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Joining of SiC, alumina and mullite by the Refractory Metal (RM) – Wrap pressure-less process

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Abstract

The aim of this work is to discuss the suitability of the joining process called "RM-Wrap" (RM= Refractory Metals, i.e. Mo, Nb, Ta, Zr) as a pressure-less and tailorable technique to join several different ceramics such as SiC, alumina and mullite ($3Al_2O_3 \cdot 2SiO_2$). In the RM-Wrap joining technique the refractory metal foil is used as a wrap containing one or more silicon foils. It is performed at 1450 °C, under flowing argon, and the resulting joining materials are in-situ formed composites made of refractory metal disilicides ($MoSi_2$, $NbSi_2$, $TaSi_2$ or $ZrSi_2$) embedded in a silicon rich matrix; their coefficient of thermal expansion has been calculated and the Laser Flash Method was used to measure the thermal diffusivity of one of them ($MoSi_2$/Si) in 25-1000 °C range, then to calculate its thermal conductivity. All the obtained joints are uniform, continuous and crack free. Some preliminary oxidation tests were carried out on all joints at 1100 °C, 6 hours in air, giving unchanged morphology of the interface and the joining materials itself; the joint strength of RM-Wrap joined SiC was measured at room temperature using three different mechanical tests: (i) single lap (SL), (ii) single lap off-set (SLO) and (iii) torsion on hourglass shaped samples (THG) (on Mo-wrap joined SiC).

Keywords

RM-wrap, Pressure-less joining, SiC, alumina, mullite, shear tests, thermal properties

Introduction

SiC, alumina and mullite are stable materials for high temperature applications, with a unique combination of properties such as lightweight, high temperature stability and chemical inertness. More and more they are used in components for energy production, defense, space and many other high-performance applications

and have great potential to replace conventional materials such as metals and superalloys in many applications. [1,2]

However, the joining of ceramics to themselves or to other materials remains a critical issue. The manufacturing of net-shape and ready to use ceramic components for advanced design solutions require large and complex parts, which can be built by joining and integrating discrete units of similar or dissimilar ceramics. [3-5]

Many joining techniques have been developed so far to join similar and dissimilar ceramics, among them: Liquid Silicon Infiltration (LSI)[6], Affordable Robust Ceramic Joining (ARCJoint TM) [7], Nano-Infiltration and Transient Eutectic Phase (NITE)[8,9], Spark Plasma Sintering (SPS) [10,11], Laser [12] or Microwave- Assisted Joining[13], Solid State Displacement Reactions (SSDR)[14], Transient-Liquid-Phase Bonding (TLPB)[15], brazing and glass-ceramic based joints [16, 3] are prominent.

The "RM-Wrap" (RM= Refractory Metals, i.e. Mo, Nb, Ta, Zr) is a novel brazing technique where the refractory metal, shaped as a wrap, is used to contain one or more silicon foils. It is a pressure-less joining process performed at 1450 °C, in an inert environment (argon flow). [17-19] The wrap is necessary to prevent the too fast spreading of molten silicon and its leaking outside the joined region during the joining process. The joining materials are in-situ formed composites made of refractory metals disilicides ($MoSi_2$, $NbSi_2$, $TaSi_2$ or $ZrSi_2$) embedded in a silicon-rich matrix. Disilicides have high melting temperature and good oxidation resistance at elevated temperature, making them a suitable choice to join ceramics.

The conventional manufacturing routes for disilicides are time consuming and prone to contamination and oxidation . [20,21] On the contrary, the RM-Wrap process is quick, free from undesired phases and has excellent reproducibility and versatility [18] the quantity of each metal can be modified and more than one refractory metal can be used in the same wrap.

Metal disilicides are characterized by a wide range of interesting properties, a few of them are highlighted here. Mo-disilicides ($MoSi_2$, Mo_5Si_3 and Mo_3Si) [22] are characterized by melting points above 2000 °C and excellent oxidation and corrosion resistance at elevated temperature due to development of a thin protective coating of SiO_2. [23] The Nb-Si phase diagram is similar to the Si-Mo one, where three (Nb_5Si_3, Nb_3Si and $NbSi_2$) compounds can be formed [24] : $NbSi_2$ exhibits higher shear strength, hardness and oxidation resistance. [25] The

