assessed.[12]

To sum up, the gaseous species taken into account in the calculations are the following: Ar, YO, YO_2, Y_2O, Y_2O_2, SiO, SiO_2, Si_2O_2, H_2, H, O_3, O_2, O, OH, HO_2, H_2O, H_2O_2, Si, Si_2, Si_3, SiH, SiH_2, SiH_3, SiH_4, Si_2H_6, YOOH, $Y(OH)_3$, $Si(OH)_4$ and $SiO(OH)_2$.

3. Thermodynamic calculations

GEMINI2 software is used to calculate the equilibrium state between a gaseous phase and a solid material. The method consists in minimizing the total Gibbs energy of the system under constant pressure conditions. The minimization method is based on a general optimization technique which has been applied to the chemical equilibrium problems.[13]

The equilibrium state is calculated in the case of a mixture of 1 mol of condensed phase with 1 mol of gaseous phase, at atmospheric pressure, in a closed system. The compositions of the initial gaseous phase are: (i) for argon: $n_{Ar} = 1$ mol; (ii) for air: $n_{Ar} = 0.8$ mol, $n_{O_2} = 0.2$ mol; (iii) for a moist environment: $n_{Ar} = 0.4$ mol, $n_{O_2} = 0.1$ mol, $n_{H_2O} = 0.5$ mol.

4. Results and discussion

4.1. *Comparison of the stability of SiO_2 and Y_2O_3*

The stabilities of Y_2O_3 and SiO_2 under argon, air and a moist environment have been quantified through the quantities of gaseous species at equilibrium predicted by a thermodynamic study. Fig. 2 shows the partial pressures of the gaseous species formed at the equilibrium over each oxide.

Under argon ($n_{Ar} = 1$ mol), the vaporization of Y_2O_3 and SiO_2 leads to the formation of gaseous YO, O and, SiO, O, O_2 and SiO_2 respectively. Their partial pressures at the equilibrium over each oxide increase with the temperature. The partial pressures of gaseous species in equilibrium over Y_2O_3 are lower than those over SiO_2 (Fig. 2a). Thus, Y_2O_3 should be more stable than SiO_2 under argon.

Under air ($n_{Ar} = 0.8$ mol, $n_{O_2} = 0.2$ mol), the volatility of Y_2O_3 and SiO_2 leads to the formation of gaseous YO_2 and, SiO_2 and SiO respectively. Their partial pressures in equilibrium with each oxide increase with the temperature. However in this case, the partial pressures of YO_2 at the equilibrium over Y_2O_3 are higher than those of SiO_2 or SiO over SiO_2 (Fig. 2b). This means that Y_2O_3 is less stable than SiO_2 under air.

Under a moist environment ($n_{Ar} = 0.4$ mol, $n_{O_2} = 0.1$ mol, $n_{H_2O} = 0.5$ mol), a reactive vaporization of Y_2O_3 and SiO_2 with water vapour occurs and leads to the formation of gaseous YOOH, $Y(OH)_3$, YO_2 and, $Si(OH)_4$, $SiO(OH)_2$, SiO_2 and SiO respectively (Fig. 2c). When the temperature increases, the partial pressures of YOOH at the equilibrium over Y_2O_3 decrease whereas those of $Y(OH)_3$ increase. In fact, this is in agreement with experiments, since the vaporization of Y_2O_3 under a moist environment occurs as two mechanisms. At low temperatures (<1200 °C), YOOH is the predominant gaseous species formed, whereas at higher temperatures, $Y(OH)_3$ becomes the major one.[12] The partial pressures of the other gaseous species increase with the temperature. By comparing the stabilities of Y_2O_3 and SiO_2, it can be noticed that the partial pressures (dash line) at the equilibrium over Y_2O_3 are lower than those over SiO_2 (dotted line), for temperatures below 1320 °C. Consequently, for these temperatures, Y_2O_3 is more stable than SiO_2. At higher temperatures, on the contrary, SiO_2 is the most stable under a moist environment.

