# Al(Si)/Al2O3 and NiAl(Si)/Al2O3 co-continuous composites obtained by low temperature reactive metal penetration of dense silica preforms

# $Al(Si)/Al_2O_3$ and $NiAl(Si)/Al_2O_3$ co-continuous composites obtained by low temperature Reactive Metal Penetration of dense silica preforms.

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**Abstract**

Interpenetrating network $Al(Si)/Al_2O_3$ composites, obtained by a reactive metal penetration process, where pure aluminum metal reacts with a dense amorphous silica preform, are an interesting class of metal/ceramic composites, with two continuous networks of metal (Al-Si alloy) and ceramic ($Al_2O_3$). These composites have high stiffness and hardness, while retaining acceptable toughness and good thermal and electrical conductivity, and can be used in wear or thermal management applications. A second infiltration step with nickel allows to substitute the Al(Si) alloy with an intermetallic, obtaining an interpenetrating network $NiAl(Si)/Al_2O_3$ composite, with very high hardness and melting point. While in the standard process the temperature for obtaining the $Al(Si)/Al_2O_3$ composites is in the 1100-1200 °C range, in this paper we studied instead the 700-1000 °C temperature range and its effect on the microstructure of the final $NiAl(Si)/Al_2O_3$ composite. After the first infiltration step, the microstructure of $Al(Si)/Al_2O_3$ composites depends on both temperature and time of the treatment. At 700-800 °C and for reaction time of 1-2 hours, the grain size is completely sub-micrometric.

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When temperature and time of reaction increase, islands with a coarser microstructure, of micrometric size, form, reaching a fully micrometric coarser microstructure at 1100-1200 °C. The islands formation is due to the transformation from transition aluminas, formed at low temperature and low reaction time, to α-alumina, while at high temperature α-alumina forms directly. In a second step, the Al(Si) metal network was replaced with an intermetallic one, by contacting the composite with liquid nickel, that reacted with the Al(Si) alloy forming an Al-Ni-Si intermetallic. The temperature and duration of the first infiltration step strongly influences not only the microstructure of the Al(Si)/$Al_2O_3$ composite but also of the final NiAl(Si)/$Al_2O_3$ one, that is finer when the first step (reaction of aluminum with silica) occurs at lower temperature.

**Keywords**

Metal-matrix composites (MMCs); Intermetallic-matrix composites (IMCs); Microstructures; Liquid metal infiltration.

## 1. Introduction

Reactive Metal Penetration (RMP) in the Al-$SiO_2$ system is a relatively simple process widely explored by many research groups [1–11]. In this process, a dense silica preform reacts with excess molten aluminum at temperatures typically ranging from 800 to 1300 °C and gives rise to near-net shape interpenetrating network composites, also called co-continuous ceramic composites ($C^4$), where two continuous networks of Al-Si alloy and $Al_2O_3$ are present. In this process, the reaction between amorphous solid silica ($SiO_2$) and liquid aluminum (Al) is the driver of the formation of the co-continuous composite

structure that replaces the original silica preform with negligible volume change (hence the near-net shape). The chemical reaction, occurring with excess aluminum, is

$$4\ Al_{(l)} + 3\ SiO_{2\ (s)} \rightarrow 3\ Si_{(in\ Al)} + 2\ Al_2O_{3\ (s)} \qquad (1)$$

where the Si formed during the reaction diffuses out through the interconnected liquid Al channels and, on cooling, precipitates in the Al matrix forming an Al-Si alloy. The kinetics of the reaction is strongly influenced by the temperature, as observed by Yoshikawa and co-workers [12] through a comparison of literature data. After a linear increase of reaction layer thickness at low temperature, a negative temperature dependence is observed between 800 and 1000 °C, then increasing again. The phenomenon seems related to the different alumina phases that nucleate from the displacement reaction: at temperatures lower than 1000 °C, γ-, θ- and δ-$Al_2O_3$ phases nucleate instead of α-$Al_2O_3$, which become the dominant phase at temperatures higher than 1000 °C. If transition alumina forms, the microstructure remains in the sub-micrometer range while the microstructure size reach the micrometer scale when α-$Al_2O_3$ is the reaction product [12].

In an Al(Si)/$Al_2O_3$ interpenetrating phase composite [13], alumina gives hardness, high Young's modulus, low thermal expansion, and a refractory character, while aluminum improves the toughness and gives thermal and electrical conductivity. For this reason, these composites were proposed mainly for wear and thermal management applications. The preparation of these composites requires the preparation of a silica preform with the proper shape and the immersion of the preform in liquid aluminum, typically at 1100-1200 °C for several hours, until the reaction is complete and the preform is completely transformed in the co-continuous composite.

