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Diffusion phenomena in the α-Si_3N_4-solid solution and 304L stainless steel static interaction couple

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Abstract

Compositional varieties of α-SiAlON a yttrium stabilized solid solution of α-Si_3N_4, were studied against 304L stainless steel through interacting couples prepared under hot pressing (1100–1300 °C, 1.8 MPa, 5 h) with respect to their chemical interactions and interface bonding formation. Interdiffusion of elements in both ceramic and steel side followed by the series of reactions those produced the interfaces between the joints were seen. Chemical behaviour of α′ vis-à-vis its compositional nitrogen content has been discussed.

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Keywords: C. Diffusion; Interface; α-SiAlON; Stainless steel

1. Introduction

Chemical interactions guide the diffusion bonding as well as the wear nature in a high pressure and high load condition of a ceramic against metals. Si_3N_4 based ceramics, owing to their good thermo-mechanical properties, oxidation resistance and compatibility towards metals at elevated temperature, became important candidate materials for wide range of applications like different engine components, wear parts such as bearings, rollers and cutting tool inserts. Structural applications in many cases require the interfacing of the ceramic components with metallic ones and hence bonding with ductile metallic structure. On the other hand, in rolling, bearing and machining operations operated at higher machining speed to meet the demand of higher productivity, the ceramic experiences high temperature and pressure at the contact surface, especially with the long chip forming metals such as steel. Chemical wear becomes most dominating in such cases. The study on chemical interactions between these ceramics and ferrous metals therefore provide most relevant information about the diffusion bonding between them as well as wear effects during tribological applications. Such studies on nature of chemical interactions, rate controlling steps, mechanisms vis-à-vis diffusion bonding and cutting performance against steel of β-Si_3N_4 [1–5] and its one solid solution β-SiAlON [6–11] (β′, $Si_{3-x}Al_xO_xN_{4-x}$, x being up to 2.1) has already been studied quite extensively.

Introduction of α-SiAlON (α′, $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, in M^{p+}, $m = px$) in composites with β/β′ brought promise for much improved cutting performances because of higher hardness contributed by the α′ phase which has been reported to display the highest hot hardness amongst this class of materials [12]. However, the chemical behaviour of this material against metals has not been assessed so far. In this paper, diffusion of different species in a static interaction couple of α-SiAlON-304L austenitic stainless steel has been studied through characterization of the bond interface.

2. Experimental

Two different compositions of α′ with one richer in oxygen [13] (Table 1) along the two dimensional extension plane Si_3N_4–Al_2O_3·AlN–Y_2O_3·9AlN of the system Y–Si–Al–O–N were produced by attrition milling for 4 h using Si_3N_4 (E10, UBE Industries, Japan), AlN (Grade A, Starck, Germany), Al_2O_3 (Ceralox Corporation, USA) and Y_2O_3 (99%, Indian Rare Earth Ltd., India) starting powders with silicon nitride

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Table 1
Compositions and denotations of α-SiAlONs expressed in equivalent substitution and their densification characteristics after firing at 1800 °C, 2 h.

Composition nos.	Equivalent substitution (%)			Density (g cm^{-3})	Porosity (%)
	Y	Al	O		
NA	2.09	9.37	2.09	3.12	4.69
OA	2.95	16.02	4.79	3.16	4.49

milling balls and isopropyl alcohol as milling media. The powder was subsequently dried, sieved and green pressed under isostatic pressure of 200 MPa into 10 mm × 8 mm × 4 mm rectangular plates and were fired at 1800 °C, 2 h and 1.5 bar nitrogen gas overpressure in graphite crucible. Density and porosity of the sintered samples were estimated by conventional water displacement method. The surfaces to be joined were prepared by polishing to 1 μm diamond finish and were characterized by XRD and SEM using EDS.

