Journal of the European Ceramic Society 22 (2002) 2561–2570

www.elsevier.com/locate/jeurceramsoc

The reaction rate at Si_3N_4/steel interfaces as a function of sintering aids

F.J. Oliveira*, R.F. Silva, J.M. Vieira

CICECO—Department of Ceramics & Glass Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

Received 30 October 2001; received in revised form 20 January 2002; accepted 20 February 2002

Abstract

The solid-state interaction between Si_3N_4 and steels can be appraised with high temperature (1000–1300 °C) static diffusion pairs. The reaction zone thickness of the ceramic side of these couples distinguishes the chemical resistance of different Si_3N_4 based compositions to the attack by iron alloys. A careful selection of the amount and composition of sintering aids for Si_3N_4 sintering may contribute to increase the chemical/diffusive wear resistance during cutting of Fe-based alloys. The reaction interfaces in diffusion couples were analysed with SEM/EDS and optical microscopy and the attack path within the ceramic was investigated by TEM on reaction interfaces of selected samples. Parabolic reaction rate constants at 1423 K vary between 7×10^{-17} m^2 s^{-1} for the least reactive system and 486×10^{-17} m^2 s^{-1} for the most reactive ceramic. The former is a Y_2O_3–SiO_2 containing Si_3N_4 ceramic while the latter is from the less refractory AlN–CeO_2 additive system. TEM analysis proved that intergranular amorphous phases are the preferential path for Fe penetration. A compilation of published kinetic data in Si_3N_4/steel interaction is thoroughly compared with the present experimental results.

Keywords: Cutting tools; Diffusion; Interfaces; Si_3N_4; Steel

---

1. Introduction

From the pioneer work of Kramer et al.[1] on the chemical stability of ceramic cutting tools in the machining of Fe-based alloys, it is expected that reinforcement phases of high chemical stability contributed to increase the chemical/diffusive wear resistance during cutting. Compounds such as HfN, BN, TiN, Al_2O_3 having a large negative Gibbs free energy of formation, fulfil these thermochemical requirements. Buljan and Wayne[2] showed that simultaneous additions of Al_2O_3 and of HfC increase the chemical resistance of silicon nitride composites to attack by Fe alloys in diffusion couple experiments. The characterisation of the interaction zones on the steel and ceramic side of the diffusion couples yields information regarding both the reaction kinetics and the chemical composition.

In a previous study aiming the production of composites[3] it was demonstrated that changes in the matrix composition due to partial dissolution of the fine particles of the reinforcement phase in the sintering liquid could induce differences of behaviour in the chemical attack by Fe alloys[4] and in the machining of steels.[5] Vleugels and co-workers assessed the effect of composition in the Si–Al–O–N system on tools used in the machining of steels.[6] Differences in the chemical composition of the sintering additives in Si_3N_4 ceramics are not yet fully clarified, although it is clear that larger amounts of sintering aids of the same additive system correspond to higher reaction rates as it happens in the (Fe, Ni)–SiC system.[7]

In this work, the effect of the composition of several matrices and of the corresponding Si_3N_4 composites on the reaction kinetics is investigated. Low carbon content steel, moderately reactive with respect to other alloys studied,[8] was selected for the diffusion couples with the different ceramics. The composition of the alloy greatly affects the reaction kinetics and different approaches have been used to model them, although for different materials: Si_3N_4[9] and SiAlONs.[10] The results are compared with compiled data published for systems containing different Si_3N_4 ceramics and for systems containing different types of alloys.

---

* Corresponding author. Tel.: +351-234-370-266; fax. +351-234-425-300.

E-mail address: filipe@cv.ua.pt (F.J. Oliveira).

0955-2219/02/$ - see front matter
PII: S0955-2219(02)00117-6

2. Experimental details

In this work, distinct Si_3N_4 based ceramics, (Table 1), were tested in diffusion couples (1000–1300 °C, 5–7 MPa, Ar atmosphere) against a low carbon steel, DIN St37K, the experimental details having been given in other publication.[4] Different amounts of CeO_2 (0.5 and 5 wt.%), AlN (3.3 and 6 wt.%), Al_2O_3 (7.5 and 12.5 wt.%), Y_2O_3 and SiO_2 (8 + 5 wt.%) were used as densification aids for Si_3N_4 hot-pressing (1500–1700 °C, 30 MPa), Table 1. Monolithic Si_3N_4 materials and homologous matrices reinforced with TiN, BN, HfN or Al_2O_3 were compared. Polished cross sections of the reaction interface were analysed with SEM/EDS (Hitachi S4100/RONTEC) and WDS-EPMA (Cameca). A TEM sample of a cross section of a M1-DIN x20Cr13 chromium containing steel diffusion couple was prepared by the usual means of grinding, drilling (GATAN), polishing (Tripod Polisher, South Bay Technologies) and precision ionic thinning and polishing (Bal-Tec). The attack path within the ceramic was investigated by TEM/EDS (300 kV Hitachi H9000-NA/RONTEC) on reaction interfaces.

3. Results and discussion

3.1. Reaction of unreinforced Si_3N_4 matrices

The microstructures of matrices M1 and M4 obtained by SEM are given in Fig. 1. They are both fully transformed from α-Si_3N_4 to β-Si_3N_4. The grain size difference and the distribution of the intergranular phases should be noted. The grain junctions contain the compound $CeSiO_2N$ in the case of M1 and the compound $Y_2Si_2O_7$ for M4, as identified by X-ray diffraction. In the case of the M2 Si_3N_4 ceramic only α-Si_3N_4 and β-Si_3N_4 could be detected. For M3, however, X-ray diffraction identified only β-SiAlON with a small value of z, the substitution degree in the general formula of the β-SiAlONs, $Si_{6-z}Al_zO_zN_{8-z}$. Accompanying the glassy phase, other minor compounds containing nitrogen can form, due to the small composition range of the compatibility triangles.[11] Fig. 2 presents the results of the reaction kinetics with steel at 1150 °C for the tested set of matrices. The y-axis values correspond to the square of the thickness of the interaction zone on the ceramic side, the Reaction Zone.[9] The large difference on the decomposition reaction of matrix M4 in the diffusion couple with the steel DIN St37K relative to the other ceramics is due to its phase composition and to its microstructure imposed by the different system of sintering additives. The nitrogen containing phases decompose in contact with steels at high temperature, precipitating oxides as SiO_2 and Al_2O_3, as in the case of M3 where the amount of CeO_2 is too low to be detected in the reaction products, or also silicates and Ce containing phases in the case of M1 and M2. Other simpler oxides such as mullite and oxides of aluminium and silicon are reaction products present in minor amounts.[12]

With respect to the results of the reaction of matrices M2 and M3, Laoui et al.[13] observed in a comparable additive system, that when partial substitution of Si–N bonds by Al–O occurs, the larger the value of z, the faster is the decomposition speed in contact with a carbon

Table 1
Composition and properties of the Si_3N_4 matrices and composites tested in the diffusion couples experiments