One of the limits of these composites is however the low melting point of the aluminum. Daehn and co-workers developed a method based on two RMP steps one after the other [14,15] to obtain higher melting point materials with co-continuous structure: in the second step liquid aluminum bronzes or liquid Ni alloys were used. In a previous works of ours [16], we developed a double process of reactive metal infiltration that allows to obtain a NiAl(Si)/$Al_2O_3$ co-continuous composites by replacing the aluminum network with nickel aluminide. The first step was to obtain a standard Al(Si)/$Al_2O_3$ co-continuous composite by reactive metal penetration of a dense silica preform at 1200 °C with liquid aluminum. Then, a high temperature step, over the NiAl melting point (1638 °C), allowed to convert the Al(Si) allow into a NiAl(Si) intermetallic. The whole two-steps process resulted near net-shape, with no appreciable size modification between the metal/ceramic and the intermetallic/ceramic composite. The obtained composites exhibited interesting mechanical and physical properties [16], due to the fact that NiAl presents a high melting point, good thermal conductivity and good oxidation and corrosion resistance [17-18]. Other authors investigated in the past interpenetrating network intermetallic/ceramic composites, however, the literature on this kind of composites is scarce. Claussen et al. [19] reacted aluminum powders with other oxides in presence of $Al_2O_3$. Rödel et al. [20] and Skirl et al. [21] infiltrated porous alumina preforms with $Ni_3Al$, Plucknett et al. [22] prepared TiC/$Ni_3Al$ composites while Henager et al. [23] used a reaction between NiAl and NiO. Other authors prepared interpenetrating network intermetallic-ceramic composites but with composition different with respect to the one proposed in this paper. In particular Schicker et al. [24] used intermetallics in the Ti-Al, Nb-Al and Fe-Al systems, obtaining higher hardness values for Ti-Al and Nb-Al system and lower values for Fe-Al system. The Fe-Al system was also explored by Subramanian et al. [25] while

Nb-Al system was studied by Klassen et al. [26]. In all these cases, powder precursors were cold-pressed and brought to high temperature. The microstructure of most of these composites however is not clearly co-continuous. Finally, Han et al. [27] prepared $Ti_3Al$-$Al_2O_3$ interpenetrating composites by hot pressing, with a co-continuous microstructure and high hardness.

In this work we investigated the properties of composites obtained by infiltrating silica with aluminum at low temperature, in the range 700-1000 °C, and the microstructure of the intermetallic/ceramic composites produced by subsequent nickel infiltration at high temperature. We observed the evolution from transition-$Al_2O_3$ to α-$Al_2O_3$, occurring during the thermal treatment of the second infiltration step and its influence on the final microstructure and properties of the NiAl(Si)/$Al_2O_3$ composites.

## 2. Materials and methods

Co-continuous ceramic composites of Al(Si)/$Al_2O_3$ composition were produced by infiltrating a preform of silica with liquid aluminum in air at temperature between 700 and 1000 °C for several hours. The preforms were made of silica glass (Helios Italquartz, Milano, Italy) with density of 2.2 g/cm$^3$ and two shapes were used: 50 mm long cylinders with a mean diameter of 20 mm and 50 x 10 x 3 mm bars. A 99.9% pure aluminum (shots, Sigma Aldrich) was used to prepare the metal bath inside an alumina crucible.

In this first RMP step, the cylindrical preforms were completely inserted into molten aluminum kept at a constant temperature in the range 700-1000 °C with steps of 100 °C, for 2, 4 and 6 hours respectively, to evaluate the kinetics for the reaction. The reaction product Si diffuses out through interconnected liquid Al channels so that an Al-Si alloy is obtained. At the end of the desired soaking period, the bath was cooled down to 680 °C

and the composites were extracted and cooled in calm air. The procedure to evaluate the thickness of infiltration is the following: samples were cross-sectioned, revealing an unreacted core and a reacted external layer, as shown in Figure 1. Each cross-section was then polished and its image digitalized. The depth of infiltration was measured from the surface in at least 20 points, since the infiltration depth is not necessary uniform along the sample. In order to investigate composition and microstructure of these composites, sectioned samples were polished down to 1 μm diamond paste using a basic liquid medium. Samples with bar shape were instead used when complete infiltration was necessary.

The second infiltration step was conducted on fully infiltrated samples in a graphite die in argon atmosphere (partial pressure of 550 mbar), at 1700 °C for 30 minutes, as described in our previous work [16]. The nickel source was a 99.5% pure powder (ABCR) with grain size comprised between 44 and 150 μm.

The size of the samples was measured before and after the two infiltration steps, together with bulk and apparent density. Porosity was measured by image analysis on optical or electron microscopy images.

