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Reactive melt infiltration as synthesis route for enhanced SiC/CoSi₂ composite materials for advanced armor systemsMario Caccia¹, Chongchen Xiang², Javier Narciso^{1,*}, Nikhil Gupta²¹Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain²Composite Materials and Mechanics Laboratory, Mechanical and Aerospace Engineering Department, Tandon School of Engineering, New York University, Brooklyn, NY 11201, USA

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Abstract: Advanced ceramics such as silicon carbide (SiC) have shown an excellent performance under impact loading, and given their low density, they have attracted attention to be used in personal armor as well as in vehicles. Sintered SiC presents, nevertheless, an elevated cost which is a direct consequence of the severe temperature and pressure conditions required to sinter it. Reactive melt infiltration is a more cost-effective way to obtain SiC-based materials. It is a pressureless technique that requires much lower temperatures (1450-1600 °C) and provides extra near-net shape capabilities, thus reducing the processing cost of the final material. The main disadvantage of this technique is that the final material presents a variable content of unreacted Si in its microstructure (5-25 vol.%). Due to its lower mechanical properties Si usually hinders the overall performance of the material. The replacement of the unreacted Si phase in SiC-based composites produced by reactive melt infiltration remains one of the biggest challenges that limits the applications of such materials. In this work, an alternative route is proposed, using Si-rich Si-Co alloys as infiltrants to replace the weaker Si phase with a tougher CoSi₂ phase. The thermo-mechanical properties of the produced composites have been measured and correlated to its microstructure. The presence of CoSi₂ showed up to 200% improvement in the impact performance of the composites.

Keywords: SiC, CoSi₂, reactive infiltration, High-strain rate compression, SHPB test

1. Introduction

Lightweight, SiC-based composites are promising materials to be used in advanced armor systems because of their high specific strength. SiC-based composites are already being used for personal and vehicle ballistic protection [1-4]. Due to their low density and high-strength, these kinds of composites show great promise for aerospace applications as well, where they could act as shields to protect vehicles against micrometeoroid and other particles impact. Furthermore, the high oxidation resistance of most SiC-based composites could lead to reusable materials that could withstand the atmosphere reentry process that involves high

temperatures and moderate pressures [5]. Sintered SiC has proven to provide outstanding impact resistance [6,7] but it is a high-cost product that can only be produced in limited geometries due to the severe sintering conditions required ($>1800\text{ }^{\circ}\text{C}$, $10\text{-}40\text{ MPa}$) [8-12]. SiC-based materials produced by reactive infiltration, also known as reaction bonded silicon carbide (RBSC), pose a more cost-effective alternative as they are produced at lower temperatures ($1450\text{-}1600\text{ }^{\circ}\text{C}$) and without the need to apply an external pressure [13-17]. Furthermore, this method provides near-net shape capabilities that make it possible to produce any desired geometry. The main drawback of these materials is that they present a variable content of unreacted Si inherent to the synthesis method. As discussed by Medvedovski [1,2], the superior ballistic performance of hot pressed SiC compared to RBSC is due to the differences in the fracture mechanism associated to their different microstructures. In RBSC, fracture occurs along the weaker Si face, resulting in an heterogeneous mixture of fine powder and chunks after failure. In hot pressed SiC, fracture occurs along the grain boundary of fine microcrystalline SiC, yielding a better ballistic performance due to the higher energy required for the fracture to progress through SiC compared to Si. For this reason, the replacement of the remaining Si phase in SiC-based composite materials obtained by reactive infiltration is a critical factor limiting the applications of these materials and remains an unsolved challenge. Since Si possesses inferior mechanical properties than SiC, it compromises the overall mechanical performance of the composite. The replacement of this phase with intermetallic compounds like MoSi_2 , WSi_2 or CrSi_2 has received attention in the development of structural ceramic matrix composites for extremely high-temperature applications [18-20]. These materials possess very high melting points (2030 , 2160 and $1570\text{ }^{\circ}\text{C}$, respectively) and deform plastically at high-temperature (above $900\text{ }^{\circ}\text{C}$ for MoSi_2 and WSi_2 and above $800\text{ }^{\circ}\text{C}$ for CrSi_2) [19]. The main drawback of these structural silicides is that they present poor ductility and toughness at room temperature, most likely due to their complex crystalline structure (tetragonal for MoSi_2 and WSi_2 and hexagonal for CrSi_2). In this context, the use of cobalt disilicide (CoSi_2) as structural silicide is interesting because, with its cubic (CaF_2) structure, it exhibits higher toughness at room temperature and might even present some ductility [21]. With a melting point of $1380\text{ }^{\circ}\text{C}$, it is still an excellent candidate for high-temperature structural applications because of its low density (4.95 g/cm^3) and because of high-temperature ductility (above $800\text{ }^{\circ}\text{C}$). Besides its superior mechanical properties compared to Si, CoSi_2 exhibits an excellent oxidation resistance to that competes with other high-temperature silicides like MoSi_2 [19]. In addition, it has been demonstrated that liquid Si-rich Si-Co alloys exhibit a high enough Si activity to