Ta-Si phase diagram shows the formation of four intermetallics: $TaSi_2$, Ta_5Si_3, Ta_2Si, and Ta_3Si. Among them, $TaSi_2$ has the best oxidation resistance due to the formation of a protective SiO_2 layer on its surface. [26] The Zr-Si phase diagram shows the formation of several phases and intermetallics ($ZrSi_2$ Zr_5Si_4, Zr_3Si_2, Zr_2Si, Zr_3Si) and an eutectic at 1370°C. [27]

An original joining technique called "RM-Wrap" was developed in our previous studies [17-19] as an alternative to obtain refractory-metals disilicide-based joints. The RM-Wrap technology has been effectively used to join C/SiC, SiC/SiC and SiC foam sandwich structures; in the present work this joining technique was successfully used to join different materials, namely SiC, alumina and mullite. To assess the reliability of the RM-Wrap process, joined SiC samples have been mechanically tested at room temperature using three different mechanical tests (single lap, SL, single lap off-set, SLO, and torsion on hourglass shaped samples, THG); moreover, oxidation tests on SiC joints were carried out at 1100 °C, 6 hours in air, as a preliminary test to investigate the suitability of these joints in working conditions. Furthermore, one of the RM-wrap joining material (MoSi2/Si) has been characterised by means of the laser flash method: the thermal diffusivity has been measured to calculate the thermal conductivity and specific heat of the joining material in 25-1000 °C range.

Experimental

Materials to be joined, i.e. SiC (density 3.1 g/cm^3, supplied by Bettini S.p.A, Italy; 98,5% purity), Al_2O_3 (density 3.8 g/cm^3, 99,5% purity, supplied by Accuratus, USA) and mullite (density 2.8 g/cm^3, supplied by Accuratus, USA) were cut to 10 mm x 10 mm x (3 to 5) mm, polished to 800 micron by grit paper, sonicated in ethanol, dried in air, then joined with the RM-Wrap technique.

The "RM-Wrap" technique consists in wrapping one Si foil (525±25 µm thick Virginia Semiconductor Electron-MEC s.r.l. Italy, 99.95% Si) in a refractory metal (Mo, Nb, Ta or Zr) (25.4 µm thick, Alfa Aesar Germany, 99.95%) foil folded as a wrap.

The optimized heating conditions were found to be 1450 °C, heating rate of 1000 °C/h, dwell of 5 minutes, natural cooling to room temperature under flowing argon (Carbolite, Gero, Germany), as reported in [2] for

Mo-Wrap. The joint thickness ranges withing 200-250 µm, measured *ex-post* joining. Compositions ranging between about 30-70 wt % Mo, Nb, Ta or Zr (balance to 100% with Si) have been tested to optimize each joining process.

Preliminary oxidation tests on joints obtained using Mo, Nb and Ta wrap were performed at 1100°C, 6 hours in air (with 10 °C/min heating rate and cooling in air), then their polished cross-sections were analysed.

Each joint morphology was analysed by FESEM, (QUANTA INSPECT 200, Zeiss SUPRATM 40™) equipped with Energy Dispersive Spectroscopy (EDS, EDAX PV 9900™).

The coefficient of thermal expansion (CTE) for the RM-wrap joining materials was calculated by the rule of mixture, according to their composition. The wrap joining material is composed by silicon and metal disilicides; the used compositions range between 30-70wt% for refractory metals (balance to 100% with Si). According to the joining material composition, the relative phase diagram and the density of the different phases, we calculated the fraction volume of the 2 phases (metal disilicide and silicon).

One $MoSi_2$/Si pellet of about 11.6 mm diameter and 2.6 mm thickness was prepared by grinding and sintering the same Si and Mo used to obtain the Mo-wrap joints, in the same quantity and with the same thermal treatment used to obtain the joints; the pellet density (3.24 g/cm^3) was measured by Archimede's method. The Laser Flash Method (LFA 467 HT ® Hyper Flash NETZSCH9) was used in order to evaluate the thermal properties of the $MoSi_2$/Si pellet between 25-1000 °C with 200 °C temperature steps at a heating rate of 4 °C·min^{-1}, under flowing Ar, mass flow 50 ml·min^{-1}. A specific SiC ring was designed, in order to minimize the backlash between the sample and the sample holder (12.7 mm diameter). This technique allows the direct determination of the thermal diffusivity and, through the Software Proteus®, the indirect determination of the specific heat and of the thermal conductivity, when the sample's density is known. The specific heat of the sample was determined by comparing its temperature increase with the reference material one (Poco Graphite Serial Nr. 21517) used to calculate the absorbed energy. [28,29] The thermal diffusivity is determined by a mathematical analysis of the measured temperature increase/time function, as explained by Parker et

al. [30] After measuring the thermal diffusivity (α), it is possible to evaluate the thermal conductivity (λ) as shown in Eq. 1.

$$\alpha(T)\rho(T)c_p(T) = \lambda(T) \quad (1)$$

Where c_p is the specific heat and ρ is the bulk density of the sample.