The microstructure of the composites was observed by Optical Microscopy and by Scanning Electron Microscopy (Leo 1450 VP) combined with EDS (Oxford 7353) analysis for assessing chemical composition. The phases present in the composites after the reaction were determined by using X-ray microdiffraction (Rigaku D/MAX Rapid) with spot size of 50-300 μm diameter. The quantity of phases was determined by Rietveld refinement using the program Maud. Vickers microhardness measurements (load 500 g) were performed on the cross section of composite samples after each RMP step with a

Leitz instrument. A mean value was obtained from at least five measurements for each sample.

## 3. Results and discussion

As stated above, it was investigated firstly the kinetics of the reaction (1) at four different temperatures: 700, 800, 900 and 1000 °C. For each temperature, cylinders of silica were inserted in the metal bath and were then extracted after 2, 4 and 6 hours. After rapidly cooling in air, the samples were sectioned, polished and images were taken by scanning to measure the thickness of the reacted zone. The images obtained are shown in Figure 1. The data collected are in agreement with the previous study of Yoshikawa and co-workers [12], and confirmed that the highest infiltration rate is achieved at 800 °C process temperature, as shown in Figure 2.

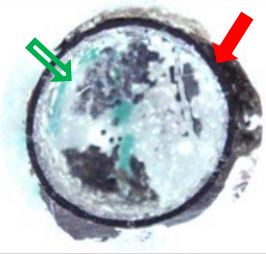
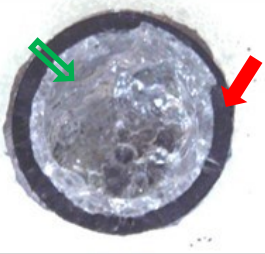
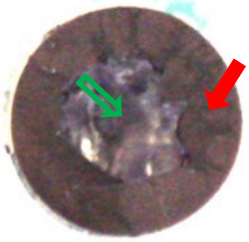
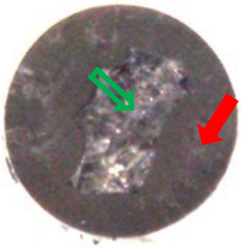
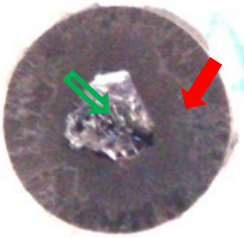
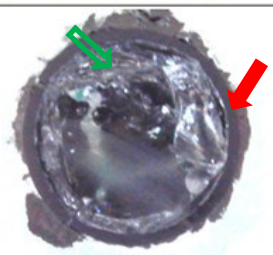
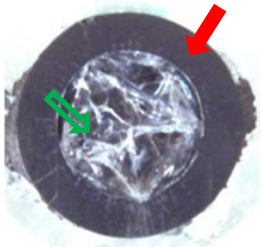
| Temperature | Infiltration Time | | |
|---|---|---|---|
| | 2 h | 4 h | 6 h |
| 700 °C |  |  |  |
| 800 °C |  |  |  |
| 900 °C |  |  |  |
| 1000 °C |  |  |  |

**Figure 1 – Photographs of samples cross sections infiltrated at various temperature for various times. Red solid arrows indicate the reacted zone, green hollow arrows indicate the unreacted zone.**