form SiC when in contact with C, thus resulting in spontaneous wetting and infiltration of C-containing porous materials, like other Si-Me (Me= Fe, Ni, Al) alloys [22-27].

In this work, the remaining Si in SiC_p/Si composites has been partially replaced by a tougher CoSi₂ phase by using Si-Co alloys as infiltrants. Different alloy compositions around the eutectic point (62.5 wt.% Si) have been used. The microstructure of the materials was investigated by scanning electron microscopy (SEM) and the different phases were identified both by energy dispersive spectroscopy (EDS) and X-ray Diffraction (XRD). The thermo-mechanical properties of the materials were characterized by thermomechanical analysis (TMA) and by 3-point bending test. The performance of the composites under impact loading was characterized by means of high strain rate compression (HSR) tests performed using a split-Hopkinson pressure bar setup with a high-speed camera attached to it to observe failure of the specimens.

2. Experimental

The composite materials were produced by infiltrating SiC_p/C porous preforms with Si-Co alloys (Si, Si90Co10, Si75Co25 and Si62.5Co37.5) using the setup shown in **Fig. 1a**. Reaction was carried out at 1450 °C using a heating rate of 3 °C/min and a holding time of 1 h in a low vacuum atmosphere (10^{-2} - 10^{-3} mbar).

The as-produced materials were characterized using SEM and XRD. The bending strength was evaluated using the 3-point bending test and the compressive behavior was evaluated using the quasi-static and the high-strain rate (HSR) compressive test as per the test scheme shown in **Fig. 1b**. A more detailed description of the setup used can be found elsewhere [28,29]. It must be noted that the HSR compression testing provides a much more realistic approach to characterize the impact response of materials than quasi-static compression. The fracture of the specimens was observed using a high-speed camera and the fracture surface was analyzed using SEM. The CTE of the composites was estimated using the rule of mixtures and was experimentally measured using TMA as per the procedure documented in [30].

Fig. 1 (a) Setup used for the reactive infiltration experiments comprising a BN-coated alumina crucible on which the preform and the alloy were placed and (b) Schematic representation of the Split-Hopkinson bar device used for HSR compressive tests.

3. Results and Discussion

3.1 Alloy characterization

Alloys were in-house prepared by melting the pure components on a BN-coated graphite cylindrical crucible under inert atmosphere (Ar). **Table 1** summarizes the nominal and experimental compositions for all the alloys prepared in this work. Nominal compositions were obtained by weighting the single pure components before melting, and experimental compositions were derived from EDX analysis of 5 SEM images of polished cross-sections of each alloy. The differences observed in some specimens are mainly attributed to Si evaporation during melting of the alloy. **Fig.2** shows representative SEM images of polished cross-sections of the different alloys prepared. The microstructures comprise a mixture of pre-eutectic Si large crystals (dark grey) embedded in a eutectic aggregate (Si+CoSi₂) of smaller grain size (dark and light grey). The composition corresponding to the eutectic point (Si_{62.5}Co_{37.5}) shows a microstructure almost free of Si crystals, confirming that the experimental composition is very close to the nominal one.

Table 1. Nominal and experimental compositions for all Si-Co alloys prepared in this work. Experimental composition was determined with SEM-EDX.