Ceramic	Matrix composition (wt.%)						Reinforcement phase	f	Density (g cm^{-3})	Hardness (GPa)	Toughness (MPa m$^{1/2}$)
	Si_3N_4[a]	CeO_2[b]	AlN[c]	Al_2O_3[d]	Y_2O_3[e]	SiO_2[f]					
M1	89	5	6	–	–	–	–	–	3.27	17.2	3.4
M1C3TN	89	5	6	–	–	–	TiN[h]	0.3	3.90	14.6	5.8
M1C3BN	89	5	6	–	–	–	BN[i]	0.3	2.97	4.5	3.7
M1C3HN	89	5	6	–	–	–	HfN[j]	0.3	6.14	15.6	6.2
M2	88.7	0.5	3.3	7.5	–	–	–	–	3.17	18.2	3.1
M2C3AL	88.7	0.5	3.3	7.5	–	–	$Al_2O_{3\ (pl)}$[g]	0.3	3.38	17.2	4.0
M3	87.5	–	–	12.5	–	–	–	–	3.16	17.5	3.1
M3C3AL	87.5	–	–	12.5	–	–	$Al_2O_{3\ (pl)}$[g]	0.3	3.37	19.1	4.6
M4	87.0	–	–	–	8.0	5.0	–	–	3.24	14.9	4.8

f, volume fraction of reinforcement.
[a] M11, HCStarck.
[b] Fluka Puriss.
[c] Grade C HC Starck.
[d] Al16SG, Alcoa.
[e] Grade C, HC Starck.
[f] Precipitated SiO_2, BDH.
[g] Platelets grade T2, Elf Atochem.
[h] Ceramyg.
[i] A01, HC Starck.
[j] Mattey Johnson, Alfa.

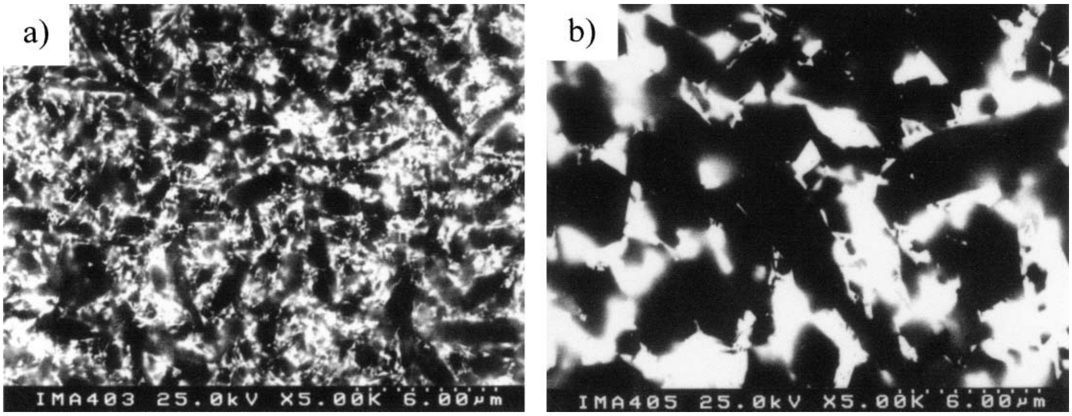

Fig. 1. Micrographs of ceramics M1 and M4, obtained using backscattered electrons in the SEM: (a) M1 (1650 °C/60 min) and (b) M4 (1750 °C/90 min). The dark grains are from Si_3N_4 whereas the bright intergranular phase in (a) and (b) respectively contains Ce and Y.

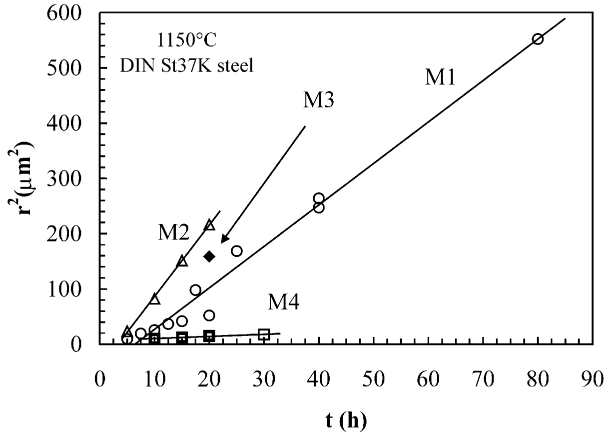

Fig. 2. Comparison of the reaction rates at 1150 °C for the diffusion couples between steel DIN St37K and the unreinforced ceramics M1, M2, M3 and M4.

steel (DIN x50 Ni Cr 13). This tendency is also observed in the reaction kinetics of the matrices M1 and M2, while the matrix M3 has increased resistance relative to the matrix M1. Some of the alumina and silica from the oxidation of the Si_3N_4 powders formed X-SiAlON during the densification matrix M3 or during cooling after hot pressing. The existence of this minor phase in the microstructure, with chemical resistance increased regarding Si_3N_4, β-SiAlON and the vitreous intergranular phase, decreases the speed of the ceramic decomposition comparatively to M2, as already pointed out in a comparable system.[14]

The intergranular phase in the M4 system, unlike the other matrix compositions consists mainly of a very stable silicate that protects the Si_3N_4 grains from attack by the iron alloys. Since most of the sintering aids are forming the silicate, the glassy phase amount is reduced, so even if M4 is the material with the largest amount of additives, (Table 1), it is also the less reactive. Fig. 3 shows the microstructure of the reaction zone of a ceramic M4-DIN St37K steel diffusion couple. The chemical microanalysis by SEM/EDS of the precipitates in the reaction zone indicates the presence of Y, Si and also Al, besides a little amount of oxygen. Although not added as a sintering aid, the Al is present due to contamination from the alumina milling media used during preparation of the Si_3N_4–additives mixture. The reaction products may consist of a mixed silicate or of a (Al,Y)–Si intermetallic material with alumina particles inside, since the oxygen signal is not as high as it would be if the particles in the micrograph of Fig. 3(a) were oxides. The glassy phase of the M4 matrix material contains some alumina that prevents all the Y and Si oxides to fully react forming the silicate. Nevertheless, the reaction rate of matrix M4 is between 15 and 25 times lower than the other matrices, Fig. 2. It should be pointed out that, in glasses of the Y-SiAlON system, an increase in temperature of approximately 80 °C decreases the viscosity of the molten glass by three orders of magnitude.[15] The differences of the ceramic M4 relative to the other matrices were revealed already during processing. It was experimentally observed that for the same densification rate to be obtained at homologous relative densities, a temperature higher by 100–150 °C is necessary in the M4 sintering additive system. These results indicate that, with an adequate selection of the additive system and processing conditions, the kinetics of reaction between silicon nitride ceramics and iron alloys can be controlled, either by producing higher chemical stability phases or by producing high viscosity vitreous phases.

The presence of a continuous layer of stable phases protecting the silicon nitride grains is, accordingly to the experimental results, the method yielding the highest chemical resistance.