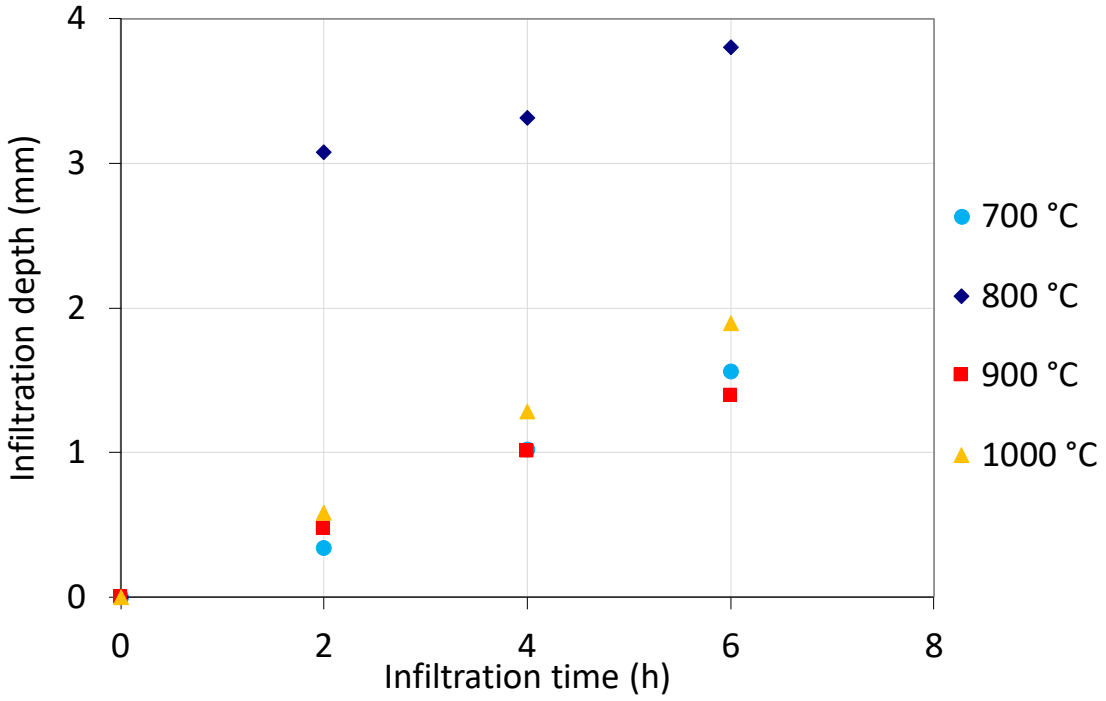



**Figure 2 – Thickness of the reaction layer versus infiltration time.**

Confirming the results of Yoshikawa [12], this negative temperature dependence seems to derive from to the specific kind of $Al_2O_3$ product phase: up to 800 °C, low-temperature ($\gamma$-/$\theta$-/$\delta$-)$Al_2O_3$ phases form, while over 900 °C $\alpha$-$Al_2O_3$ phase is the main reaction product. It was also observed, as in Yoshikawa case, that this transformation takes place isothermally in a time-dependent manner.

X-ray microdiffraction patterns for a sample infiltrated at 800 °C for 6 h are reported in Figure 3, showing, with numbers from 1 to 5, five positions along the infiltration front. The number 1 represent the just infiltrated material (in an inner position, around 3.5 mm from the outer sample surface), while the number 5 the external part, where the composite remained almost all the 6 h at 800 °C (around 0.2 mm from the outer sample surface). It is evident that going to the inside (shorter time after composite formation) to the outside (longer time after composite formation) the fraction of $\alpha$-$Al_2O_3$ phase increases. This was calculated by Rietveld analysis and the plot is shown in Figure 4. It must be considered

however that the quality of the Rietveld is low, due to low signal-to-noise ratio of microdiffraction analysis, so these numbers are affected by a significant uncertainty. The infiltration times is inversely proportional to the distance from outer surface, so the higher $\alpha$-$Al_2O_3$ phase content corresponds to the zone that was infiltrated first, and remained for the longest time at the infiltration temperature.

It is thus possible to see that transition-$Al_2O_3$ (in Figure 3 indicated as $\theta$-$Al_2O_3$) are predominant at low infiltration times or close to the infiltration front, while $\alpha$-$Al_2O_3$ phase begins to develop only after a few hours, or at a certain distance from the silica/Al interface. This confirms that the transition-$Al_2O_3$ phases are not stable, but tends to become $\alpha$-$Al_2O_3$ after a certain induction time, as also confirmed by specific studies on the transformation of gibbsite or boehmite to $\alpha$-$Al_2O_3$ [28-30].