The joints were tested by single lap (SL) shear test in compression, according to [31] on five samples. The commercial Scotch-Weld DP490 epoxy adhesive was used to attach the specimens to the aluminium fixtures and cured for 45 min at 90 °C. The joined specimen size was 10 mm x 10 mm x (3 to 5) mm. Furthermore, the single lap off-set (SLO) (adapted from ASTM-D905-08 [32]) was also used to measure the joint strength of RM-Wrap joined SiC with specimen size of 5 mm x 10 mm x 5 mm (3 mm offset); with this configuration, no adhesive was necessary. The mechanical tests were performed at room temperature with a compression machine (SINTEC D/10) with a cross-head speed of 0.5 mm/min. Mo-Wrap joined SiC samples were also tested by torsion: SiC hourglass shaped samples with a circular joined area of 4 mm or 5 mm in diameter (referred to as THG-4 and THG-5, respectively) were joined one by one or machined (by Morise Ltd. Japan) to obtain THG-4 and THG-5 hourglasses from a joined 35 mm x 8 mm x 4 mm specimen. A custom-made torsional testing machine developed at Politecnico di Torino (Italy) was used to test the SiC joints in torsion. [33]

~~The X-Ray Diffraction (XRD) analysis was carried out on the fracture surfaces of each joined sample after mechanical test (X'Pert Phillips diffractometer, with Cu Kα radiation, and the XRD spectra were analyzed by using X'Pert High Score Plus software).~~

Results and discussion

Following the success of RM-Wrap in joining SiC-based composites and foams[17-19], its scope has been extended to another refractory metal (Zr) and to other substrates (silicon carbide, alumina and mullite).

The use of silicon has the dual function of providing the liquid phase necessary to wet the faying surfaces and to form the disilicides by reacting with the refractory metal. In all the cases, the joining materials were in-situ formed composites made of disilicides homogenously dispersed in a Si rich matrix. The presence of free (un-reacted) Mo, Nb, Ta or Zr must be avoided because of their poor oxidation resistance. Likewise, the presence of free silicon may be not desirable for some applications, but a certain amount of silicon was necessary to achieve a good wettability and crack-free continuous joints. In this work, the amount of free, unreacted silicon was minimized by gradually reducing its amount inside each wrap, but always trying to avoid the presence of unreacted refractory metal. The best compromise was obtained with 65-68 wt.% Si + 32-35 wt.% Mo, 67-69 wt.% Si + 31-33 wt.% Nb, 50-51 wt% Si + 49-50 wt% Ta and 71wt.% Si + 29 wt.% Zr (Si-Zr eutectic composition), respectively. A higher amount of the refractory metal resulted in an insufficient amount of silicon matrix, thus leading to discontinuous joints.

The RM-Wrap SiC-SiC joint microstructures are shown in Figure 1 (Mo-Wrap), Figure 2 (Nb-Wrap) and Figure 3 (Ta-Wrap): the round shaped disilicides particles are uniformly embedded in the Si rich matrix, which shows an excellent wettability on Mo at temperature above its melting point [34] and can easily infiltrate and hinder the formation of pores between $MoSi_2$ particles. Likewise, all the joining material/SiC interfaces are continuous, and no cracks are visible within the joint area, thus indicating that the CTE mismatch between RM silicides/Si and SiC did not affect the integrity of the joint. The joints showed an excellent wettability on SiC surfaces and continuous and robust interfaces (Figure 1-3).

As expected, the Zr-wrap joining material (Figure 4) is characterized by a typical eutectic microstructure with needle-shaped $ZrSi_2$ and Si phases, evidenced in the Si-Zr phase diagram in Figure 5. Recently, Naikade M. et al.[35] has shown that Si0.92Zr0.08 eutectic alloy has good wettability on SiC and slower spreading in comparison with the instantaneous spreading of the pure molten silicon. The same results were obtained with the Zr-wrap, with all the joining material well confined in the joined region.