Alloy	Nominal composition (wt.%)		Experimental composition (wt.%)	
	Si	Co	Si	Co
Si62.5Co37.5	62.71	37.29	62.43	37.57
Si62.5Co37.5	62.60	37.40	64.61	35.39
Si62.5Co37.5	63.20	36.80	63.65	36.35
Si75Co25	75.17	24.83	74.37	25.63
Si75Co25	75.03	24.97	68.86	31.14
Si90Co10	90.00	10.00	89.69	10.31
Si90Co10	89.97	10.03	85.95	14.05

Fig.2 Representative SEM images of polished (a) Si90Co10, (b), Si75Co25 and (c) and Si62.5Co37.5 alloys.

The toughness of the different alloys was qualitatively assessed using the Vickers microindentation test. **Fig.3** shows optical micrographs of the impression after indentation. From left to right, the impressions were made in pure CoSi_2 , Si62.5Co37.5 alloy, Si75Co25

alloy and pure Si. There is a clear increase in toughness with the relative amount of CoSi_2 in the alloy characterized by the decrease in radial crack density around the impression.

Fig. 3 Vickers microindentation test on Si-Co alloys with different Si content. From left to right pure CoSi_2 , $\text{Si}_{62.5}\text{Co}_{37.5}$, $\text{Si}_{75}\text{Co}_{25}$ and pure Si.

3.2 SiC_p/C preform characterization

SiC_p/C preforms were kindly supplied by Petroceramics [3], and they consist of a bimodal mixture of α -SiC particles (280 and 1000 FEPA grain size which is equivalent to 36.5 and 4.5 μm , respectively) bonded by a carbon matrix. These preforms were made by mechanically mixing α -SiC (black SiC, 99.5% SiC + oxides) with 10 wt.% phenolic resin. The mixture was uniaxially pressed at 140 MPa and 150 $^{\circ}\text{C}$ to promote cross-linking of the resin. After that, the pressed mixture was pyrolyzed under a nitrogen atmosphere at 700 $^{\circ}\text{C}$. Samples were supplied in the shape of bars with dimensions of 50 $\times$ 8 $\times$ 4 mm³. **Table 2** summarizes the results of the characterization of the preform.

Table 2. Results of the characterization of the SiC_p/C preform.

Composition (wt. %)		Bulk density (g/cm ³)	Density* (g/cm ³)	Porosity (Vol.%)	D ₅₀ ** (μm)
α -SiC	C				
95.30	4.70	2.10-2.20	3.10	30	1.30

*Density is measured by Helium pycnometry

**D₅₀: Average pore diameter measured by Hg porosimetry

The composition was obtained by thermogravimetric analysis (TGA) in oxidizing atmosphere ($\text{N}_2:\text{O}_2 = 4:1$) in the range 25-800 $^{\circ}\text{C}$. XRD indicated that α -SiC is the only crystalline phase present in the preform (**Fig. 4a**), exhibiting a mixture of the 4H and 6H polytypes. The bulk density of the preform ranges from 2.10-2.20 g/cm³, while the density measured by helium pycnometry is 3.10 g/cm³. Considering these density values, open porosity was calculated to be around 30%. **Fig. 4b** shows an optical micrograph of a polished cross-section of the preform, where the α -SiC phase is depicted in white, the C phase in grey and the porosity in black. A random distribution of the phases and the porosity is clearly observed. Mercury

porosimetry showed a narrow pore size distribution around a pore size of 1 μm ($P = 1$ MPa). The intrusion curve and the pore size distribution derived from it are shown in **Fig. 4c**.

Fig.4 (a) XRD pattern for the SiC_p/C preform, (b) optical microscopy image of a polished cross-section of the SiC_p/C preform, and (c) intrusion curve and pore size distribution obtained from mercury porosimetry.