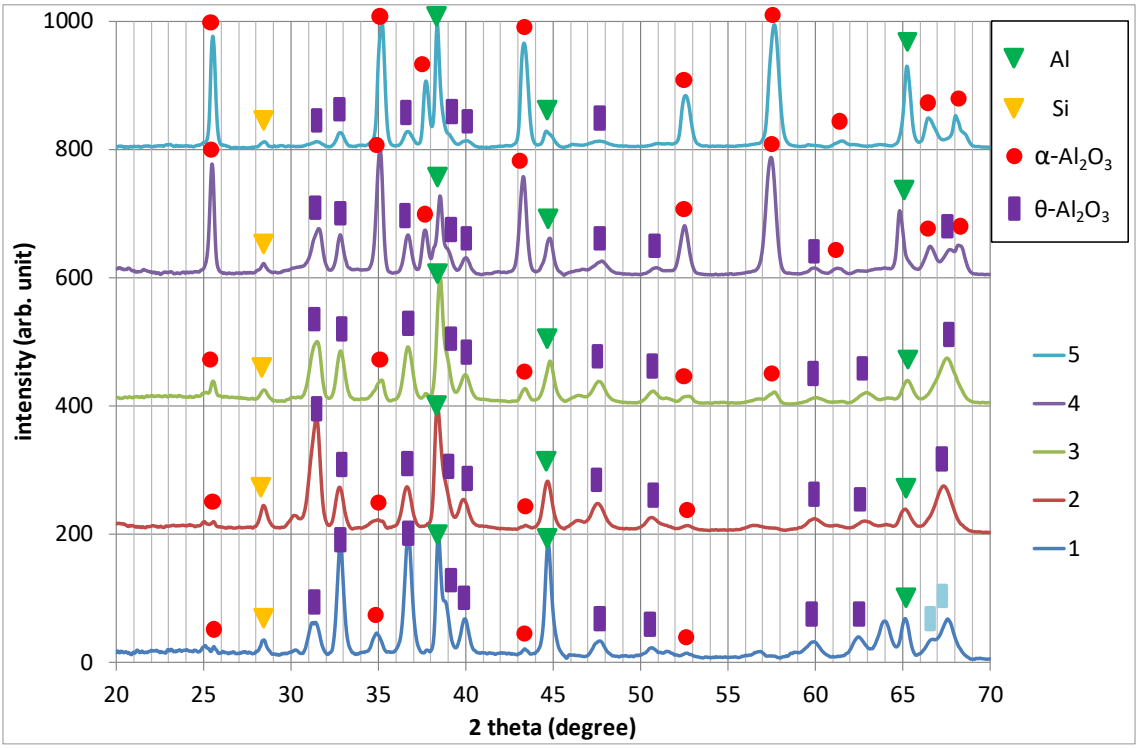



**Figure 3 –X-ray microdiffraction patterns of different zones in the cross section of the composite Al(Si)/$Al_2O_3$ obtained by infiltration at 800 °C for 6 h, with numbers from 1 to 5 as reported in legenda. Number 1 corresponds to the front of infiltration, while number 5 corresponds to the outer surface.**

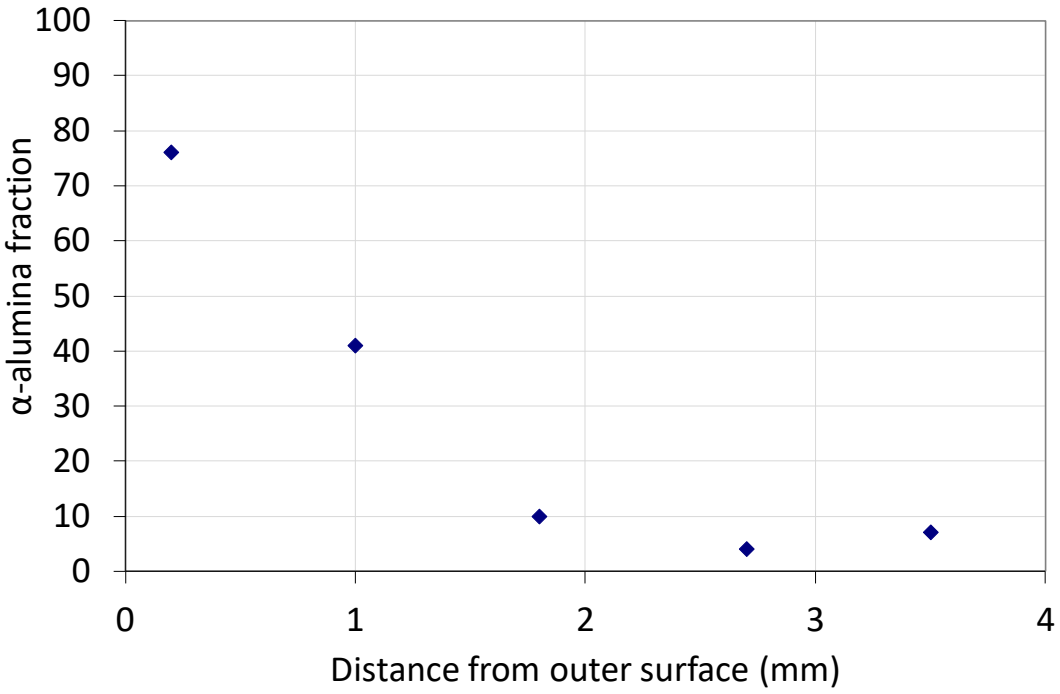



**Figure 4 – Fraction of α-$Al_2O_3$, calculated by Rietveld, as a function of the distance from the outer surface for the sample infiltrated for 6 hours at 800 °C. The infiltration front is at around 3.8 mm.**