3.2. *Reaction of Si_3N_4 composites*

Similarly to the high stability phases formed by the reaction between Y_2O_3 and SiO_2 in ceramic M4, composites can be made to improve the chemical resistance

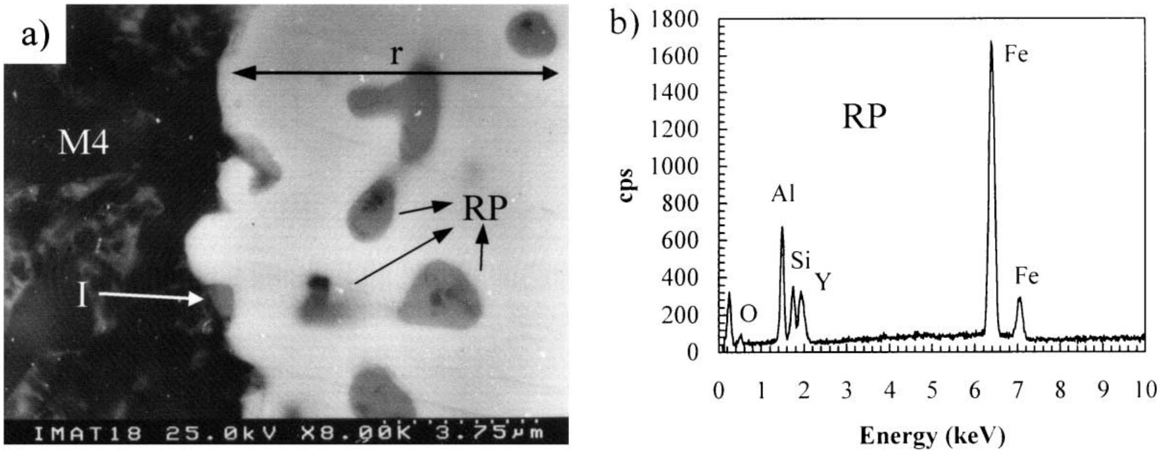

Fig. 3. (a) SEM photomicrograph of the microstructure of the reaction zone of a M4-DIN St37K steel diffusion couple (1185 °C, 80 h); (b) EDS spectrum of the reaction products (RP) in the reaction zone. *r*—thickness of the reaction zone; *I*—reaction interface.

of the Si_3N_4 based materials. If the reinforcement phase does not react, it stays in the reaction zone, forming a composite with the metallic matrix. The attack of the ceramic by Fe is conditioned on the presence of the reinforcement particles, resulting an attack interface with high roughness. The reaction of the Si_3N_4 composites with carbon steel DIN St37K at 1150 °C depends on the nature of the reinforcement phase but also on the composition of the matrix. The reaction constants, *Kr*, of the kinetics equation, $r^2 = 2Kr\ t$, of the matrices and composites are plotted in Fig. 4. For the composites with matrix M1 the reactivity is at least equal to or larger than that of the un-reinforced matrix, (Fig. 4). Alternatively, for the diffusion couple with the alumina platelets there is an increase of the chemical resistance of the composite in comparison to the un-reinforced matrix, (Fig. 4). The presence of the alumina platelets decreases the parabolic rate constants relative to the un-reinforced matrix.

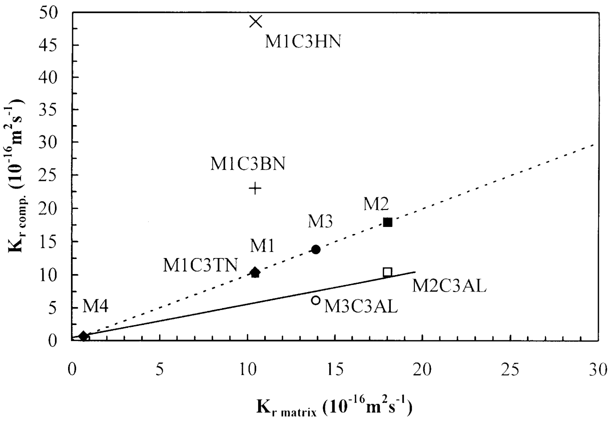

Fig. 4. Reaction constants, *Kr*, of the composites in comparison to the reaction constants of the respective matrices. Diffusion couples with the steel DIN St37K at 1150 °C (trace-line corresponds to the identity *Kr* comp. = *Kr* matrix).

Relative to matrix M1, particles of TiN are thus considered essentially inert from the standpoint of the reactivity of the diffusion couples of the M1C3TN composite with the steel, the ratio between the reactivity of the matrix and of the composite being nearly 1, (Fig. 4). The reaction rate of the composite M1C3BN occupies an intermediate position, being more reactive than the matrix M1 or the composite M1C3TN, but much less than M1C3HN, with particles of HfN, (Fig. 4). ZrO_2 is always associated with HfO_2,[16] so it is possible that somehow the catalytic effect of ZrO_2 on the oxidation kinetics of Si_3N_4[17] also contributes for the fastest reaction rates observed in the diffusion pairs. Fine BN may dissolve in the sintering liquid, increasing the liquid amount, and thus, the reaction rates.[18] The composites of Si_3N_4–Al_2O_3(pl), M2C3AL and M3C3AL are more resistant to attack by Fe than their respective matrices. The inert tabular Al_2O_3 reinforcing particles exert a net improvement in the chemical resistance of the ceramic. In the case of the composite M3C3AL, the reaction of fine alumina from the platelets during sintering increases the amount of X-SiAlON relative to the unreinforced matrix.

Unlike the silicates in ceramic M4, the high stability particles added do not protect their matrices and may even increase the reactivity toward attack by Fe, due to some dissolution of the dispersed phase or reaction of minor components. It can be concluded by comparing the results of the ceramic reaction kinetics that, for a given Fe alloy, it is the composition of the intergranular phase of the matrix of the composite more than the dispersed second phase that determines the speed of attack of the Si_3N_4 by the alloy. More important than the amount of sintering additive is the thermochemical stability of the reaction products forming a continuous and protective layer around Si_3N_4 grains during the densification.

3.3. Composition at interfaces

The decomposition of a dense silicon nitride ceramic in contact with iron alloys at high temperature involves more reactions than the well-known decomposition of Si_3N_4 itself. Previous TEM investigations of M1-pure Fe diffusion couples[12] has shown that the sintering aids react in different ways, precipitating mixed oxides but also metallic Ce. This indicated that both oxidising and reducing reactions accompany the decomposition of Si_3N_4 as a consequence of interfacial thermodynamic equilibrium imposed by the mass and electro-chemical balances. In the TEM micrograph in Fig. 5(a) one alumina marker is visible as also are the reaction products in the reaction zone of the diffusion couple. None of the elements from the sintering aids is dissolved in the metallic matrix of the reaction zone, [Fig. 6(i)]. The chemical analysis by EDS of non-metal particles shows that the reaction products are mixed oxides containing Si, Al and Ce from the decomposition of the ceramic and Fe and Cr from the metal, [Fig. 6(ii)]. These large and more abundant particles in the reaction zone, rich in Ce, Al and oxygen, are probably $CeAlO_3$ oxide, a transient phase that appeared in the hot pressing of Si_3N_4 ceramics of the CeO_2-AlN additive system.[19] Smaller particles, [Fig. 6(iii)], in the reaction zone do not contain any Ce, being most probably silica or mullite. These compounds are neither homogeneous in their distribution, composition, size or type of agglomerates. They coalesce during the recession of the interface into the ceramic as the Si_3N_4 is being consumed, leaving the more chemically resistant new oxide compounds in small islands in the metal. After formation, the initial oxides stay further away from the reaction interface, and thus, further away from the oxygen source. It is thus expected different distribution of the reaction products in diffusion couples prepared for different reaction times.