3.3 $\text{SiC}_p/\text{Si-CoSi}_2$ composite materials

Infiltration of the SiC_p/C preforms proceeded spontaneously and full infiltration was achieved within 1 hour dwell time at 1450 $^{\circ}\text{C}$. The density of the infiltrated specimens varies from 2.8-3.1 g/cm^3 depending on their CoSi_2 content. Residual open porosities between 2-5% were estimated based on density measurements. **Fig.5** shows representative SEM backscattered electron images of polished cross-sections of the different composite materials with their corresponding XRD patterns. Si, CoSi_2 and α -SiC are the only phases identified, and no unreacted carbon was observed or detected. Dense microstructures are observed in all cases, and random distribution of the CoSi_2 phase is found. The size of the CoSi_2 and Si domains vary depending on their relative content. Nevertheless, the size of those phases is rather large in all materials, being several orders of magnitude higher than the size of the reinforcement (α -SiC). In the case of the $\text{SiC}_p/\text{Si}62.6\text{Co}37.5$ there are areas which consist of only CoSi_2 and

SiC (see **Fig.5**). No phase debonding is observed between any of the phases in spite of the difference in CTE between the CoSi_2 and the $\alpha\text{-SiC}$ phase [31,32]. All this suggests that the composites should be machinable using electro discharge machining, since they are dense enough and all the phases have electrical resistivities within the operational range of an EDM machine [33,34].

Fig. 5 Representative SEM images of polished cross-sections of the different composite materials and their corresponding XRD pattern. The materials were obtained with (a) Si90Co10 alloy, (b) Si75Co25 alloy and (c) Si62.5Co37.5 alloy respectively.

3.4 Thermomechanical properties of the composites

The rule of mixtures provides a first-order approximation for the calculation of the CTE of a composite material. It can be expressed as

$$CTE_C = V_p \cdot CTE_p + (1 - V_p) \cdot CTE_m \quad (1)$$

where CTE_C , CTE_p and CTE_m are the coefficient of thermal expansion of the composite, the reinforcement (α -SiC) and the matrix respectively (Si-Co alloys), and V_p is the volume of particle reinforcement ($V_p = 0.7$). The CTE of the matrix, in this case the different Si-Co alloys, can also be estimated using a similar expression considering the different phase contents that can be estimated using the lever rule from the phase diagram. The values of CTE of the pure phases used are provided in **Table 3**, where the values for Si and SiC have been measured in this work.

Table 3. CTE values of the different phases at room temperature.

Phase	CTE ($\times 10^{-6} \text{K}^{-1}$)
Si	1.96
SiC	2.00
CoSi ₂	14.4 [29]

Fig. 6a shows the measured CTE values for the different composites as a function of the Si content in the matrix (dots) and the theoretical value of the CTE of the composites calculated using the rule of mixtures (dashed line). Even though the rule of mixtures is a simplified model which does not consider the thermoelastic deformations that occur in the composite as other more complex models like the Kerner [35] or Schapery [36] models, in this case, where the elastic modulus and Poisson's ratio of the different phases are similar [37], it provides an adequate description of the thermal response of the system. The CTE at room temperature for all composites containing CoSi₂ falls in the range of $1.6\text{-}3.6 \times 10^{-6} \text{K}^{-1}$, which remains lower than most metal superalloys used for high-temperature applications [38]. CTE is a critical parameter for aerospace applications, as these materials are often subjected to numerous thermal cycles e.g. the international space station will undergo around 175,000 thermal cycles from 125 °C to -125 °C during its 30-year life as it moves in and out of Earth's shadow [39].

Fig. 6b shows the thermal response curve (after 3 cycles from 25-900°C) obtained from the TMA for the SiC/Si and the SiC/Si62.5Co37.5 composites. The absence of a hysteresis cycle

suggests excellent thermal compatibility between the phases and that no residual stresses are being developed upon thermal cycling. This is in good agreement with the microstructural analysis that shows no signs of phase debonding.

(a)

(b)

Fig. 6 (a) CTE of the different composites measured in this work (dots) and the calculated CTE using the rule of mixtures (dashed line), (b) Thermal response curve for the SiC/Si and SiC/Si62.5Co37.5 composites obtained from the TMA. The error bars represent the experimental error of the measurement.