4.2. *Stability of the different phases in the Y_2O_3–SiO_2 system*

In order to verify the interest of a such material as an EBC, its thermal stability has to be compared to SiO_2, which is formed by oxidation of silicon based ceramics. For this purpose, partial pressures of gaseous species in equilibrium over a material have

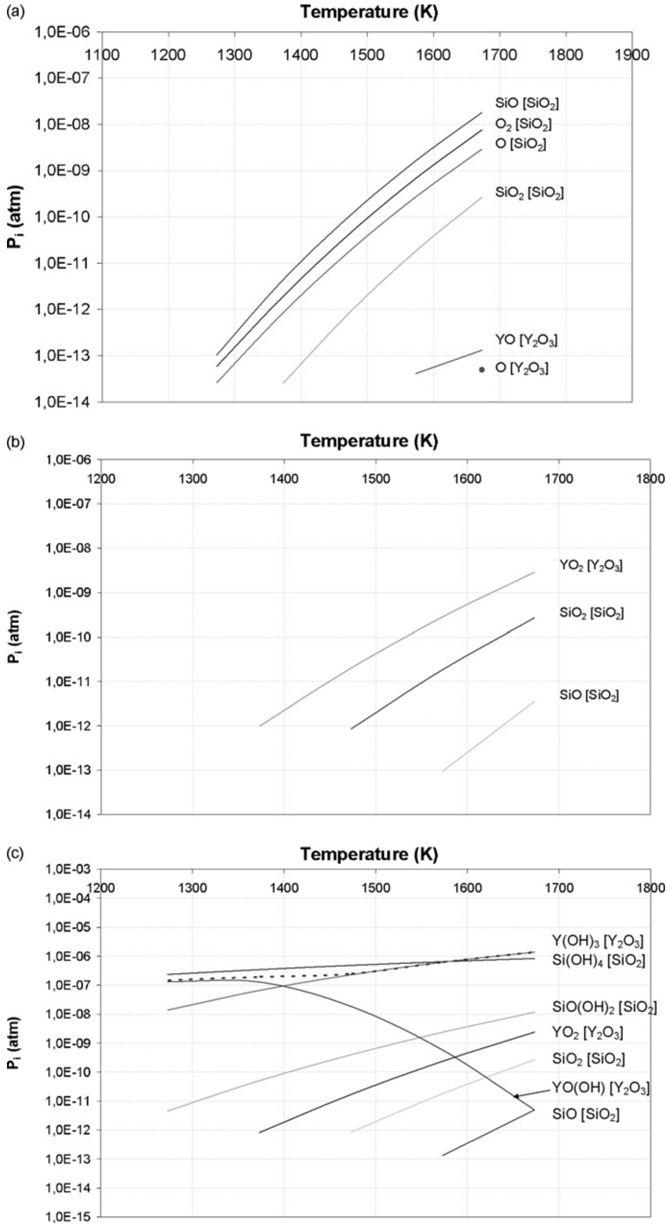

Fig. 2. Stability of Y_2O_3 and SiO_2 revealed through the variation of partial pressures of different gaseous species formed under (a) argon, (b) air ($n_{Ar} = 0.8$ mol, $n_{O_2} = 0.2$ mol), (c) a moist environment ($n_{Ar} = 0.4$ mol, $n_{O_2} = 0.1$ mol and $n_{H_2O} = 0.5$ mol).

been evaluated by running thermodynamic calculations using parameters corresponding to experimental conditions (temperature, total pressure, quantity of matter). The thermal stability of a material increases when partial pressures are lower than those in equilibrium over SiO_2. This is the result of the strong solid state bonding between yttrium and silicon oxides.

The materials considered correspond to the different phases of the system Y_2O_3–SiO_2.