Ce has a significant role on the overall reaction, as is demonstrated by the distinct reaction rates of ceramics containing Y_2O_3 or CeO_2 as sintering additives in M1, M2 and M4. The chemical analysis of the ceramic of the diffusion couple, Fig. 5(b), evidences that Fe diffuses into it to some extent, [Fig. 6(v)]. In the reaction interface the steel may be in contact with both the Si_3N_4 grain but also with oxidised glassy phase that does not contain any Ce, Figs. 5(c), (d) and 6(iv). Ce was also found in the metallic matrix, but only far away (>50 μm) from both the reaction interface and the reaction zone. Although not present as a pure metal as in the case of M1-pure Fe diffusion couples,[12] it may appear in its elemental form but dissolved in the Fe–Cr alloy.

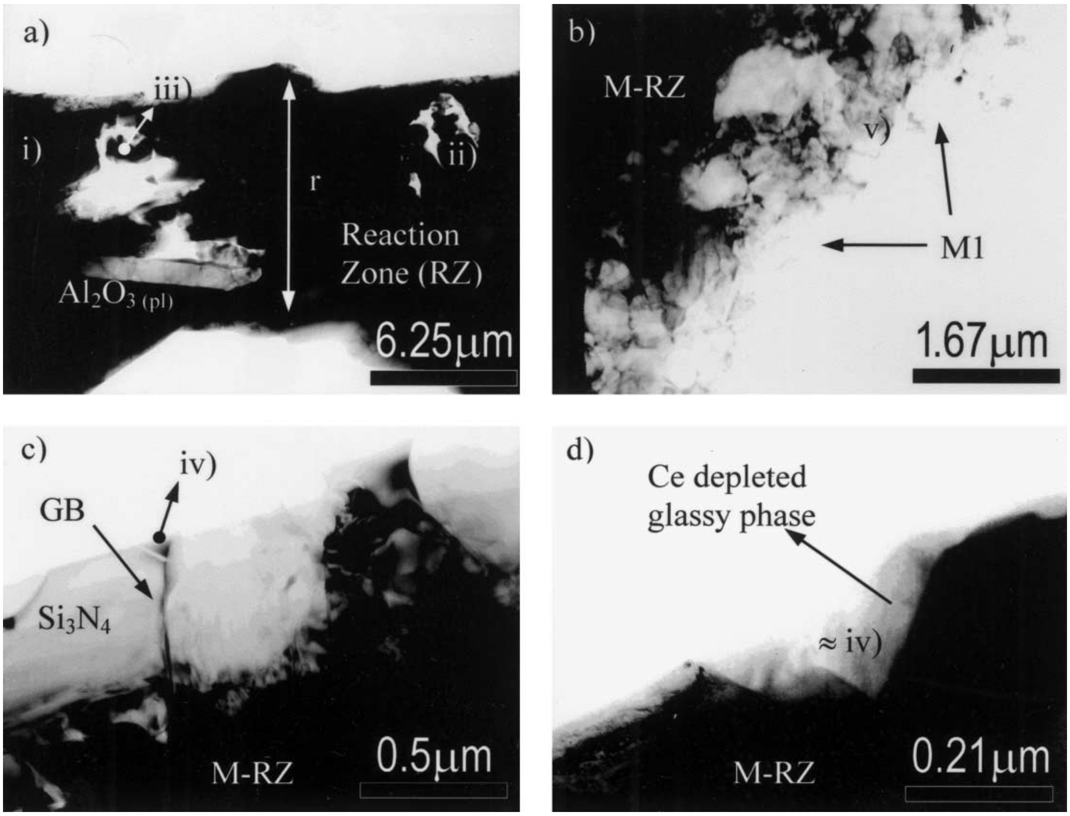

Fig. 5. TEM micrographs of a M1-DIN x20Cr13 diffusion couple showing the positions of the chemical analysis presented in Fig. 6(i)–(v). (a) Reaction Zone with alumina platelet marker; (b) microstructure of ceramic and of interface; (c) details of the interface between steel and Ce depleted ceramic; (d) vitreous zone at the interface with the metal. M—RZ: metal in Reaction Zone, *r*—reaction zone thickness.

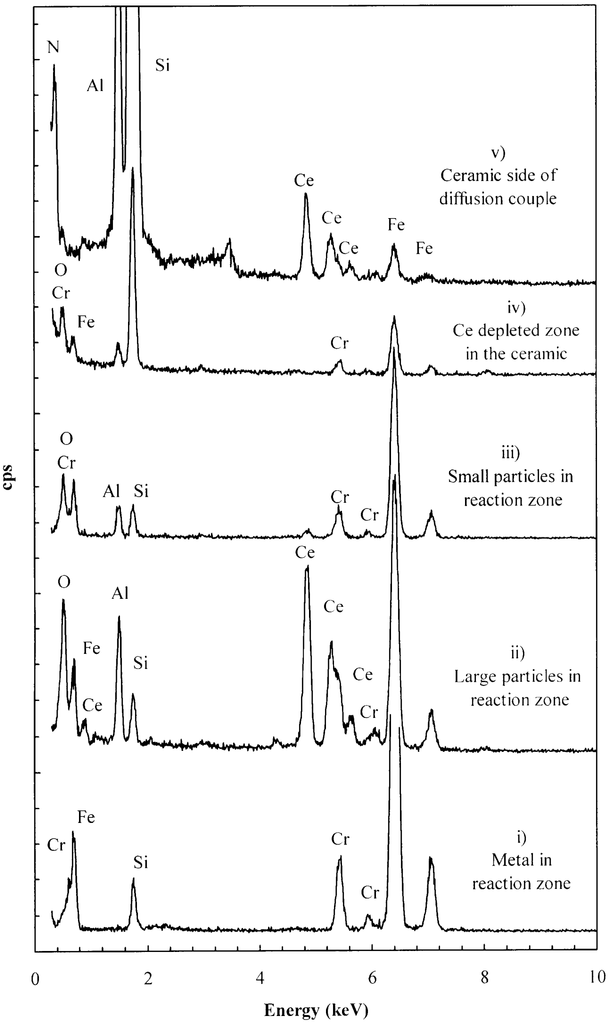

Fig. 6. EDS spectra of the phases present in the reaction zone (analysis of zones indicated in the TEM micrographs of Fig. 5).