Fig. 7a shows the bending strengths measured for the different composite materials. An initial decrease in bending strength is observed when introducing Co in the infiltrating alloy compared to pure Si. However, the bending strength increases for higher contents of CoSi₂ in

the material. This could be attributed to the formation of large pre-eutectic Si domains that promote crack propagation along the large grain boundary decreasing bending strength. **Fig. 7b** shows the bending strength of the materials vs. the content in pre-eutectic Si, where a direct relation between both parameters is clearly observed. Although the Si phase has been partially replaced by the tougher CoSi_2 phase, fracture in these materials remains dominated by the presence of Si along which cracks progress. However, the results show clearly that increasing the content in CoSi_2 has a beneficial impact on the bending strength of the composite. A more detailed study with other Si-Co alloy compositions, which is outside the scope of this work, would be necessary to fully replace the Si phase

(a)

(b)

Fig. 7(a) Bending strength calculated from 3-point bending test for all composites. **(b)** Bending strength vs. content in pre-eutectic Si for the different composite materials. Error bars indicate standard deviation.

Based on these results, only the compressive behavior of the sample produced with the eutectic alloy (SiC/Si62.5Co37.5) and pure Si(SiC/Si) will be discussed.

3.5 HSR compression behavior of the composites

High strain rate compressive tests were conducted using a split-Hopkinson pressure bar system. The strain rate developed is not only a function of the gas pressure but depends also on the size and material of the specimen, which makes it rather difficult to directly control all the parameters. Therefore, the strain rate is recovered from the test results. Strain rates between $500\text{--}1500\text{ s}^{-1}$ were achieved in the present tests. Low strain rates of the order of $10^{-3}\text{--}10^{-1}\text{ s}^{-1}$ can be achieved in tension or compression using a universal testing machine. However, intermediate strain rates, namely values between $10\text{--}500\text{ s}^{-1}$, are much more difficult to obtain [40,41]. The drop-weight and pendulum tests may be located in the range of intermediate strain rate, but they do not provide full stress-strain response curves which are of great interest in strain rate-dependant material's modeling [41]. One of the most challenging aspects of using the SHPB method for testing materials is achieving accurate measurements of the different mechanical parameters (elastic modulus, peak stress, strain-to-failure). In order to obtain significant values of these parameters, it is necessary to have a homogeneous distribution of stress within the sample during the whole test and to achieve a constant strain rate. Because ceramic materials and ceramic composites fail catastrophically in a few microseconds and because a constant strain rate is usually achieved only around failure, the measured elastic moduli are considered not realistic and will not be discussed. The peak stress and the strain-to-failure values, however, are obtained within constant strain rates as shown in **Fig. 8a**, guaranteeing their accuracy. **Fig. 8a** shows, as an example, the strain vs. stress curve obtained for the SiC/Si62.5Co37.5 sample under high strain rate loading and the strain vs. strain rate for the same specimen. **Fig. 8b** shows the calculated stress in the front and back faces of the specimen. The coincidental curves indicate a homogeneous distribution of stress within the specimen during the whole experiment. The material shows a pure brittle behavior with failure occurring during the elastic regime and no evidence of ductile deformation.

Fig. 8 (a) Stress vs. strain and strain vs. strain rate curves for the SiC/Si62.5Co37.5 sample and (b) front and back stress in the specimen.

Failure of brittle materials like ceramics and ceramic-based composites under compressive loading is intimately associated to initial microcracking at defects in the microstructure like pores, inclusions, reinforcement or grain boundaries [42-44]. It was stated by Lankford that the compressive strength of ceramics and ceramic composites is strain-rate-dependent at strain rates above a certain critical value of strain rate [43]. In the case of sintered α -SiC, a HSR sensitivity in compressive strength is observed above 10³ s⁻¹ strain rate [43].

Most ceramics' compressive strengths at low strain rates follow a law according to

$$\sigma_c \propto \dot{\epsilon}^{\frac{1}{1+n}} \quad (2)$$

where σ_c is the compression strength, $\dot{\epsilon}$ is the strain rate and n is the stress intensity exponent in the macroscopic tensile crack velocity relationship, varying from 50-200 [43]. This equation describes a relatively strain rate-insensitive process controlled by thermally-activated growth of microcracks. At higher strain rates, this equation differs in a great manner from the experimental values, and it was proposed by Grady et al. [45] that the compressive strength at high strain rates for ceramics correlates better to an expression like