The morphology and size of the $Al_2O_3$ phase depends also significantly on the specific alumina phase. At higher temperature, 900 °C and above, where there is the direct formation of α-$Al_2O_3$, the microstructure is micrometer-sized (mean size around 5 μm), as shown in Figure 5a, where the light phase is α-$Al_2O_3$ and the dark phase is the Al(Si) alloy. At lower temperature, 800 °C and below, where the initial phases forming are transition-$Al_2O_3$, the typical grain size is several tens or hundreds of nanometers. This is represented in Figures 5b-5c, where the gray phase is due to the finer microstructure of transition-$Al_2O_3$ intermingled with the Al(Si) alloy. The lighter isolated zones correspond instead to a microstructure similar to the one of Figure 5a, where α-$Al_2O_3$ is interconnected with the Al(Si) alloy. In fact, the α-$Al_2O_3$ formed during the isothermal permanence at 800 °C has a larger grain size than the transition one. Thus, this

transformation entails a grain growth, while the reaction at temperature higher than 900 °C, that forms directly α-$Al_2O_3$, bring to the formation of much larger grain size, in the micrometric range, that does not significantly change even extremely long permanence at very high temperature [2-4,12].

To confirm the microdiffraction data, geometrical and apparent density, porosity and micro-hardness were measured on thin samples infiltrated 6 h at 800 °C, and compared with data measured on samples obtained by the high temperature process, at 1200 °C [8]. From the data of bulk, apparent and theoretical [17] density, together with the porosity, it is possible to calculate the ratio between transition-$Al_2O_3$ and α-$Al_2O_3$, and compare it to the value calculated by Rietveld refinement of XRD spectra. The results, shown in Table 1, show good accord, even if it must be considered that the α-phase fraction results are affected by a significant uncertainty. This confirms the fact that at 800 °C a transition to α phase occurs.