This analysis confirms that the more refractory the oxides formed during sintering and the lower the solubility of the metallic element in the Fe alloys, the lower the reactivity of these ceramics is in contact with the steels. The Fe and Ce interdiffuse through the intergranular phase of the Si_3N_4 ceramic, the Ce reaching the metal and diffusing further away from it into the metal, leaving a depleted zone near the attack or reaction interface on the ceramic side.

3.4. Intergranular diffusion

Due to the existence of the vitreous intergranular phase, it is possible that Fe can diffuse several micrometers inside the ceramic, as it happens in machining tests,[20] in the case of the low stability M1 matrix. The results of the micro-probe element analysis revealed the existence of a Fe concentration profile inside the ceramic. The concentration of the Fe, present just in the ceramic vitreous phase, was corrected to account for the volume fraction and density of the glass, (Fig. 7). Fe reaches about 40 μm inside the ceramic after reaction at 1150 °C for 30 h, and approximately 20 μm for a reaction time of 10 h. The interdiffusion in the vitreous phase depends on the coefficients of diffusion of all the present species, and the depth of diffusion of the Fe is determined by the requirement for local equilibrium.

In Fig. 8 values of diffusion coefficients of several elements in Si_3N_4, in the intergranular phase of Si_3N_4 ceramics and in some silica glasses are compiled, to help elucidate the effect of the glassy phase on the reaction with metals. It should be noted that the data for the diffusion coefficients of Si and N in Si_3N_4 are quite different among diverse authors. This is due to the large difference between the values of the effective diffusion coefficient obtained by hot pressing, and those measured in silica glasses or in Si_3N_4 grains.

While Si and N have very low diffusion coefficients in the intergranular phase of the ceramic, cations as Fe^{2+} or Ca^{2+} and anions as O^{2-}, possess large diffusion coefficients in glasses. The activation energy for the diffusion in these systems approaches the values recorded for the reaction kinetics of diffusion couples with M1 ceramic[8] only for the data obtained by hot pressing or for the diffusion of Fe in oxynitride glasses. The values of the rate constants of the decomposition reaction in the systems M1-DINx20Cr13 and M3C3AL-DIN St37K, are compared in Fig. 9 with the values of the rate constants of passivating oxidation of Si_3N_4 ceramics with additive system of CeO_2 and AlN. M1-AC1 and M3C3AL-DIN St37K are, among the diffusion couples systems, the more and the less reactive, respectively.[4,8] It should be noted that the rate of oxidation in the passivating regime approaches that of the Si_3N_4 decomposition reaction, (Fig. 9). This result suggests that the formation of a passive layer of vitreous nature in the ceramic surface decreases the reactivity with respect to the Fe alloy. This

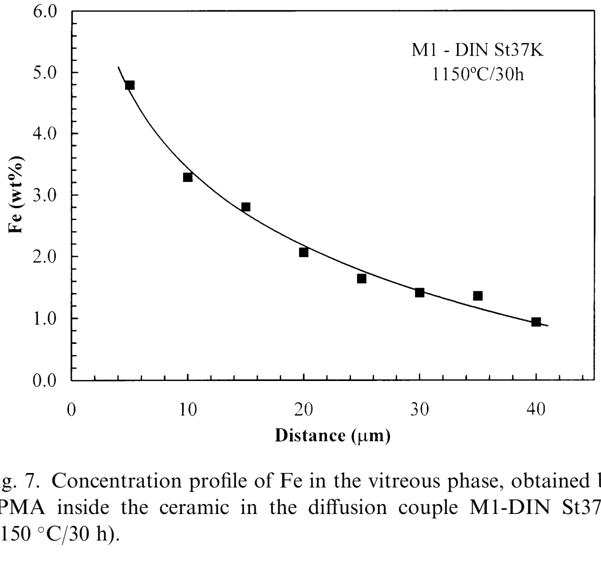

Fig. 7. Concentration profile of Fe in the vitreous phase, obtained by EPMA inside the ceramic in the diffusion couple M1-DIN St37K (1150 °C/30 h).