$$\sigma_c \propto \dot{\epsilon}^{1/3} \quad (3)$$

Fig. 9a shows the compressive strength measured for the SiC_p/Si composite samples at different strain rates. The compressive strengths measured for the SiC/Si composites are inferior to those reported for hot pressed SiC because of the presence of Si in the RBSC specimens as previously discussed. However, the behavior observed is similar to the one described for sintered α -SiC [42]. An initial rather insensitive to strain rate stage is observed, that transitions into a highly strain-rate-dependent state above 10^3 s^{-1} . Unlike for sintered α -SiC, the dependency of the compressive strength with the strain rate observed experimentally is much higher, following the expression

$$\sigma_c \propto \dot{\epsilon}^{4.5} \quad (4)$$

The lack of constitutive models for ceramic containing composite materials makes it hard to interpret this higher strain rate sensitivity and more work is needed in this field to develop analytical models to describe such materials.

For comparison, the HSR compressive stress of the SiC/Si and SiC/Si62.5Co37.5 composite materials were normalized by the quasi-static compressive stress (σ/σ_0). **Fig. 9b** shows the normalized compressive stress vs. strain rate for both materials, where the SiC/Si62.5Co37.5 clearly outperforms the pure SiC/Si composite, showing an increase in high-strain rate compressive strength up to 3 times higher compared to the low-strain rate compressive strength, whereas SiC/Si only shows an increase of only 1.5. The increase in high-strain rate compression strength can be associated to a transition from an interparticle (in low-strain rate compression) to an inter/intraparticle fracture mechanism, as evidence from the *post mortem* SEM analysis of the specimen (**Fig. 9c** and **Fig. 9d**). The better performance of the SiC/Si62.5Co37.5 samples can be directly attributed to the higher fracture toughness of the CoSi₂ phase that replaced the Si. Since, almost all Si content is replaced at this composition level, further increase in the Co content is not expected to continue the trend of improvement in properties. It is evident from Fig. 9c that the cracks tend to bend around the particles and propagate primarily in the matrix, which results in lower mechanical properties. Increase in

the strain rate changes the deformation and failure mechanisms and transgranular failure is observed in Fig. 9d, where the crack propagates through the particles that have higher mechanical properties and the material demonstrates improved strength. Similar transition in failure mechanism at high strain rates has been observed in other particulate composites [28].

Fig. 9 (a) Normalized compressive strength vs. strain rate for the SiC/Si and (b) SiC/Si62.5Co37.5 composites, (c) SEM image of a fracture surface of a SiC/Si62.5Co37.5 after low-strain rate compression and (d) after high-strain rate compression.

Conclusions

SiC_p/Si-CoSi₂ composite materials were successfully synthesized by reactive melt infiltration of Si-Co alloys into SiC_p/C preforms. The microstructure and mechanical properties of the different composites were analyzed and correlated, where substantial evidence is provided to assure that the introduction of CoSi₂ in these composites can improve the mechanical performance of the material, especially under impact loading, where the compressive strength under high-strain rate increases up to 200% for the composites

containing CoSi_2 . The thermal expansion behavior of the composites has been investigated, and the results show an excellent thermal compatibility between the different phases, yielding CTEs between $2\text{--}4 \cdot 10^{-6} \text{ K}^{-1}$.

The combination of the properties measured for these composites makes them ideal candidates for next generation advanced protection systems of both ground and aerospace vehicles.

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References

- [1] E. Medvedovsk, Ballistic performance of armour ceramics: Influence of design and structure. Part 1, *Ceram. Int.* 36 (2010) 2103-2115.
- [2] E. Medvedovsk, Ballistic performance of armour ceramics: Influence of design and structure. Part 2, *Ceram. Int.* 36 (2010) 2117-2127.
<http://www.petroceramics.com/index.php/markets/security-defence>
- [4] US patent, US 4876941 A, Composite for protection against armor-piercing projectiles (1989).
- [5] H. Hermann, Operational limits for reusable space transportation systems due to physical boundaries of C/SiC materials, *Aerosp. Sci. Technol.* 7 (2003) 551-559.
- [6] J. Lankford, Mechanisms responsible for strain-rate-dependent compressive strength in ceramic materials, *J. Am. Ceram. Soc.* 64(1981) 33-34.
- [7] J. Lankford, C.R. Blanchard, Fragmentation of brittle materials at high rates of loading, *J. Mater. Sci.* 26 (1991) 3067-3072.
- [8] M. Srinivasan, *Structural Ceramics*. London, Academic Press, 1989.
- [9] S. Prochazka, R.M. Scanlan, Effect of boron and carbon on sintering of SiC, *J. Amer. Ceram. Soc.* 58 (1975) 72.
- [10] F. Lange, T.K. Gupta, Sintering of SiC with boron compounds, *J. Amer. Ceram. Soc.* 59 (1976) 537-538.