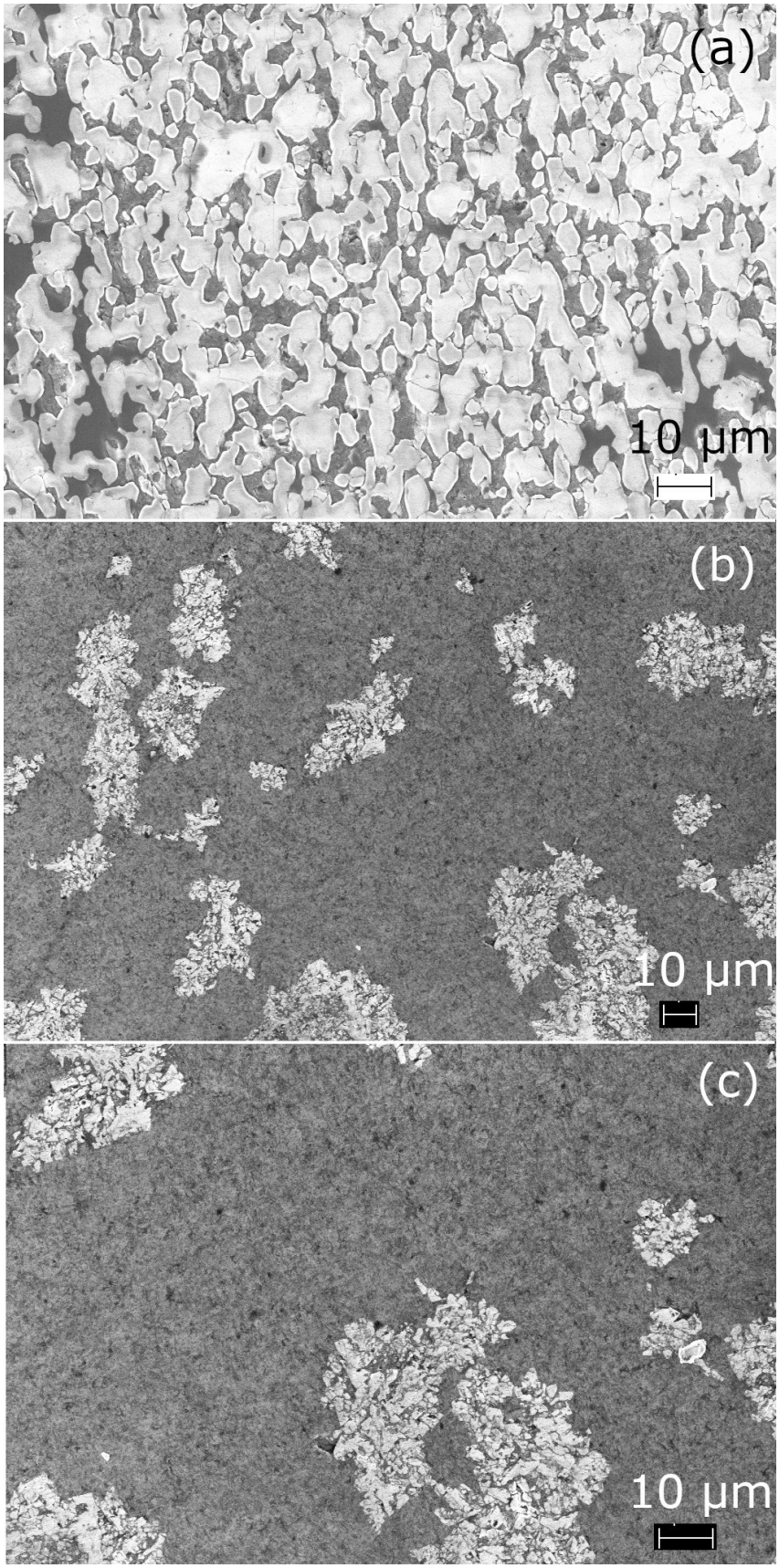



**Figure 5 – Microstructure of Al(Si)/$Al_2O_3$ obtained at 1200 °C for 3 hours (a) and at 800 °C for 6 hours (b/c), showing the two typical sizes of the microstructure.**

**Table 1 - Density and microhardness of C[4] composites obtained at 1200 °C [8] and 800 °C by $SiO_2$ and pure Al, together with calculated α-phase fraction.**

| Infiltration temperature and time | Bulk density ($g/cm^3$) | Apparent density ($g/cm^3$) | Porosity (%) | Vickers microhardness [HV-500] | α fraction by density (%) | α fraction by XRD (%) |
|---|---|---|---|---|---|---|
| 1200 °C, 3 h [8] | 3.39 | 3.46 | 2.5 | 445 | 100 | 100 |
| 800 °C, 6 h | 3.23 | 3.28 | 3.5 | 510 | 70 | 76 |

Since the composition of the composites obtained at 800 °C and 1200 °C is rather similar (mostly, at 800 °C, or completely, at 1200 °C, α-$Al_2O_3$ and Al(Si) alloy), it is reasonable to compare their properties mainly based on porosity and microstructure. The finer microstructure brings to an increase of the hardness mean value of the composites.

Finally, the composites obtained at 800 °C for 6 h from the bar-shaped preforms were submitted to the second infiltration step to obtain the intermetallic/ceramic co-continuous composites. During this second process, the samples remained at 1700 °C for 30 min: all the residual transition $Al_2O_3$ present transformed in the α-phase and the crystals assumed a rounder shape. Looking at the SEM images reported in Figure 6, the NiAl(Si)/$Al_2O_3$ composites obtained show a very similar microstructure in shape to those obtained from 1200 °C derived composites, but with a finer network size. The mean grain size obtained from samples prepared at 800 °C is around 5 μm, while the samples prepared at 1200 °C present a mean grain size around 10 μm. The lighter phase is NiAl(Si) while the darker one is the ceramic phase [16,31].