The interaction of silicon carbide with refractory metals results in the formation of carbide(s) and silicide compounds, if they are more thermodynamically stable than SiC; reactions are extensive at temperature above 1000°C, as reported in[36] and the kinetics for solid state diffusion is normally fast enough at T above

1200°C.[37] In case of Nb/SiC interface, it has been reported that the typical reaction layer sequence is SiC/Nb_xSi_yC/NbC_z/NbO/Nb [38]; in fact, not only silicon and carbon can be detected on the SiC surface, but also a thin layer of SiO2. These reaction layers (carbides and silicides) have been found also by other authors at the Ta/SiC , Mo/SiC, Zr/SiC interfaces. [39,40] Nevertheless, the data reported in literature refer to temperature comparable with that used in our joining process (1450°C), but the solid-state diffusive reaction at SiC/RM interface involved dwelling time from few hours to hundreds of hours.[40,41] Moreover, the absence of applied pressure during the "refractory metal (RM) – wrap" joining process does not foster the diffusive process at the interface. Furthermore, the presence of Si at the interface can hinder the formation of carbides; for instance, in case of Mo, it has been reported [42] that Si diffuses towards Mo faster than C, thus leading to silicides formation.

In conclusion, the formation of a distinct layer of RM-carbide layer (i.e. MC_x or MSi_yC_z) was not observed up to now in our joined samples, but it cannot be ruled out that, immediately adjacent to SiC, a nano-layer of carbide exists.

In order to evaluate their oxidation resistance and thermal stability, SiC joined by Mo-, Nb- and Ta-Wraps were tested at 1100 °C for 6 hours in air; this thermal treatment simulates possible operating conditions for SiC-based components in aerospace [43] and the creep of the silicon matrix advices against their use at higher temperatures. The FESEM analysis of the cross-sections of the joints after the oxidation tests is shown in Figure 1(d) (Mo-Wrap), Figure 2(c) (Nb-Wrap) and Figure 3 (c) (Ta-Wrap).

All the joints were apparently not affected by this preliminary heat treatment, since no cracks, debonding or formation of new phases (i.e. SiO2 [44]) were observed. Actually, it was reported that $MoSi_2$ forms gaseous oxidation products and silica at 1100 °C, but none of them have been detected in this work. It is possible that a negligible silica layer was polished away during sample preparation. It must be underlined that the oxidation of $MoSi_2$ is a very complex process. In the temperature range of 375° to 600°C, MoO_3 whiskers and SiO_2 clusters will form, causing the disintegration of bulk $MoSi_2$ (pesting). At higher temperatures, MoO_3 is volatile.[45,46] However, none of these reactions were observed during Mo-wrap joining.

Mo-Wrap was successful and for the first time used to join oxide-based ceramics: alumina-to-alumina (Figure 6 a) and mullite to SiC joints (Figure 6 b).

The coefficient of thermal expansion (CTE) for the RM-wrap joining materials ($MoSi_2$/Si, $NbSi_2$/Si , $TaSi_2$/Si, and $ZrSi_2$/Si), calculated by the rule of mixture according to their composition [47] and the RM-wrap compositions (as volume ratio between RM silicides and silicon) are summarized in Table 1, also showing those of the joined materials for comparison purposes: except Ta-wrap, all the other wraps range at about 3.9 – 4.5 x 10^{-6} $°C^{-1}$, making them suitable joining materials for SiC-carbide based materials. Ta-wrap, with a CTE of about 6.3 x 10^{-6} $°C^{-1}$ may offer interesting opportunities for alumina-to-mullite or alumina-to-SiC joints, given its intermediate value: research is ongoing on this respect.

Despite of the CTE mismatch with alumina, no cracks in the joining material or debonding at the joining material/alumina and joining material/mullite interfaces were observed (Figure 6) . There might be several possible uses of this joining technology for alumina-based components and these mullite-to-SiC joints could be used to obtain thermal barrier coatings in various high temperature applications.