4.2.1. Under argon

Under argon ($n_{Ar} = 1$ mol), the volatilisation of phases in the Y_2O_3–SiO_2 system leads to the formation of gaseous YO_2, SiO, O, O_2 and SiO_2. It can be mentioned that the Y-based gaseous species are different from those at the equilibrium above Y_2O_3. Actually, YO_2 is the predominant species under dry air. The small partial pressure of O or O_2 in the system at the equilibrium can explain its presence under argon. Moreover, the presence of gaseous O or O_2 can increase the partial pressures of gaseous Y-bearing species, since Y_2O_3 is less stable under air than under argon. Besides, if phases of Y_2O_3–SiO_2 system are introduced as an EBC, the interface coating/Si-based ceramics may be oxidized by O or O_2 coming from the decomposition of Y_2O_3 and SiO_2.

Fig. 3 shows the values of partial pressures in equilibrium with $Y_2O_3 + Y_2SiO_5$, Y_2SiO_5, $Y_2SiO_5 + Y_2Si_2O_7$, $Y_2Si_2O_7$ and $Y_2Si_2O_7 + SiO_2$ under argon.

For the systems $Y_2O_3 + Y_2SiO_5$ (Fig. 3a) and Y_2SiO_5 (Fig. 3b), partial pressures of SiO, O, O_2 and SiO_2 at the equilibrium over $Y_2O_3 + Y_2SiO_5$ or Y_2SiO_5, are lowered by at least two magnitude orders with regard to those over SiO_2. Consequently, these phases show a real interest since an increased thermal stability is highlighted compared to silica. However, it can be noticed the respective rise of the quantity of residual Y_2O_3 in function of temperature, because of the higher stability of Y_2O_3 compared to SiO_2. Now, if Y_2SiO_5 coated a silicon based ceramics, Y_2O_3 would be formed due to the favored volatilisation of SiO_2 under $Si(OH)_4$ form. So an increase of the coefficient of thermal expansion would be occurred, and the coating and the Si-based ceramics should not be compatible. Therefore, cracks and/or decohesion of the coating can be created.

For the systems $Y_2SiO_5 + Y_2Si_2O_7$ (Fig. 3c) and $Y_2Si_2O_7$ (Fig. 3d), partial pressures of SiO, O, O_2 and SiO_2 at the equilibrium over $Y_2SiO_5 + Y_2Si_2O_7$ or $Y_2Si_2O_7$, are lowered by at least one magnitude order with regard to those over SiO_2. Consequently, as previously, these phases are interesting since an increased thermal stability is observed compared to silica. Moreover, it can be noticed the rise of the quantity of residual Y_2SiO_5 in function of temperature, because of again the higher stability of Y_2O_3. Contrary to the previous case, the formation of Y_2SiO_5 is not catastrophic for the coating, since a significative modification of CTE is not induced. Thus its CTE remains similar to those of $Y_2Si_2O_7$ and Si-based ceramics.

For the system $Y_2Si_2O_7 + SiO_2$ (Fig. 3e), partial pressures of SiO, O, O_2 and SiO_2 at the equilibrium over $Y_2Si_2O_7 + SiO_2$, are similar to those above SiO_2. So the stability of this system follows the silica's one. In this case, the interest of use this material as an EBC is extremely limited.

4.2.2. Under air

Under air ($n_{Ar} = 0.8$ mol, $n_{O_2} = 0.2$ mol), the vaporization of phases in the system Y_2O_3–SiO_2 leads to the formation of gaseous YO_2, SiO and SiO_2.

Fig. 4 shows the values of the partial pressures in equilibrium with $Y_2O_3 + Y_2SiO_5$, Y_2SiO_5, $Y_2SiO_5 + Y_2Si_2O_7$, $Y_2Si_2O_7$ and $Y_2Si_2O_7 + SiO_2$ under air.