For preparation of the interaction couple, the ceramic samples were encapsulated in grade 304L stainless steel powder (referred to as SS in the following sections) inside graphite die of 40 mm diameter. Boron nitride as high temperature lubricant was used to avoid reaction of steel with carbon of the die and punch. The samples were hot pressed at a pressure of 1.8 MPa for 5 h in a temperature range of 1100–1300 °C with an average heating and cooling rate of 20 °C/min and by maintaining 1 bar nitrogen pressure inside the furnace. Ram pressure was withdrawn immediately when cooling started.

The diffusion-bonded samples were cross sectioned and polished to 1 μm diamond finish and etched with suitable reagent for the studies of optical and scanning electron microscopy. EDS analysis was performed at the ceramic–steel interfaces. The phases at the interfaces were also identified by XRD using Cu Kα radiation. Vicker's microhardness tests were

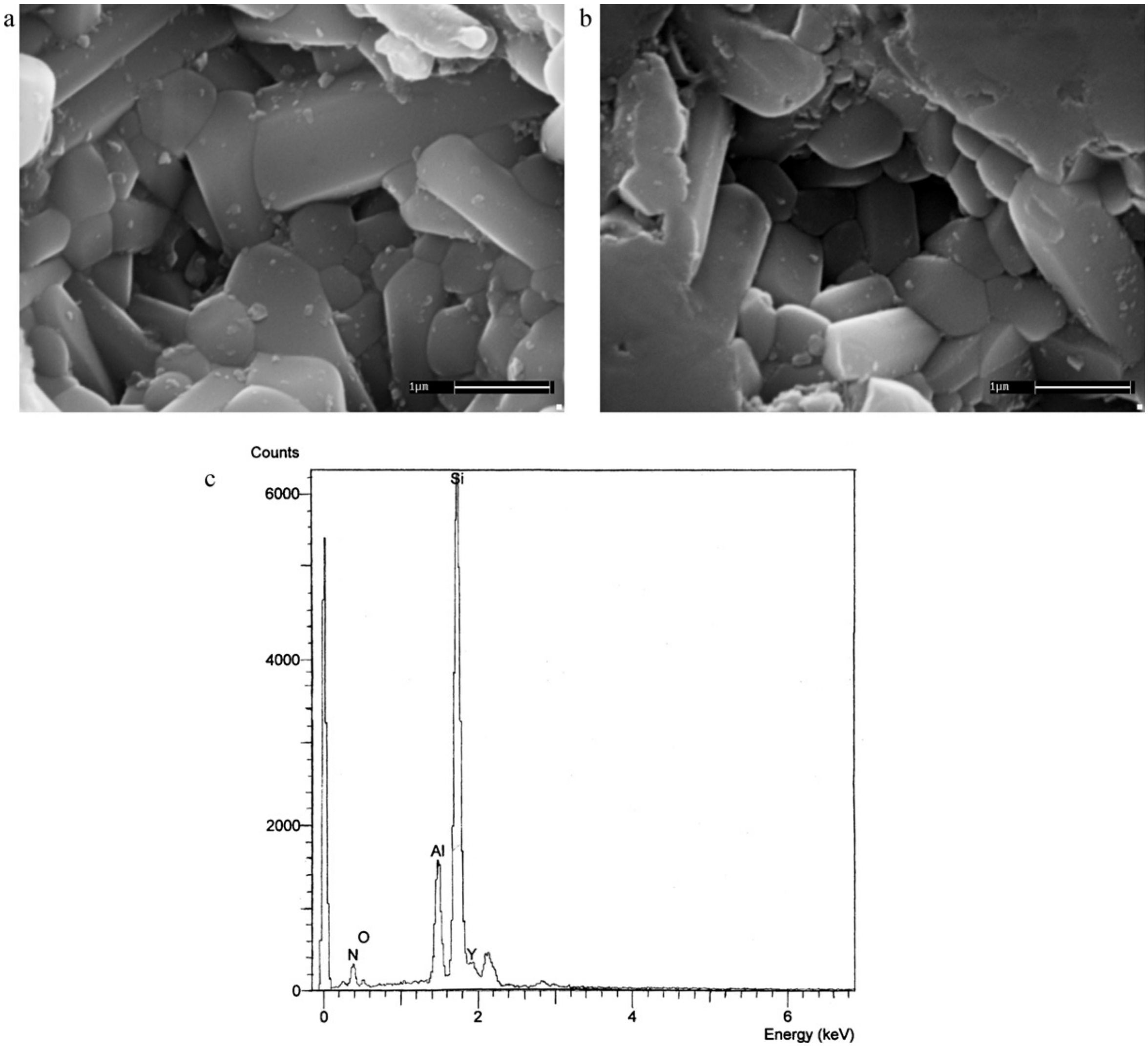

Fig. 1. Electron micrographs of (a) NA, (b) OA and (c) EDS spectrum of OA SiAlON.

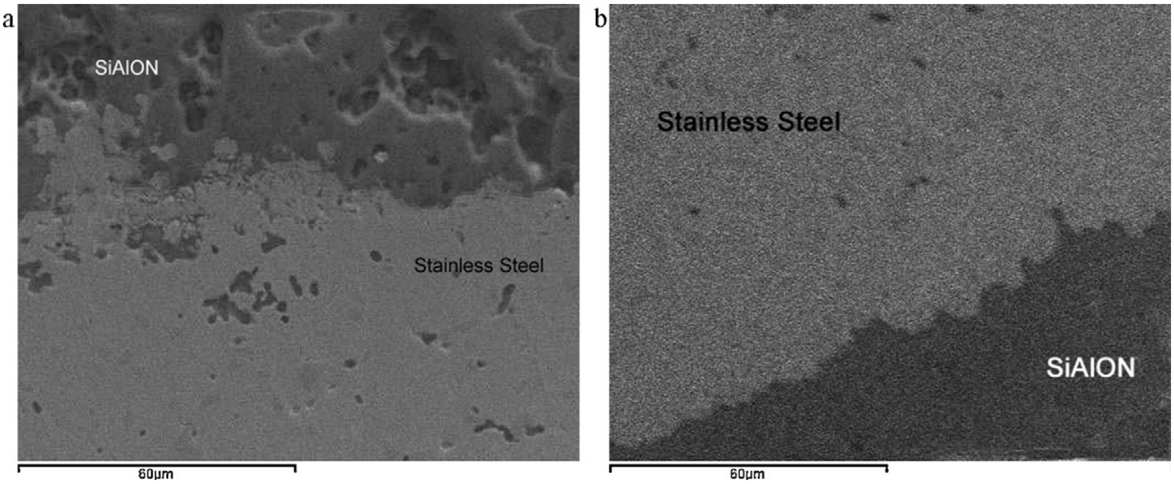

Fig. 2. Electron micrographs of α-SiAlON-304L stainless steel interface: (a) NA and (b) OA.

carried out across the bonding interface employing 100 g and 1000 g load on the steel and ceramic surfaces, respectively.

3. Results

The results of physical characterization and microscopy of the two α′ used in this study are given in Table 1 and Fig. 1a and b. The figures represent some elongated α′ grains typically in the range of 2–3 µm in NA are present in otherwise mostly smaller grains of size around 1 µm or less. The grains are more equiaxed in nature in case of OA. Phase characterization is also confirmed through XRD and through EDS patterns taken randomly, one typical of the latter measurement are shown in Fig. 1c.