In order to calculate the thermal diffusivity of the sample, the Cape-Lehman model was used[48], which consider a two–dimensional heat flow and the heat loss to evaluate the radiation effect above 500 °C. Moreover, the convection from the test sample to the ambient gas flow was taken into account. The thermal diffusivity of the $MoSi_2$/Si pellet ranges between 38 mm^2/s at room temperature and 8 mm^2/s at 1000°C, as shown in Figure 7 (a). The decrease *versus* temperature increase is most likely due to phonon scattering enhancement at higher temperatures. The standard deviation of the thermal diffusivity values for each temperature point is in the order of magnitude of 0.1 mm^2/s.

The specific heat of the $MoSi_2$/Si pellet was measured by using a reference sample (i.e. Poco Graphite Serial Nr. 21517): it ranges between 0.63 J/gK at room temperature and 0.89 J/gK at 1000°C as shown in Figure 7 (b). Finally, the thermal conductivity of the $MoSi_2$/Si pellet was calculated and varies between 77 W/mK at RT and 24W/(mK) at 1000 °C, Figure 7 (c). The thermal conductivity values of the $MoSi_2$/Si pellet is higher

than those available in the literature for the $MoSi_2$ [49,50], most likely due to the contribution of the silicon matrix.

The mechanical strength of the RM-Wrap SiC joints was measured at room temperature using three different tests: (i) single lap (SL), (ii) single lap off-set (SLO) and (iii) torsion on hourglass shaped samples (THG). It is worth mentioning that all the SiC joints did not break during the single lap tests (SL, SLO): the specimen were detached from the aluminium fixtures during the SL test, or SiC crushed during SLO tests. As a consequence, it was not possible to measure their joint strength by means of these lap tests.

As previously reported [51], lap shear tests (SL and SLO) are useful for comparative purposes, i.e. when the joining strength of a similar set of samples is to be compared. Moreover, the results in case of brittle materials are strongly related to the size and the shape of joined samples and fixtures. Both SL and SLO has been found inappropriate for measuring the RM-Wrap joint strength of SiC-based samples: even though the specimens mostly failed in the fixtures rather than in the joining seam, this behaviour might be due to a high stress concentration close to the joined region, rather than a high mechanical strength of the joint. Due to this uncertainty, SL and SLO tests were replaced by torsion test.

The torsion test can properly measure the shear strength of brittle joined materials, but the shear strength can only be calculated when the failure starts and propagates inside the joining material. If this is not the case, then either the test method is not correctly done, or the substrate and joint strength are similar. A custom-made torsional testing machine built at Politecnico di Torino in 2006 was used to test the different joints in torsion: details and comparison with other tests can be found in[33].

In this work, SiC hourglasses of two different sizes (4 and 5 mm in diameter) were joined by Mo-Wrap, and named as THG-4 and THG-5 respectively. The fractured surfaces after torsion test are shown in Figure 8 (b,c): the fracture initiates and propagates inside the SiC substrates, as evidenced in particular in Figure 8(c): the hourglass is partially crushed after torsion and some SiC parts are missing, leaving an irregular shape (see "SiC surface" with red arrows in Figure 8(c)) . This can be due to a certain misalignment of hourglasses joined one by one by Mo-wrap, thus giving to mixed mode loads together with torsion one. To obtain a reliable

shear value with torsion, the joints must be perfectly aligned: a few micrometres lateral shift in sample position may result in mixed shear along with bending load, thus unreliable results ranging between 21-32 MPa.

In order to understand if this fracture behaviour under torsion was due to a sample misalignment during the joining process or to the similar mechanical strength of both, some joined SiC tiles (Figure 9 a) were prepared, machined to obtain hourglasses (Figure 9 b) and then tested in torsion. In this case the fracture propagated inside the joined area only (Figure 9 c, d), probably initiated by a macroscopic defect induced in the joined region by machining; the machining of a brittle joining material such as a RM-disilicide reinforced silicon matrix composite, may induce significant defects (cracks, disilicides detachment from the silicon matrix, etc..) on the external region of the joint, thus affecting the mechanical strength of the joints.

However, the obtained values of 14 ± 5 MPa, with a partially cohesive/adhesive fracture (Figure 9 c, d) is at the moment the only pure shear strength result available for these joints at room temperature. Further tests are ongoing to completely characterize the mechanical strengths of them by other mechanical tests and at higher temperature.