For the domains $Y_2Si_2O_7$ (Fig. 4a), $Y_2SiO_5 + Y_2Si_2O_7$ (Fig. 4b) and Y_2SiO_5 (Fig. 4c), the partial pressures of YO_2, SiO_2 and SiO at the equilibrium over these systems are lowered by at least one magnitude order with regard to those over Y_2O_3 and SiO_2. Consequently, these phases are interesting since an

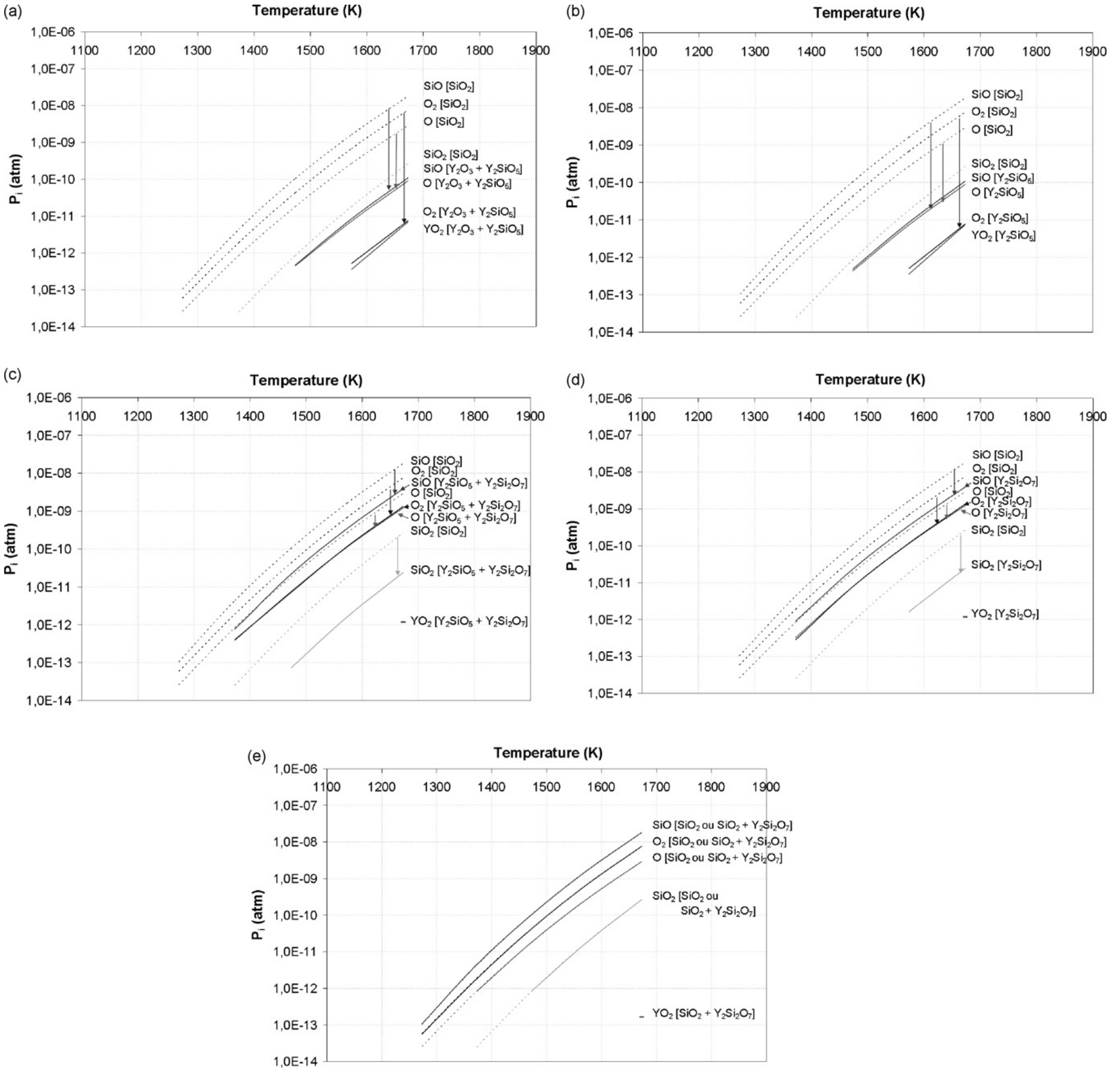

Fig. 3. Stability of (a) $Y_2O_3 + Y_2SiO_5$, (b) Y_2SiO_5, (c) $Y_2SiO_5 + Y_2Si_2O_7$, (d) $Y_2Si_2O_7$, (e) $Y_2Si_2O_7 + SiO_2$ revealed through the variation of partial pressures of different gaseous species formed under argon.