The hot pressing temperature was selected in the higher side (1100–1300 °C) of common diffusion bonding studies (∼1000–1200 °C), as to provide a maximum kinetically accelerated diffusion/reaction to take place while the pressure was kept in a minimum level just to avoid the detachment of the dissimilar surfaces because of thermal coefficient mismatch. Results of interaction are most prominent in case of 1300 °C for the reason of kinetic acceleration and are used as representative data for analyzing in detail in the following sections. SEM of interfaces obtained between SS and two different α′ varieties are shown in Fig. 2a and b. In some places of both SiAlONs, although non uniform, interfaces appear to be continuous and coherent for some distance indicating diffusion reaction between the two phases. Some porosity can be seen in the SS side in case of nitrogen richer α′. Images of optical microscopy (Fig. 3a) reveal bigger grain size in SS in diffusion couple with NA. For both diffusion couples, some wider metal protruded zone has been observed in places, one typical of such in OA–SS is presented in Fig. 3b.

To identify diffusion of different elements such as Fe, Cr and Ni in ceramic and Si, Al, Y in steel, EDS element line-scan was taken for both diffusion couples at various locations across the diffusion interface. One representative line-scan for each of the samples is presented in Fig. 4a and b. Tables 2 and 3 represent the detailed EDS quantitative analysis across the interface. The general trend of diffusion pattern may be divided into two parts: the first one is a decrease/increase in elemental concentration over a zone, the sharpness of the fall/hike being different for different species, and then the second part consists of a continuous layer of the diffusing species over a certain distance away from the interface in the opposite material. The diffusion of Si into stainless steel is the most extensive, that of Fe, Cr into

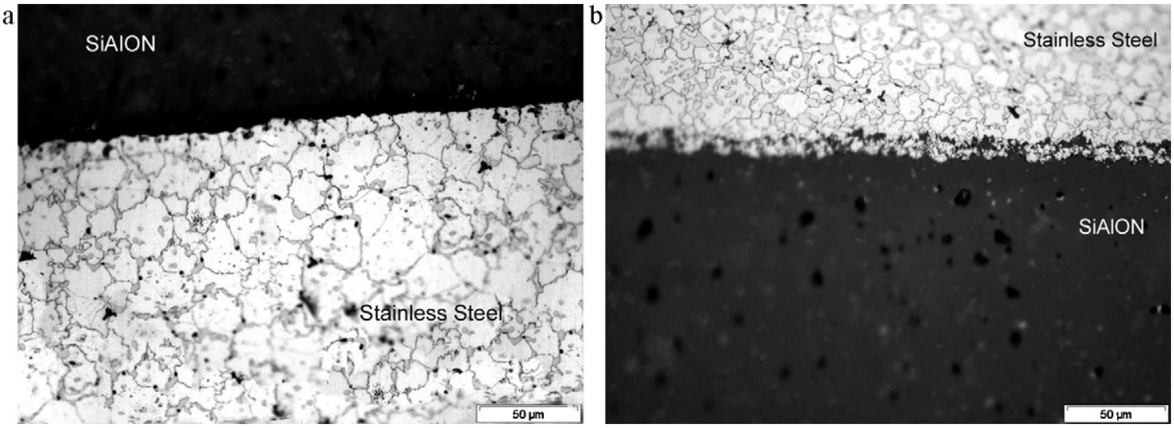

Fig. 3. Optical micrographs of α-SiAlON-304L stainless steel interface: (a) NA and (b) OA.