~~The X-ray diffraction analysis on fracture surfaces after mechanical tests, confirmed the formation of RM disilicides and silicon as the only phases, as already reported in [1] for RM-Wrap joined C/SiC.~~

Conclusions

A pressure-less tailorable joining technique named “RM-Wrap” (Refractory metals = RM, i.e. Mo, Nb, Ta, Zr) was successfully used to join SiC, alumina and mullite. Morphological analyses showed continuous, crack free and well bonded interfaces with a joining microstructure consisting of *in-situ* formed composites made of a silicon rich matrix with disilicides of molybdenum ($MoSi_2$ in case of Mo-Wrap), niobium ($NbSi_2$ in case of Nb-Wrap), tantalum ($TaSi_2$ in case of Ta-Wrap) and zirconium ($ZrSi_2$ in case of Zr-wrap). Thermal and oxidation stability of SiC joints were carried out at 1100 ^{o}C for 6 hours. FESEM analysis before and after this thermal ageing showed unaffected joint interfaces and microstructure. CTE have been calculated for all RM-wraps

and thermal diffusivity, thermal conductivity and specific heat have been measured or calculated for $MoSi_2$/Si.

SiC joints were mechanically tested in three different modes SL in compression, SLO in compression and torsion on hourglass shaped samples: a shear strength of 14 ± 5 MPa was measured at room temperature by torsion on Mo-wrap joined SiC hourglass samples, only when obtained by machining from a joined tile.

For the first time, refractory metal disilicides based materials have been exploited in joining of SiC, alumina and mullite. It can be concluded that RM-Wrap joining offers many attractive advantages and its scope can be further extended: a summary of all RM-wrap joints obtained until now is shown in Figure 10.

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References

[1] Boch P, Chartier T. Alumina, mullite and spinel, zirconia (Ch 6). In: Boch P, Niepce J-C, editors. Ceramic Materials: Processes, Properties and Applications. ISTE Publication; 2007.

[2] Torrecillas R, Calderón J M, Moya J S, Reece M J, Davies C K L , Olagnon C, Fantozzi G. Suitability of mullite for high temperature applications, J Eur Ceram Soc. 1999; 19: 2519-2527.

[3] Bansal N P, Lamon J. Ceramic Matrix Composites: Materials, Modeling and Technology. John Wiley & Sons; 014.

[4] Ferraris M. Joining and Machining of CMCs. In: Beaumont P W R, Zweben C H, editors. Comprehensive Composite Materials II. Elsevier, Oxford. 2018; 293-307.

[5] Singh M, Kondo N, Asthana R. Chapter 12 - Manufacturing of Ceramic Components using Robust Integration Technologies, Green and Sustainable Manufacturing of Advanced Material. Elsevier, Oxford. 2016; 295-308.

[6] Krenkel W, Henke T, MasonN . In-situ joined CMC components. Key Engineering Materials, Trans Tech Publ. 1997; 313-320.

[7] Singh M. A reaction forming method for joining of silicon carbide-based ceramics. Scripta Mater. 1997; 37[8]: 1151-1154.

[8] Katoh Y, Kohyama A, Nozawa T, Sato M. SiC/SiC composites through transient eutectic-phase route for fusion applications. J Nucl Mat. 2004; 329: 587-59.

[9] Shimoda K, Hinoki T, Kohyama A. Effect of additive content on transient liquid phase sintering in SiC nanopowder infiltrated SiCf/SiC composites. Compos Sci Technol. 2011; 71(5): 609-615.

[10] Fan J, Chen L, Bai S, Shi X. Joining of Mo to $CoSb_3$ by spark plasma sintering by inserting a Ti interlayer. Mater Lett. 2004; 58 (30) :3876-3878.

[11]Rizzo S, Grasso S, Salvo M, Casalegno V, Reece M J, Ferraris M .Joining of C/SiC composites by spark plasma sintering technique. J Eur Cer Soc. 2014; 34 (4): 903-913.

[12] Lippmann W, Knorr J, Wolf R, Rasper R, Exner H, Reinecke A M , Nieher M, Schreiber R. Laser joining of silicon carbide—a new technology for ultra-high temperature resistant joints. Nucl Eng Des. 2004; 231 (29: 151-161.

[13] Aravindan S, Krishnamurthy R . Microwave Joining of $Al2O_3$-ZrO_2 Composites. 1999. Paper presented at: 23rd Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: B: Ceramic Engineering and Science Proceedings. Wiley Online Library. 1999; 71-78.