- [11] J. Lis, Y. Miyamoto, R. Pampuch, K. Tanihata, Ti₃SiC-based materials prepared by HIP-SHS techniques, *Mater. Lett.* 22 (1995) 163-168.
- [12] E. Gomez, J. Echeberria, I. Iturriza, F. Castro, Liquid phase sintering of SiC with additions of Y₂O₃, Al₂O₃ and SiO₂, *J. Eur. Ceram. Soc.* 24 (2004) 2895–2903.
- [13] J.N. Ness, T.F. Page, Microstructural evolution in reaction-bonded silicon carbide, *J. Mater. Sci.* 21 (1986) 1377-1397.
- [14] A.J. Whitehead, T.F. Page, Fabrication and characterization of some novel reaction-bonded silicon carbide materials, *J. Mater. Sci.* 27 (1992) 839-852.
- [15] J.N. Ness, T.F. Page, The structure and properties of interfaces in reaction-bonded silicon carbides. In: R.E. Tressler, G.L. Messing, C.G. Pantano, R.E. Newnham, editors. *Tailoring Multiphase and Composite Ceramics*, Boston: Springer, 1986.
- [16] M. Caccia, J. Narciso, SiC manufacture via reactive infiltration. In: John Wiley & Sons, editors. *Processing and Properties of Advanced Ceramics and Composites VI: Ceramic Transactions*. Wiley, 2014.
- [17] M. Caccia, J. Narciso, Production of SiC materials by reactive infiltration, *Mater. Sci. Forum* 783-786 (2014) 1863-1866.
- [18] R. Arpón, J.F. Narciso, F. Rodríguez-Reinoso, M. Komatsu, Synthesis of mixed disilicides/SiC composites by displacement reaction between metal carbides and silicon. *Mater. Sci. Eng. A* 380 (2004) 62-66.
- [19] D.M. Shah, D. Berczik, D.L. Anton, R. Hecht, Appraisal of other silicides as structural materials, *Mater. Sci. Eng. A* 155 (1992) 45-57.
- [20] J.F. Narciso-Romero, R. Arpón-Carballo Synthesis of a (MoSi₂, Mo₅Si₃)/SiC composite using an in situ solid-state displacement reaction between Mo₂C and Si, *J. Ceram. Soc. Jap.* 108 (2000) 957-959.
- [21] K. Ito, H. Inui, T. Hirano, M. Yamaguchi, Room temperature deformation of CoSi₂ single crystals, *Mater. Sci. Eng. A* 152 (1992): 153-159.
- [22] M. Caccia, S. Amore, D. Giuranno, R. Novakovic, E. Ricci, J. Narciso, Towards optimization of SiC/CoSi₂ composite material manufacture via reactive infiltration: Wetting study of Si–Co alloys on carbon materials, *J. Eur. Ceram. Soc.* 35(2015) 4099-4106.
- [23] A. Camarano, M. Caccia, J.M. Molina, J. Narciso, Effects of Fe addition on the mechanical and thermo-mechanical properties of SiC/FeSi₂/Si composites produced via reactive infiltration, *Ceram. int.* 42 (2016) 10726-10733.
- [24] O. Coloma-Esteban, M. Caccia, A. Camarano, J. Narciso, Manufacture of SiC/ZrSi₂ composite materials: assessing thermal compatibility between matrix and reinforcement. In:

Advances in High Temperature Ceramic Matrix Composites and Materials for Sustainable Development. Ceramic Transactions, Wiley: 2017.