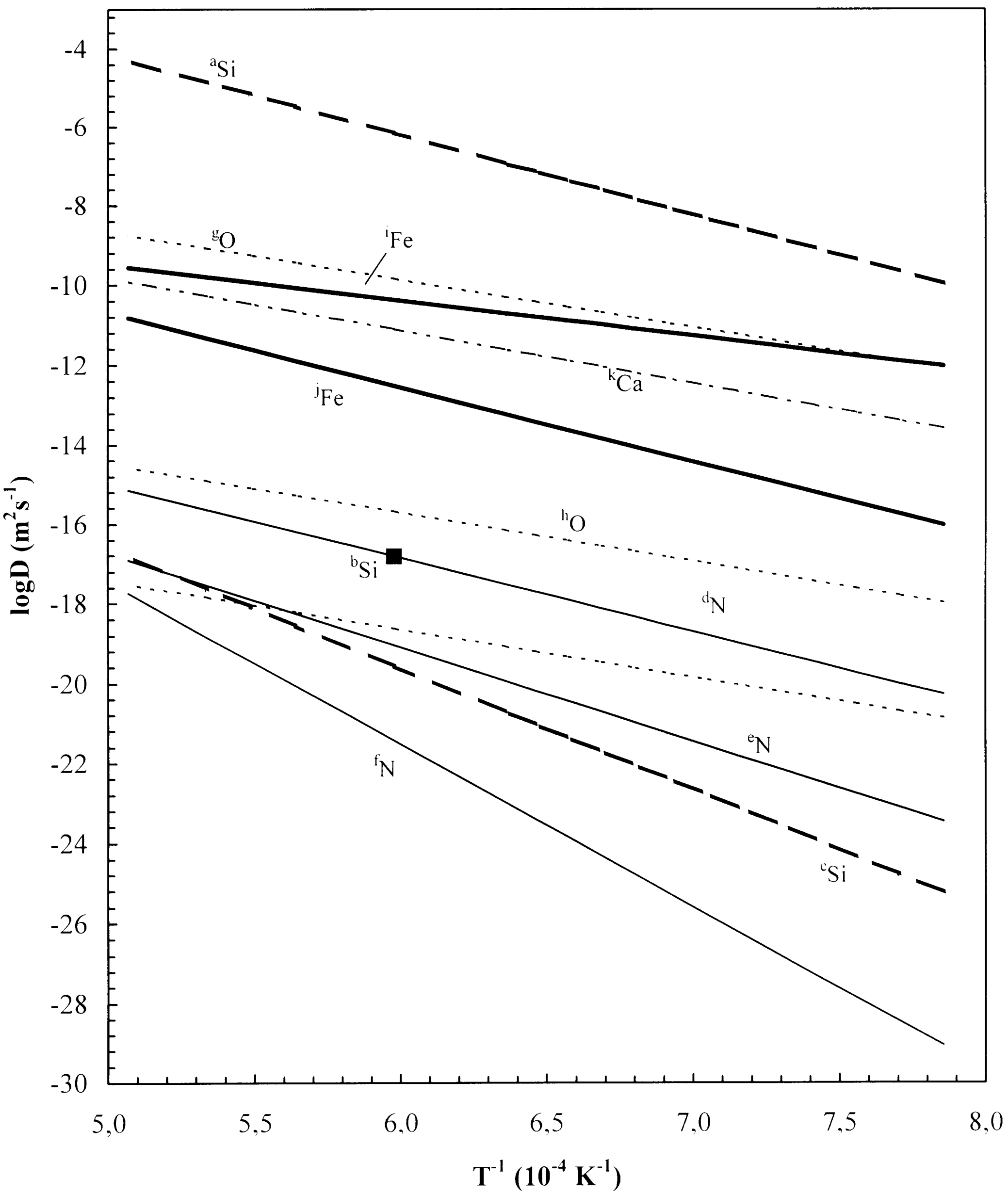

Fig. 8. Diffusion coefficients in Si_3N_4 and glasses: $(Si_3N_4+Si)^a$;[27] $(\beta\text{-}Si_3N_4)^{b,f}$;[27] (glass, $SiO_2)^{c,h}$;[28] (GB, HP)^d;[29] (GB, HP)^e;[28] (glass, Si–Na–Ca–O)^{g,i,k};[28] (glass, Si–Y–N–O)^j[30] (GB—Si_3N_4 ceramic grain boundary, HP—uniaxial hot-pressing).

decrease is related to the reaction products, what is compatible with the effect of the composition of the ceramics or of the composites in the reaction kinetics as discussed above. The comparison of the results in Fig. 9 suggests that the Si and N diffusion coefficients for the transport in the ceramic when increased by the presence of the Fe, coincidentally will be comparable to the diffusion coefficients of Fe and Si in the metallic alloy.[21] The values of the activation energy for the formation of the reaction zone are similar to the values measured for the diffusion of N in the vitreous phase, as obtained by hot pressing and other methods. These close values indicate that for sufficient fast diffusion in the alloy the overall reaction-diffusion control will be on the ceramic side, whereas the opposite is true if the reaction is hindered by slow diffusion or build up of reaction products on the metal side. The activation energy for the oxidation of ceramics of approximate composition is also similar showing that the ceramic composition controls different types of processes.

3.5. Reaction in other Si_3N_4-alloy systems

In Fig. 10 the effect of the temperature on the reaction rate constants of different systems is plotted. Data is from the present work and from literature. The data includes values for reaction rates of silicon nitride ceramics with sintering additives such that the substitution degree

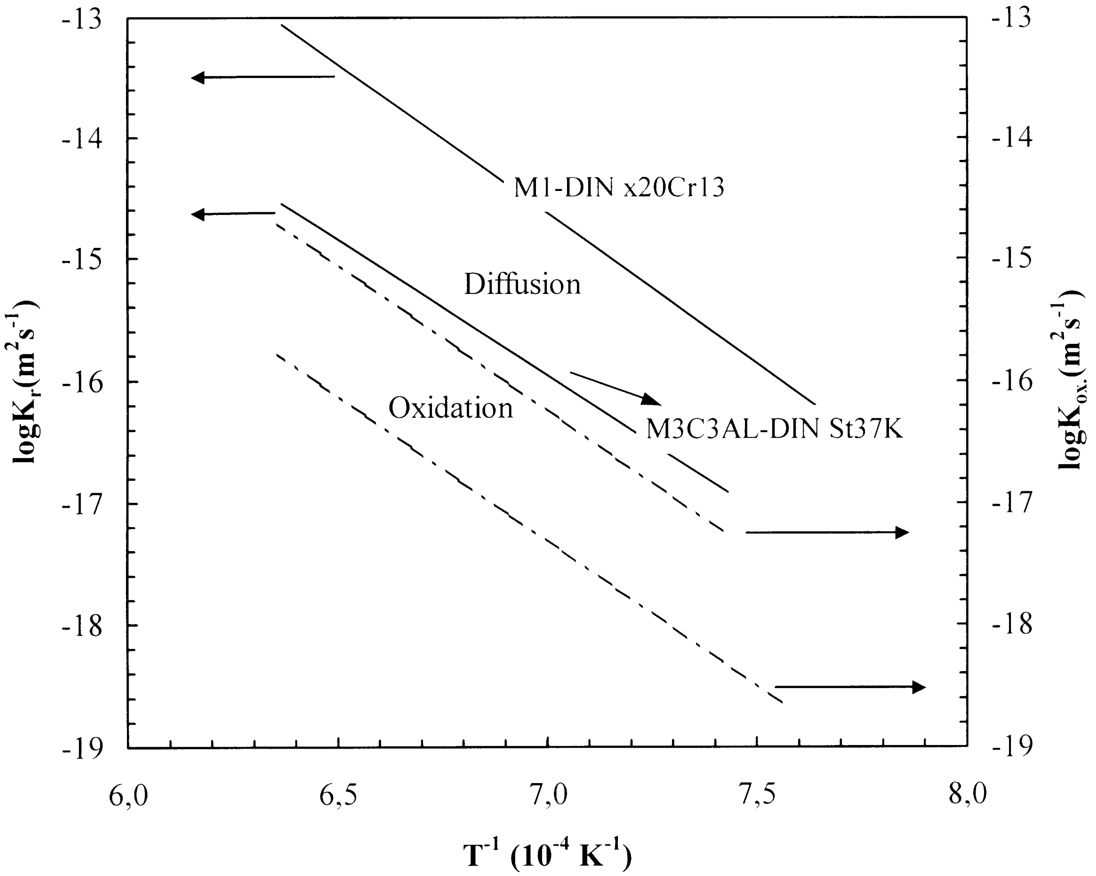

Fig. 9. Reaction constants in diffusion couples between the ceramic M1 and the steel DIN x20Cr13 and the composite M3C3AL and the steel DIN St37K, and constants of oxidation in passivation regime, for Si_3N_4 ceramics of the same system of additives of ceramic M1 (CeO_2–AlN), the less oxidation resistant containing more liquid phase.[29]

in SiAlONs is nearly zero. The data range represented in Fig. 10, includes the values corresponding to the most and the least reactive metals towards ceramic M1, steels DIN x20Cr13 and DIN C105W1, respectively.[8] In the different diffusion couple systems, ceramics with the same composition are represented by the same symbol.