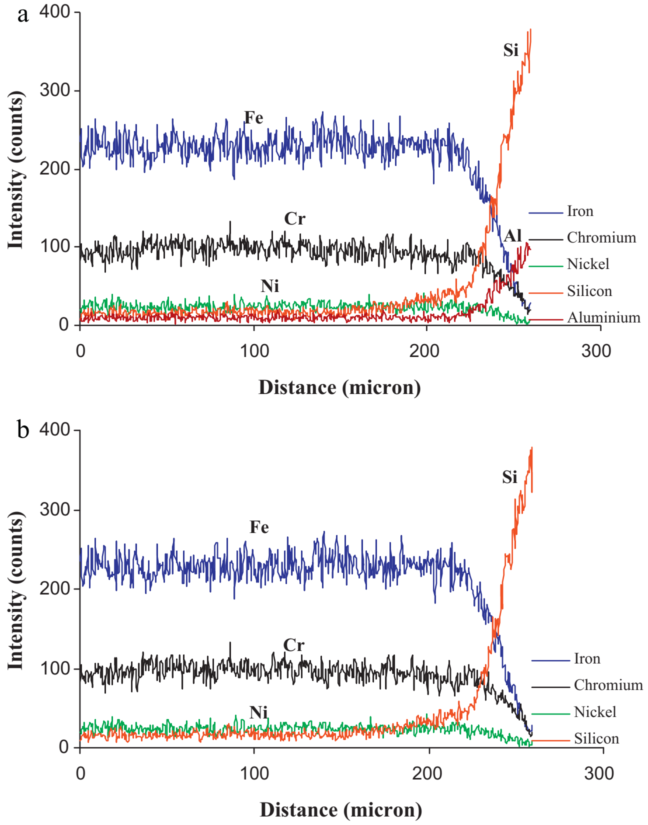

Fig. 4. EDS line scan of α-SiAlON-304L stainless steel interface: (a) NA and (b) OA.

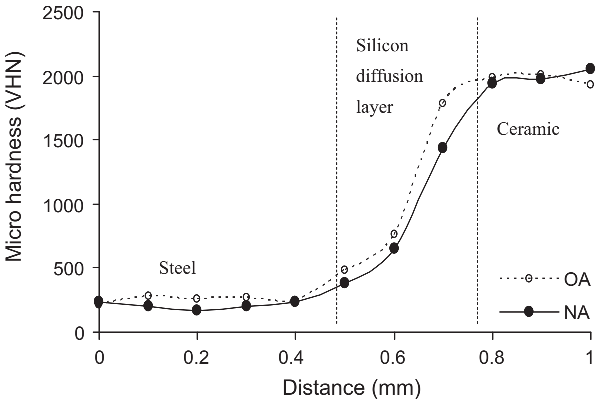

Fig. 5. Microhardness survey across α-SiAlON-304L stainless steel interface.

Table 2
Quantitative analysis of the EDS profile (wt.%) across 304-NA diffusion couple.

Distance (μm)	Al	Si	Fe	Cr	Ni	Y
0	11.25	82.37	0	0	0	6.38
25	8.41	77.29	6.85	5.1	0.73	1.62
50	0.74	7.8	71.82	13.05	6.59	0
75	2.3	3.14	70.22	14.83	8.07	1.44
100	0	0.21	74.63	16.96	8.2	0
125	0	0.72	72.58	17.25	9.45	0
150	0	2.02	71.32	16.68	9.98	0
175	0	6.27	70.44	14.76	8.53	0
200	0	5.53	66.7	17.73	10.04	0
225	0	4.39	70.66	15.28	9.67	0
250	0	4.12	71.1	15.83	8.95	0
275	0	1.11	70.54	17.93	10.42	0
300	0	1.53	70.53	18.78	9.16	0

Table 3
Quantitative analysis of the EDS profile (wt.%) across 304-OA diffusion couple.

Distance (μm)	Al	Si	Fe	Cr	Ni	Y
0	10.31	80.51	0	0	0	9.18
25	8.59	77.42	5.79	3.85	0.14	4.21
50	1.48	6.7	66.07	17.22	8.53	0
75	1.63	4.24	63.78	17.3	9.46	3.59
100	0.1	2.73	71.27	15.27	10.63	0
125	0	1.91	72.68	15	10.41	0
150	0	1.32	73.38	14.47	10.83	0

SiAlON is limited, Al and Ni is still lesser and Y is the least. Thus, the figures are self explanatory about the diffusion/reaction layer thickness which are predominantly dominated by the silicon diffusion. It is to be mentioned here that this distance is not uniform over all locations across the interface. Hence, EDS analysis was carried out at an interval of 25 μm from ceramic to stainless steel side across the interface at 10 different locations and summation of the distance in stainless steel side where Si wt.% is greater than 1 and both Fe, Cr concentration is appreciably high in ceramic side is considered as total diffusion layer thickness. Average of 10 such data was used to approximate the layer thickness and the same is estimated to be as 285 μm in SS–NA and 150 μm in SS–OA diffusion couple.