- [25] R. Voytovych, V. Bougiouri, N.R. Calderon, J. Narciso, N. Eustathopoulos, Reactive infiltration of porous graphite by NiSi alloys, *Acta Mater.* 56 (2008) 2237-2246.
- [26] N.R. Calderon, R. Voytovych, J. Narciso, N. Eustathopoulos, Wetting dynamics versus interfacial reactivity of AlSi alloys on carbon, *J. Mat. Sci.* 45 (2010) 2150-2156.
- [27] N.R. Calderon, R. Voytovych, J. Narciso, N. Eustathopoulos, Pressureless infiltration versus wetting in AlSi/graphite system, *J. Mat. Sci.* 45 (2010) 4345-4350.
- [28] D.D. Luong, O.M. StrbikIII, V.H. Hammond, N. Gupta, K. Choc, Development of high performance lightweight aluminum alloy/SiC hollow sphere syntactic foams and compressive characterization at quasi-static and high strain rates, *J. Alloys Compd.* 550 (2013) 412-422.
- [29] E. Woldeesenbet, N. Gupta, A. Jadhav, Effects of density and strain rate on properties of syntactic foams, *J. Mater. Sci.* 40 (2005) 4009-4017.
- [30] R. Arpón, J.M. Molina, R.A. Saravanan, C. García-Cordovilla, E. Louis, J. Narciso, Thermal expansion behaviour of aluminium/SiC composites with bimodal particle distributions. *Acta Mater.* 51 (2003) 3145-3156.
- [31] D. Smeets, G. Vanhoyland, J. D'Haen, A. Vantomme, On the thermal expansion coefficient of CoSi_2 and NiSi_2 , *J. Phys. D: Applied Physics*, 42 (2009) 235402.
- [32] K. Schmidt, C. Zweben, R. Arsenault, ASTM special technical publication, Philadelphia, PA, no 1080. 1990.
- [33] C.D. Lien, M. Finetti, and M.A. Nicolet, Electrical properties of thin Co_2Si , CoSi and CoSi_2 layers grown on evaporated Si, *J. Electr. Mater.*, 13 (1984) 95-105.
- [34] S. Grasso, T. Saunders, H. Porwal, B. Milsom, A. Tudball, M. Reece, Flash spark plasma sintering (FSPS) of α and β SiC, *J. Am. Ceram. Soc.* 99 (2016) 1534-1543
- [35] E.H. Kerner, Effective moduli calculations of isotropic composites, *Proc. Phys. Soc. Lond. B* 69 (1956) 808.
- [36] R.A. Schapery, Thermal expansion coefficients of composite materials based on energy principles, *J. Comp. Mater.* 2 (1968) 380-404.
- [37] M. Nakamura, Elastic constants of some transition-metal-disilicide Single Crystals, *Metal Mater. Trans. A* 25A (1994).
- [38] P. Hidnert, Thermal expansion of some nickel alloys, *J. Res. Nat. Bur. Stand.* 58 (1957) 89-92.
- [39] S. Rawal, Metal-matrix composites for space applications, *JOM*, 53 (2001) 14-17.

- [40] N.Gupta, D.D. Luong, P.K. Rohatgi, A method for intermediate strain rate compression testing and study of compressive failure mechanism of Mg-Al-Zn alloy, *J. App. Phys.* 109 (2011) 103512.
- [41] B. Song, W.W. Chen, W.Y. Lu, Mechanical characterization at intermediate strain rates for rate effects on an epoxy syntactic foam, *Int. J. Mech. Sci.* 49 (2007) 1336–1343.
- [42] G. Ravichandran, G. Subhash, A micromechanical model for high strain rate behavior of ceramics, *Inter. J. Sol. Struct.* 32 (1995) 2627-2646.
- [43] J. Lankford, Mechanisms responsible for strain-rate-dependent compressive strength in ceramic materials, *J. Am. Ceram. Soc.* 64 (1981) 33-34.
- [44] J. Lankford, High strain rate compression and plastic flow of ceramics, *J. Am. Ceram. Soc.* 15 (1996) 745-750.
- [45] D.E. Grady, Shock properties of high-strength ceramics. *Constitutive Laws: Experiment and Numerical Implementation*, In: *Proceedings of the second international conference on structural stability and dynamics*. Singapore, World Scientific, 2002.