increased thermal stability is observed compared to that of single oxides. For $Y_2Si_2O_7$ (Fig. 4a), it can be mentioned that the ratios of the partial pressures between YO_2 and SiO_2 are similar to the stoichiometric ratio between Y and Si. This feature presents an interest since no new solid phases would be formed. For the domains $Y_2SiO_5 + Y_2Si_2O_7$ (Fig. 4b) and Y_2SiO_5 (Fig. 4c), the partial pressures of YO_2, SiO_2 and SiO are the same over these two systems. In fact, as YO_2 has a partial pressure higher than the other gaseous species, a preferential vaporization of Y-based compound occurs and leads to the formation of $Y_2Si_2O_7$. The formation of this compound is not catastrophic for the coating, since Y_2SiO_5, $Y_2Si_2O_7$ and Si-based ceramics have similar coefficient of thermal expansion.

For the system $Y_2O_3 + Y_2SiO_5$ (Fig. 4d), Y_2O_3 is less stable than SiO_2 and yttrium silicates under air. Consequently, partial pressures of YO_2 at the equilibrium above $Y_2O_3 + Y_2SiO_5$ are fixed by Y_2O_3, and are higher than those over SiO_2. For the domain $Y_2Si_2O_7 + SiO_2$ (Fig. 4e), SiO_2 is less stable than $Y_2Si_2O_7$. Therefore partial pressures of SiO_2 and SiO are fixed by SiO_2. These two domains are not interesting for an application as an EBC, since their stability is worse or similar to SiO_2.

4.2.3. Under a moist environment ($P_{H_2O} = 50\,kPa$, P_{atm})

Under a moist environment ($n_{Ar} = 0.4$ mol, $n_{O_2} = 0.1$ mol, $n_{H_2O} = 0.5$ mol), the vaporization of phases in the system