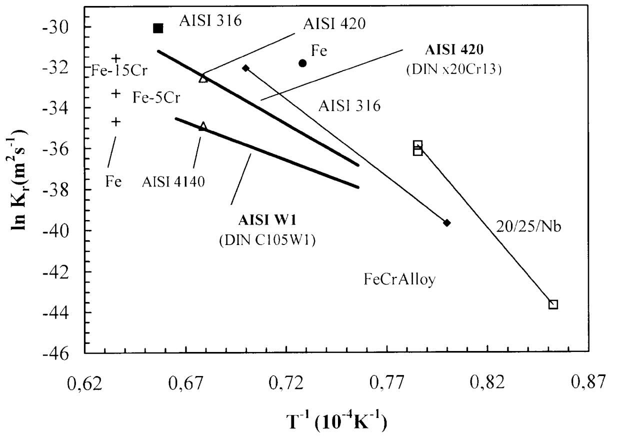

Fig. 10. Effect of temperature on the reactivity of silicon nitride ceramics in contact with different Fe alloys; references: Δ,[10] +,[22] •,[25] ◆,[26] ■,[31] □;[32,33] bold traces represent reaction with ceramic M1;[8] same ceramic has same symbol.

When the content of alloying elements, such as Cr or other nitride and carbide forming elements increases, the reactivity of such an alloy in contact with the same ceramic also increases relatively to reaction with pure iron. This is clear in the data obtained from Peteves and co-workers.[22] Carbide and nitride former elements in iron alloys, such as Cr, Mo or V[23,24] are also α-Fe phase stabilizers. As sustained in a previous publication, the transition from γ-Fe to α-Fe results in an increase of the reaction speed,[9] and thus two concurrent mechanisms are expected to contribute to the increase of reactivity.

The data obtained in the present work is compatible with the published data, obtained in similar conditions (Fig. 10). The largest difference is observed for the single-point experiments of Peteves[22] and of Heikinheimo and co-workers.[25] Peteves et al.[22] used a nitrogen atmosphere that allows the formation of a CrN layer between the ceramic and the alloy, which changes the reaction control to the diffusion of N in that layer. The reaction rate is thus decreased with respect to atmospheres without nitrogen. The results of Heikinheimo[25] are not compatible with the other studies of diffusion couples between pure

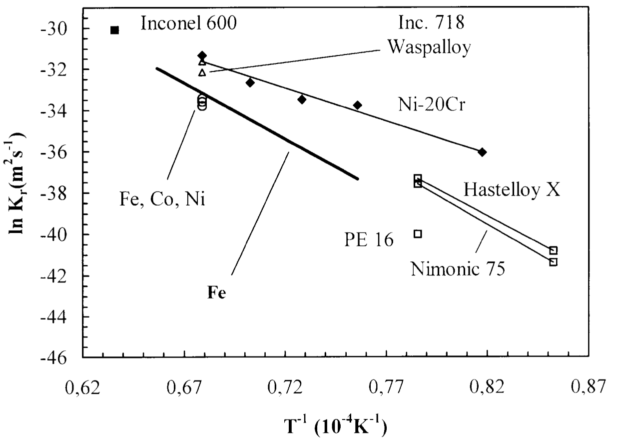

Fig. 11. Effect of temperature on the reactivity of silicon nitride ceramics in contact with pure Fe, Co, Ni and Ni base alloys; references: □,[32] Δ,[33] ○,[34] ◆,[35] ■;[36] bold traces represent reaction with ceramic M1;[8] same ceramic has same symbol.

iron and Si_3N_4 ceramics. This result suggests that the intergranular phase of a MgO containing ceramic is less protective than the one obtained with other sintering additive systems. However, it should be noted that in other works involving Si_3N_4 with MgO as a sintering additive there are not such large differences in reactivity.[18,26]

The effect of the alloy base metal composition on the reaction rate constants is presented in the Arrhenius plot of Fig. 11. Data are from reaction of Si_3N_4 ceramics with pure Fe, pure Co, pure Ni and Ni based alloys. For a given Si_3N_4 ceramic the reactivity with pure Fe, Co or Ni is nearly the same. The same result was obtained for the reaction of SiC with Ni and Fe, with enhanced reaction rates being observed only for diffusion couples with binary Fe–Ni compositions close to 50:50.[7] For the Ni base alloys there is a tendency for increased reactivity with the amount of Cr or carbide forming elements in solution, although the results are not very different from those observed in the diffusion couples with the iron alloys, (Fig. 10). Again, since the data correspond to diffusion couples with different ceramics, it is difficult to attribute the differences between the reaction rate constants obtained by all the authors to the composition of the alloy alone.

4. Conclusions

The Y_2O_3–SiO_2 (M4) additive system is the less reactive in contact with iron at high temperature followed, in this order, by the CeO_2–AlN (M1), the Al_2O_3 (M3) and the CeO_2–AlN–Al_2O_3 systems.

The alumina platelets in the M2 and M3 matrix composites result in a net increase in chemical resistance whereas TiN behaves as an inert and HfN and BN composites have increased reactivity relatively to their corresponding unreinforced matrices.

The most effective method of chemical protection is the formation of a continuous layer of stable crystalline phases or high viscosity glassy phases as in the M4 system.

The decomposition of the ceramics results in the formation of new oxides or intermetallics in the reaction zone in the newly formed Fe–Si alloy. In the M1 ceramic reaction progress is due to interdiffusion of Fe and Ce in the glassy phase, resulting in a cerium depleted zone near the reaction interface. The activation energies for the reaction with iron or for oxidation are approximate in ceramics with the same types of additives.

The large differences in the kinetic reaction constants for different Fe–Si_3N_4 ceramic diffusion couples are due both to the composition of the alloy or to the composition of the additives, since the diffusion coefficients of Fe and N in oxynitride glasses are close to the interdiffusion coefficients of Fe–Si in α-Fe(Si) alloys.

Ni and Co base alloys behave in the same manner of Fe base alloys in the contact with Si_3N_4 ceramics.

Acknowledgements

F.J. Oliveira acknowledges Program Praxis XXI of Foundation for the Science and Technology of Portugal, the post-doc grant BPD/20157/99 that allowed him to prepare the manuscript.

References

1. Kramer, B. M. and Judd, P. K., Computational design of wear coatings. *J. Vac. Sci. Technol.*, 1985, **3**(6), 2439–2444.
2. Buljan, S. T. and Wayne, S. F., Silicon nitride-based composite cutting tools: material design approach. *Adv. Ceram. Mater.*, 1987, **2**(4), 813–816.
3. Oliveira, F. J., Silva, R. F. and Vieira, J. M., Densification and microstructural evolution in a reactive silicon nitride/alumina platelet system. *Key Engineering Materials*, 1997, **127–131**, 377–384.
4. Oliveira, F. J., Silva, R. F. and Vieira, J. M., Dissolution of Si3N4-Al2O3(pl) composite tool materials in carbon steels. *Key Engineering Materials*, 1997, **132–136**, 2068–2071.
5. Oliveira, F. J., Silva, R. F. and Vieira, J. M., Improved wear resistance of Si3N4 tool inserts by addition of Al_2O_3 platelets. Private communication.
6. Vleugels, J., Jacobs, P., Kruth, J. P., Vanherck, P., Mong, W. D. and Van Der Biest, O., Machining of steel with sialon ceramics: influence of ceramic and workpiece composition on tool wear. *Wear*, 1995, **189**, 32–44.
7. Schiepers, R. C. J., van Beek, J. A., van Loo, F. J. J. and de With, G., The interaction between SiC and Ni, Fe, (Fe,Ni) and steel: morphology and kinetics. *J. Eur. Ceram. Soc.*, 1993, **11**, 211–218.
8. Oliveira, F. J., Silva, R. F. and Vieira, J. M., Interfacial reaction kinetics of silicon nitride/iron alloys diffusion couples in the range 1050 °C–1250 °C. In *Interfacial Science in Ceramic Joining* (as part of the NATO Advanced Research Workshop Interfacial Science in Ceramic Joining, Bled, Slovenia, 12–15 November) (NATO ASI Series 3. High Technology, Vol. 58) ed. A. Bellosi, T. Kosmac and A. Tomsia. Kluwer Academic, 1997, pp. 203–209.
9. Oliveira, F. J., Silva, R. F. and Vieira, J. M., Thermochemistry of contacts between silicon nitride ceramics and steels. *Acta Mater.*, 2000, **48**(18–19), 4659–4665.