Microhardness measurements were taken at an interval of 100 μm from ceramic to steel side across the interface. The hardness values are quite homogeneous in the ceramic side and are ~2000 VHN for both the samples (Fig. 5). The hardness values drastically reduce from SiAlON to steel phase and reaches to a value in the range of ~200–250 VHN. Adjacent to the ceramic–steel interface, a sharp hardness gradient can be observed within a narrow region for both the samples, indicating the width of the interface.

The characterization of different phases through XRD is presented in Fig. 6. The strongest lines could be detected from XRD patterns are for α-SiAlON and austenite. The diffraction examinations also show the existence of mainly silicides of Fe (Fe_3Si) and Cr–Si–nitrides ($Cr_{6.5}N_{2.5}Si$, $Cr_3N_5Si_2$) along with Cr–nitride (CrN).

4. Discussions

During hot pressing, a clear appearance of interface in some of places, and therefore bonding, are evident. From the differential rate of diffusion of individual species it can be inferred that decomposition of SiAlON has taken place. Larger diffusivity of Si in the metal side is the resultant of two counter effects: it is favoured by the presence of Cr alloying in steel [14]

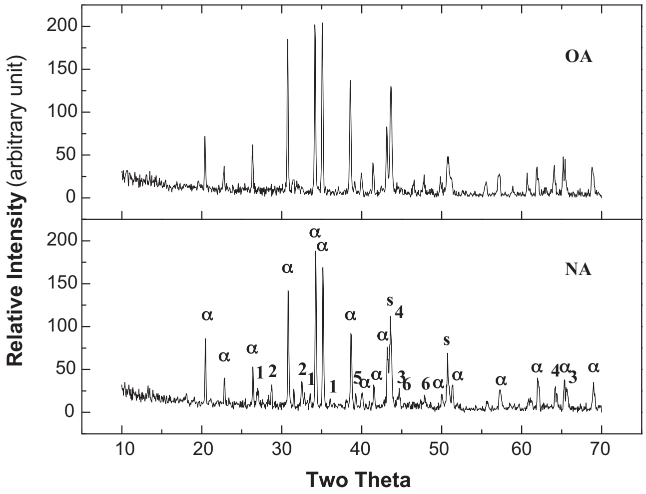

Fig. 6. X-ray diffraction patterns of α-SiAlON-304L stainless steel surface after reaction around interface; α-α-SiAlON, s-stainless steel, 1, β-Si_3N_4; 2, YAM; 3, Fe_3Si; 4, CrN; 5, $Cr_{6.5}N_{2.5}Si$; 6, $Cr_3N_5Si_2$.

while the dissolution of it is counteracted by the solution of nitrogen in steel [9]. Nitrogen liberated from dissociation of SiAlON from the ceramic side, in excess to dissolution to austenite, produces metal nitrides [10,11]. The presence of β-Si_3N_4 in XRD in NA is the outcome of reprecipitation process of Si (Si_{Fe}) after reaction with this nitrogen (N_{Fe}). In the presence of Fe–Si liquid where Fe is seen through Mossbauer spectroscopy to be bonded to both Si and N and is believed to be acting as the nitrogen carrier to the reaction site, β-form of Si_3N_4 is the only expected phase [15]. However, the other sample (OA) containing higher oxygen did not show the reprecipitation of the β-Si_3N_4, and this composition is lesser prone to decomposition as evidenced through diffusion layer thickness of Si and Fe. In some earlier work [5,9], the presence of α-Fe in smaller zone of the interface has been reported. The formation of the ferritic phase is favoured by the dissolution of Si. In this work, however, no such phase could be detected. One reason may be the presence of Ni which is strong austenite stabilizer.