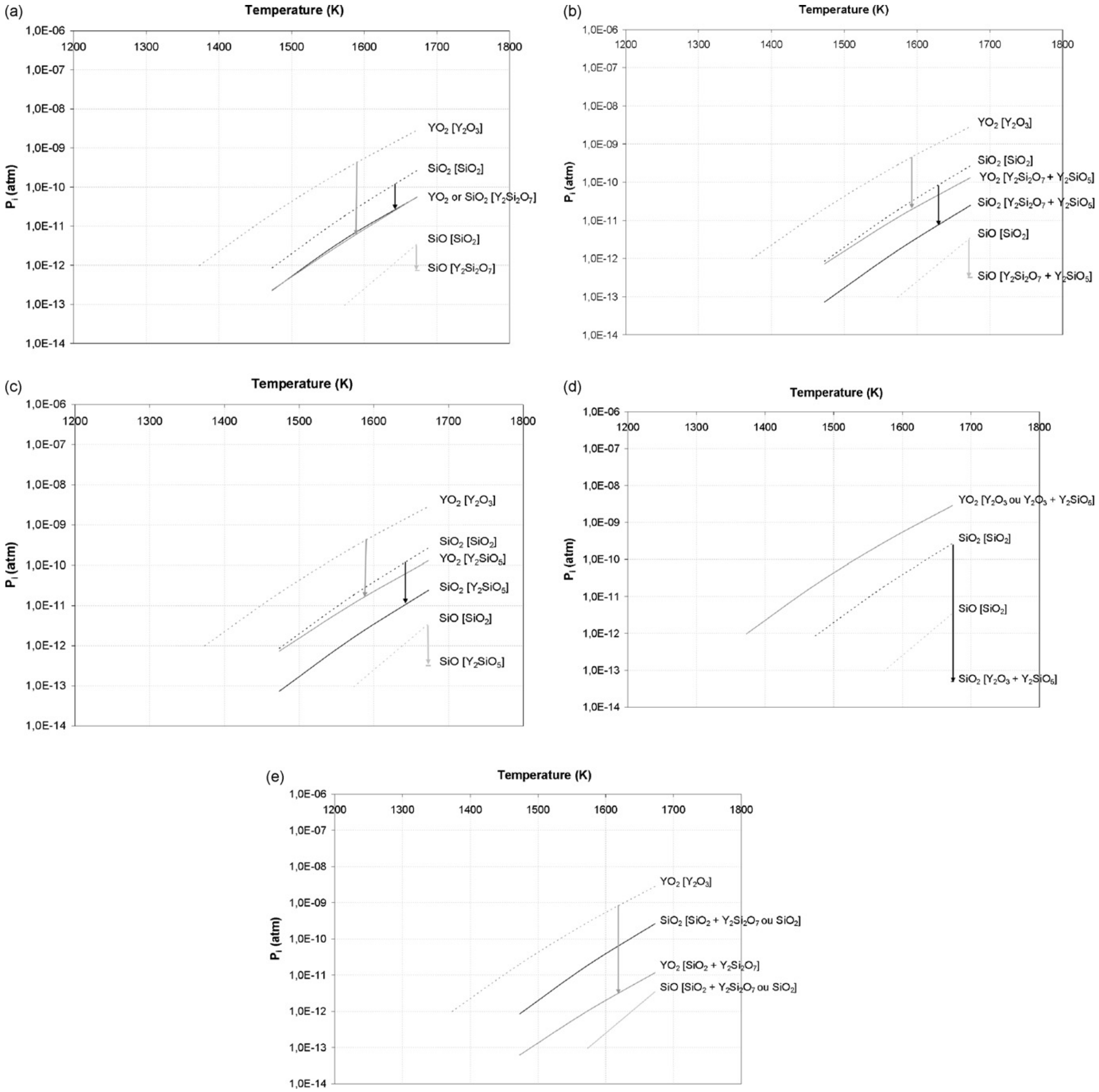

Fig. 4. Stability of (a) $Y_2Si_2O_7$, (b) $Y_2SiO_5 + Y_2Si_2O_7$, (c) Y_2SiO_5, (d) $Y_2O_3 + Y_2SiO_5$ and (e) $Y_2Si_2O_7 + SiO_2$ revealed through the variation of partial pressures of different gaseous species formed under air.

Y_2O_3–SiO_2 leads to the formation of gaseous YOOH, $Y(OH)_3$, YO_2, $Si(OH)_4$, $SiO(OH)_2$, SiO_2 and SiO.

Under a moist environment, the tendencies are similar to those under air. As previously, partial pressures of YOOH, $Y(OH)_3$ and YO_2 at the equilibrium over $Y_2O_3 + Y_2SiO_5$ are fixed by those expected over Y_2O_3, and higher than those above SiO_2 at high temperatures (>1300 °C). Moreover, for the domain $Y_2Si_2O_7 + SiO_2$, partial pressures of $Si(OH)_4$, $SiO(OH)_2$, SiO_2 and SiO are fixed by those expected over SiO_2. These two domains are not interesting for an application as an EBC, since their stability is not enhanced with respect to that of SiO_2.

Fig. 5 shows the values of partial pressures at the equilibrium above Y_2SiO_5, $Y_2SiO_5 + Y_2Si_2O_7$ and $Y_2Si_2O_7$ under a moist environment.