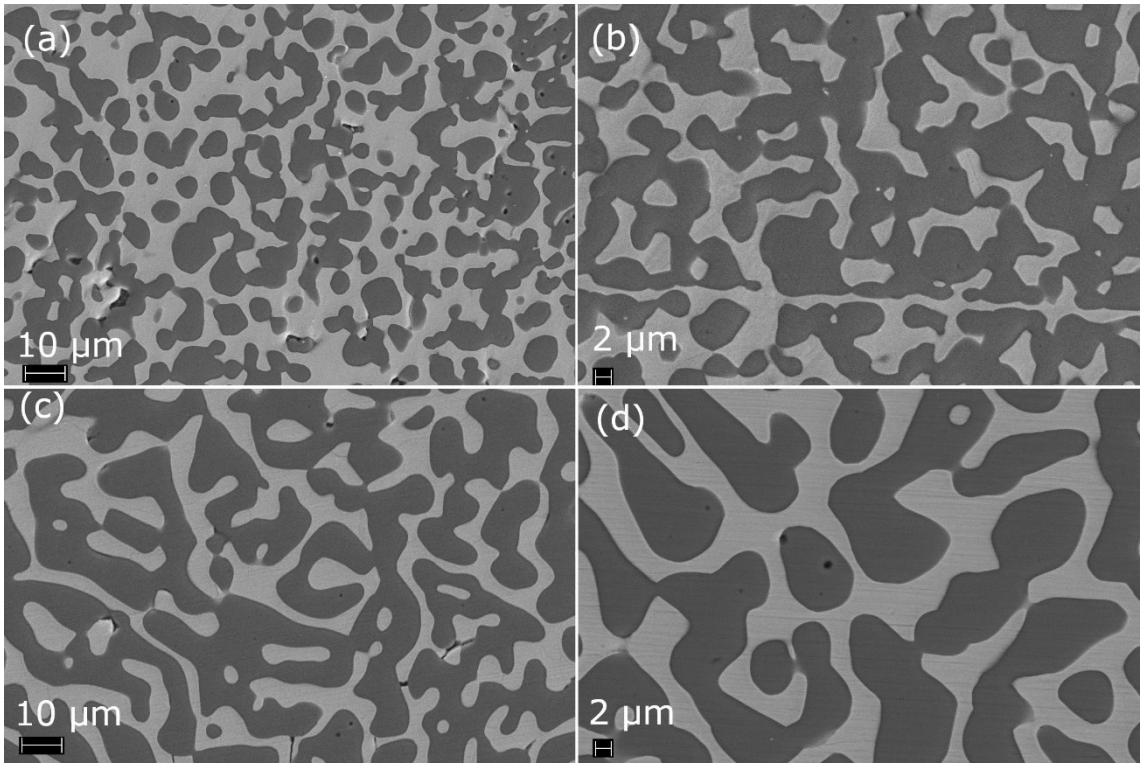



**Figure 6 - Microstructure of composites after the second high temperature infiltration step with Ni powder: comparison of different networks size between NiAl(Si)/$Al_2O_3$ derived from Al(Si)/$Al_2O_3$ composites obtained at 800 °C (a,b) and 1200 °C (c,d).**

Hence, we can deduce that starting from a finer ceramic structure will bring to a finer intermetallic-ceramic interpenetrated grains. This consideration is confirmed by the microhardness tests: the mean value exhibits a small increase from 990 to 1070 HV.

As discussed in the introduction, the literature on these composites is not very large. The microstructure obtained in this work is similar to the one observed by Del Rio et al. [15], the only authors who prepared intermetallic/ceramic composites with a method similar to the one proposed in this paper. Claussen et al. [19] obtained also analogous microstructures, but they reacted powders of aluminum with other oxides in presence of $Al_2O_3$. Other authors [20-23, 26] obtained instead microstructures closer to a standard composite with high ceramic content, with limited evidence of a co-continuous structure. Moreover, since the interest of most of these authors was in toughening ceramics, no

hardness value was given. Hardness was measured by Schicker et al. [24], who obtained higher hardness values (around 14-17 GPa) for Ti-Al and Nb-Al systems and lower values (0.5-0.6 GPa) for the Fe-Al system. The Fe-Al system was also explored by Subramanian et al. [25], who also obtained smaller hardness (300-400 HV). The Ti-Al system was studied by Han et al. [27] who obtained hardness in the 12-15 GPa range. In all cases, however, the preparation procedure was different, since Subramanian worked on Fe-Al-$Fe_2O_3$ precursors, cold-pressed and heat treated, while Schicker used an attrition milled MeO-Al powder mixture, where Me was Ti, Nb or Fe, again cold pressed and then heat treated. Han used a hot-pressing approach on high-energy milled powders.

Thus, it is difficult to properly compare these composites with the literature. The lack of significant It seems however that an approach that avoids high energy milling or hot pressing can be interesting for obtaining composites with interpenetrating network and high melting point, as the NiAl(Si)/$Al_2O_3$.

## Conclusions

In this work co-continuous NiAl(Si)/$Al_2O_3$ composites were produced by a two-step reactive infiltration technique, consisting first in an infiltration of an amorphous silica preform with liquid Al and then by a second infiltration step with nickel at a temperature higher than the NiAl melting point.

In the first part of the work, the infiltration kinetics of the silica preform with aluminum was studied at low temperature, in the range 700-1000 °C. It was observed that a maximum value of the infiltration rate occurs at 800 °C, confirming literature data. This is due to the fact that up to 800 °C transition alumina forms during the reaction between molten Al and the silica preform. At higher temperature α-$Al_2O_3$ forms, and the

infiltration rate slows down; an infiltration temperature of 1200 °C is required to obtain again high infiltration rates. The microstructure immediately after reaction with molten Al at 800 °C is characterized by submicrometer-sized grains of transition $Al_2O_3$ and Al(Si) alloy. Islands of micrometer-sized co-continuous structure of α-$Al_2O_3$ and Al(Si) alloy are also observed. After a few hours at 800 °C however, the transition alumina slowly converts to the α phase, but the microstructure size remains smaller than the one obtained by an infiltration at 1200 °C, providing a small increase in hardness.

In the second part of the work, silica samples were infiltrated first with liquid aluminum at 800 °C for 6 hours, obtaining an Al(Si)/$Al_2O_3$ composite. Then, in a second step of reactive infiltration, at 1700 °C, the aluminum-silicon alloy was replaced by a NiAl(Si) intermetallic by contacting the composite with nickel. The samples obtained from the Al(Si)/$Al_2O_3$ composites made at 800 °C present, after transformation in intermetallic/ceramic composites, a finer microstructure in comparison to the ones derived from the Al(Si)/$Al_2O_3$ at 1200 °C. The smaller grain size is reflected in a small increase of hardness.

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