10. Vleugels, J., Van Der Perre, L. and Van Der Biest, O., Influence of alloying elements on the chemical reactivity between Si-Al-O-N ceramics and iron-based alloys. *J. Mater. Res.*, 1996, **11**(5), 1265–1276.
11. Jack, K. H., Sialons: a study in materials development. In *Non-Oxide Technical and Engineering Ceramics*. Elsvier Science, London, 1986, pp 1–30.
12. Oliveira, F. J., Silva, R. F. and Vieira, J. M., The structure of the reaction zone in Fe-Si_3N_4 diffusion couples In *Proceedings of the IXth CIMTEC—International Ceramic Congress and Forum on New Materials*, ed. P. Vincenzini. Faenza Editrice, 1999, pp. 245–258.
13. Laoui, T., Vleugels, J. and Van der Biest, O., Effect of secondary phase on SiAlON/steel chemical interaction, Mater. *Sci. Eng. A*, 1994, **183**, L19–L21.
14. Zhou, Y., Vleugels, J., Laoui, T., Ratchev, P. O. and van der Biest, O., Preparation and properties of X-SiAlON. *J. Mat. Sci.*, 1995, **30**, 4584–4590.
15. Rouxel, T., Huger, M. and Besson, J. L., Rheological properties of Y-Si-Al-O-N glasses—elastic moduli, viscosity and creep. *J. Mat. Sci.*, 1992, **27**, 279–284.
16. Desmaison-Brut, M., Montintin, J., Valin, F. and Boncoeur, M., Mechanical properties and oxidation behaviour of HIPed hafnium nitride ceramics. *J. Eur. Ceram. Soc.*, 1994, **13**, 379–386.
17. Falk, L. K. L., Hermansson, T. and Rundgren, K., Microstructure of hot-pressed Si_3N_4-ZrO_2(+Y_2O_3) composites. *J. Mat. Sci. Let*, 1989, **8**, 1032–1034.
18. Oliveira, F. J., *Stability of Ce-SiAlON composites in contact with iron alloys*. MSc Thesis UMIST, Manchester, 1995.
19. Silva, R. F., *Cinética de sinterização e desgaste de pastilhas de corte do sistema Si_3N_4-CeO_2-AlN. PhD Thesis*. University of Aveiro, Portugal, 1992.
20. Kannatey-Asibu Jr., E., On the performance of the silicon nitride cutting tool in machining steel. *J. Man. Syst*, 1990, **9**(2), 159–168.
21. Oikawa, H., Review on lattice diffusion of substitutional impurities in iron: a summary report, Technol. *Rep. Tohoku Univ*, 1982, **47**(2), 215–224.
22. Peteves, S. D. and Suganuma, K., Solid state bonding of Si3N4 ceramics with Fe-Cr alloy interlayers. *Structural Ceramics Joining II*, 1992, **35**, 229–238.
23. Krauss, G., *Materials Science and Technology*, 1992, **7**, 2–40.
24. Pickering, F. B., *Materials Science and Technology*, 1992, **7**, 337–399.
25. Heikinheimo, E., Isomaki, I., Kodentsov, A. and van Loo, F. J., Chemical interaction between Fe and silicon nitride ceramic. *J. Eur. Ceram. Soc.*, 1997, **17**, 25–32.
26. Stoop, B. T. J. and Den Ouden, G., Diffusion bonding of silicon nitride to austenitic stainless steel with metallic interlayers. *Metall. Mater. Trans. A*, 1995, **26**(1), 203–208.
27. Kunz, K. P., Sarin, V. K., Davis, R. F. and Bryan, S. R., Self-diffusion of silicon-30 and nitrogen-15 in alfa phase silicon nitride. *Mat. Sci. Eng. A*, 1988, **105–106**, 47–54.
28. Weiss, J. and Kaysser, W. A., Liquid phase sintering. In *Progress in Nitrogen Ceramics*, ed. F. L. Riley. Martinus Nijhof, The Netherlands, 1986, pp. 169–186.
29. Silva, R. F., Moreira, A. P., Gomes, J. M., Miranda, A. S. and Vieira, J. M., The role of nitrogen in the intergranular glass phase of Si_3N_4 on high temperature applications and wear. *Mat. Sci. Eng. A*, 1993, **168**, 55–59.
30. Das, P. K., Sanyal, A. S. and Mukerji, J., Comparison of the diffusion behaviour of sodium and iron in oxide and oxynitride glass pairs in the yttrium aluminosilicate system. *J. Chem. Glas.*, 1995, **36**(4), 191–193.
31. Hussain, P., Abed, A. and Hendry, A., Joining of sialon to stainless steel. *Brit. Ceram. Proc.*, 1995, **55**, 53–62.
32. Bennet, M. J. and Houlton, M. R., The interaction between silicon nitride and several iron, nickel and molybdenum-based alloys. *J. Mat. Sci.*, 1979, **14**, 184–196.
33. Adhoum, H. and Broussard, D., Interaction of ceramic cutting tools with nickel-based alloys. *Mat. Sci. Eng. A*, 1989, **109**, 379–387.
34. Vleugels, J., Laoui, T., Vercammen, K., Celis, J. P. and Van Der Biest, O., Chemical interaction between a sialon cutting tool and iron based alloys. *Mat. Sci. Eng. A*, 1994, **187**, 177–182.
35. Moretto, P., Moulaert, M., Glaude, P., Frampton, P., Ceccone, G. and Peteeves, S. D., *Designing Ceramic Interfaces II*, 1993, 519–538.
36. Colin, C., Bienvenu, Y., Bartout, J. D. and Koutny, J. L., Solid-state bonding of silicon nitride in direct contact with Inconel 600: relationship between processing conditions, interfacial microstructure and shear strength of joint. In *Hot Isostatic Pressing '93*, ed. L. Delaey and H. Tas. Elsevier Applied Science, London, 1994, pp. 125–132.