For the domains Y_2SiO_5 (Fig. 5a), $Y_2SiO_5 + Y_2Si_2O_7$ (Fig. 5b) and $Y_2Si_2O_7$ (Fig. 5c), the partial pressures of YOOH, $Y(OH)_3$, YO_2, $Si(OH)_4$, $SiO(OH)_2$, SiO_2 and SiO at the equilibrium over these systems are lowered by at least one magnitude order with regard to those over Y_2O_3 and SiO_2. Consequently,

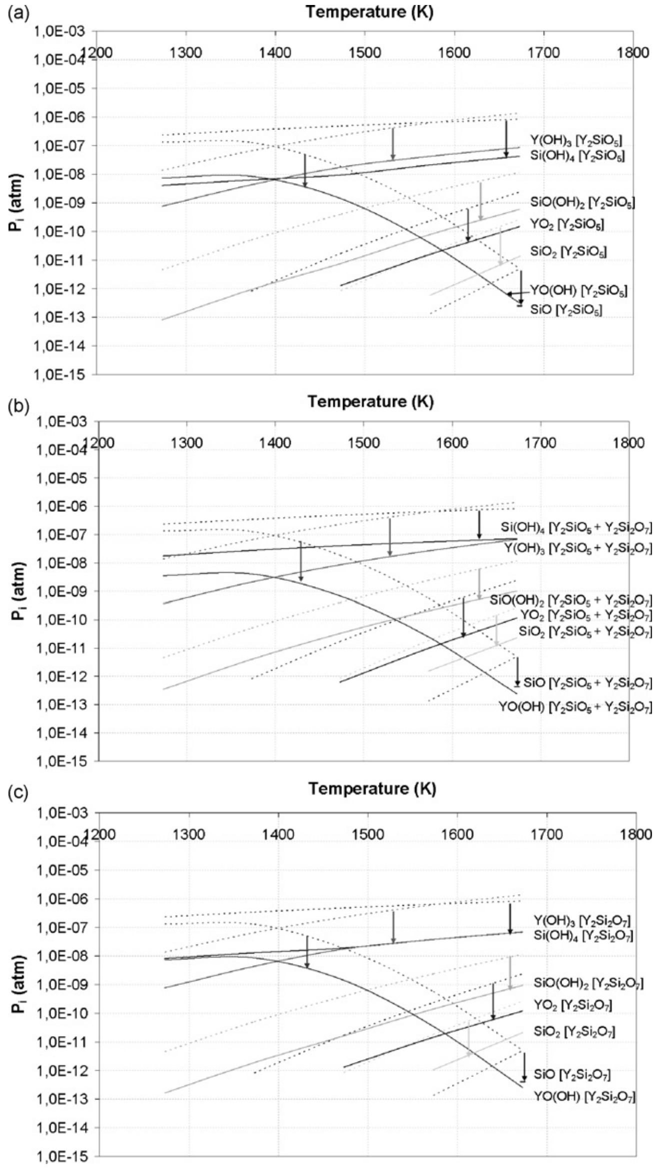

Fig. 5. Stability of (a) Y_2SiO_5, (b) $Y_2SiO_5 + Y_2Si_2O_7$, (c) $Y_2Si_2O_7$ revealed through the variation of partial pressures of different gaseous species formed under a moist environment ($n_{Ar} = 0.4$ mol, $n_{O_2} = 0.1$ mol and $n_{H_2O} = 0.5$ mol).

the increase of the observed thermal stability shows the interest of these phases compared to silica. For the domains Y_2SiO_5 (Fig. 5a) and $Y_2Si_2O_7$ (Fig. 5c), it can be mentioned that the ratios of the partial pressures between yttrium bearing species and silicon bearing species are similar to the stoechiometric ratio between Y and Si. Consequently, between 1000 °C and 1400 °C, yttrium silicates are stable compounds in moist environments (at atmospheric pressure with a water vapour pressure of 50 kPa).

5. Conclusions

Thermodynamic calculations have been realized in order to quantify the stability of the Y_2O_3–SiO_2 system in different atmospheres (argon, air, moisture). It appears that yttrium silicates (Y_2SiO_5 and $Y_2Si_2O_7$) are candidate materials for use as an EBC. Actually, they vaporize less than each single oxide (SiO_2 or Y_2O_3). Their stability is related to the strong solid state bonding between yttrium and silicon oxides. Future works consist in realize corrosion tests on these materials as EBC in order to confirm these calculations.

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