So far as the decomposition of α′ is concerned, apart from Si and N, formation of the other elemental species is not evidenced much through diffusion. In the oxide form, stability of Al_2O_3 and Y_2O_3 (free energy at 1200 °C is −1155 kJ/gmol, −1489.4 kJ/gmol, respectively) being higher than that of Si_3N_4 (−266.6 kJ/gmol), dissociation of Al_2O_3 and Y_2O_3 from SiAlON and diffusion of Al or Y into the steel is not expected [16]. This is supported by the fact that the presence of yttrium aluminate (YAM) is detected in XRD.

As evidenced from the EDS analysis, interdiffusion of elements occurs in the reaction layer from both sides of the interacting couple. The diffusion fronts of metals are predominantly demonstrated by Fe, followed by Cr. One general observation is that the extent of diffusion of Fe is much restricted (about 3–6 times lesser) in ceramic if compared to that of Si in metal side. This may be explained through the presence of Al–O bond in ceramic. The thermit process may be referred to in this connection where Al–O bond formation is more thermodynamically favoured to release Fe, substituted by Al. In this case, because of the presence of Al–O bond in ceramic, the oxygen chemical potential acting as the driving force for the diffusing Fe may be neglected and it may be assumed that the presence of Al atoms act as the barrier in front of diffusing metal front. For the similar reason of the stability of Al–O bond, the diffusion of Al is also very restricted. Hence the higher cationic substitution in SiAlON composition would be preferable for lesser tendency of diffusion, thereby leading towards lesser tendency for adhesive wear during cutting operations. It may be mentioned here that α′ offers higher cationic substitution than its own anions, the valency being compensated through the stuffing cation, in this case, Y.

At the applied reaction temperature (1300 °C), being above the subsolidous temperature, it is expected that a Fe–Si eutectic liquid is formed in the interface and interaction of the metal front is thus through liquid medium. Results of this interaction are the formation of different ferro-silicides at temperature below 1100–1150 °C and the possible phases during cooling may be FeSi, Fe_2Si, Fe_3Si, Fe_5Si_3. In the present study, not all the predicted intermetallic phases could be identified excepting Fe_3Si which is consistent with earlier findings [5] as happened in case of Si_3N_4–steel interaction. The other intermetallic compounds produced at the ceramic–steel interface mainly consists of silicides and nitrides of Cr as described above. Because Cr nitride is not stable at 1000 °C in the absence of external nitrogen pressure [17], it is evident in case of nitrogen rich composition (NA) that the parent α′ decomposes to provide enough nitrogen pressure to stabilize CrN phase. That the nitrogen pressure was high enough was also evidenced through the presence of porosities. However, Ni being strong austenite stabilizer is less likely to come out from austenite phase and participate in diffusion reaction.

In both cases, the formation of the interface with graded hardness from steel on one end to the ceramic on the other side is expected to bring advantage [10,11]. Due to this hardness gradient, a gradation of properties exists from ceramic to steel through the reaction layer. Thus the reaction layer might help in reducing the effect of thermal expansion mismatch between α′ (3.6×10^{-6}/°C) and steel (17.3×10^{-6}/°C) and thereby help in accommodating residual stresses during cooling and favours diffusion bonding. From both the diffusion layer thickness presented here (nearly double in case of NA, Tables 2 and 3) and the general impression under microscopy, it may be inferred that nitrogen richer compositions favour larger extent of diffusion.

5. Conclusion

α-SiAlON decomposes in a process similar to β-Si_3N_4/β-SiAlON materials against steel, with preferential diffusion of Si and N into steel and transition components of the metal pair Fe and Cr towards the ceramic. A series of chemical interactions take place with the resultant formation of an interface layer of intermediate hardness. The composition of α′ determines the extent of interaction. The nitrogen richer α′ compositions favour higher decomposition while on the other hand, the higher oxygen content in α' brings lesser tendency towards it.

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