[14] Radhakrishnan R, Bhaduri S, Henager Jr C, Brimhall J. Synthesis of Ti_3SiC_2S/SiC and $TiSi_2$/SiC composites using displacement reactions in the Ti-Si-C system. Scripta Mater. 1996; 34 (12).

[15] MacDonald W, Eagar T. Transient liquid phase bonding. Annu Rev Mater Res. 1992; 22 (1): 23-46.

[16] Ferraris M, Salvo M, Isola C, Appendino Montorsi M, Kohyama A. Glass-ceramic joining and coating of SiC/SiC for fusion applications. J Nucl Mat. 1998; 258-263 (PART 2 B): 1546-1550.

[17] Gianchandani P K, Casalegno V, Salvo M, Ferraris M, Dlouhý I. Refractory Metal, RM – Wrap: a tailorable, pressure-less joining technology. Ceram Int. 2019; 45(4): 4824-4834.

[18]Gianchandani P K, Casalegno V, Smeacetto F, Ferraris M. Pressure-less joining of C/SiC and SiC/SiC by a MoSi2/Si composite. Int J Appl Ceram Tec. 2017; 14 (3): 305-312.

[19] Gianchandani P K, Casalegno V, Salvo M, Bianchi G, Ortona A. Ferraris M. SiC foam sandwich structures obtained by Mo-wrap joining. Mater Lett. 2018; 221: 240-243.

[20] Prasad N E, Wanhill R . Aerospace Materials and Material Technologies. Springer, Singapore; 2017.

[21]Wiltner B, Klöden T, Weißgärber T, Hutsch, Kieback B, Reaction temperatures within Mo–Si powder mixtures and their influencing factors. Int J Refract Met H. 2013; 37: 73-81.

[22] Okamoto H, Mo-Si (Molybdenum-Silicon). J Phase Equilib Diff. 2011; 32 (2) : 176-176.

[23]Cherniack G B, Elliot A G. High-Temperature Behavior of $MoSi_2$ and Mo_5Si_3. J Am Cer Soc. 1964; 47 (3): 136-141.

[24]Schlesinger M E, Okamoto H, Gokhale A B, Abbaschian R. The Nb-Si (Niobium-Silicon) system. J Phase Equilib. 1993; 14 (4): 502-509.

[25] Todai M, Hagihara K, Kishida K, Inui H, Nakano T. Microstructure and fracture toughness in boron added NbSi2(C40)/$MoSi_2$(C11b) duplex crystals Scripta Mater. 2016; 113 [Supplement C] 236-240.

[26] Yeh C L, Wang H J. A comparative study on combustion synthesis of Ta–Si compounds. Intermetallics. 2007; 15 (10) : 1277-1284.

[27]Okamoto H. The Si-Zr (Silicon-Zirconium) system. J Phase Equilib. 1990; 11 (5): 513-519.

[28] ASTM E 1461-13, Standard test method for thermal diffusivity by the flash method, 2013.

[29] ASTM E 2585-09, Standard practice for thermal diffusivity by the laser flash, 2009.

[30]Parker W, Jenkins R, Butler C, Abbott G. Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. J Appl Phys. 1961; 32 (9): 1679-1684.

[31]Ferraris M, Ventrella A, Salvo M, Avalle M, Pavia F, Martin E. Comparison of shear strength tests on AV119 epoxy-joined carbon/carbon composites. Compos Part B-Eng. 2010; 41 (2): 182-191.

[32] ASTM D905-D908, Standard Test Method for Strength Properties of Adhesive Bondsin Shear by Compression Loading.2013; ASTM Int., West Conshohocken, PA USA

[33] Ferraris M, Salvo M, Rizzo S, Casalegno V, Han S, Ventrella A, Hinoki T, Katoh Y. Torsional shear strength of silicon carbide components pressurelessly joined by a glass-ceramic. Int J Appl Ceram Tec. 2012; 9 (4): 786-794.

[34]Zhang Y, Ni W, Li Y. Effect of siliconizing temperature on microstructure and phase constitution of Mo–$MoSi_2$ functionally graded materials. Ceram Int. 2018; 44[10]: 11166-11171.

[35]Naikade M, Fankhänel B, Weber L, Ortona A, Stelter M, Graule T. Studying the wettability of Si and eutectic Si-Zr alloy on carbon and silicon carbide by sessile drop experiments. J Eur Cer Soc. 2019; 39 (4): 735-742.

[36] Chou T C, Joshi A. High temperature interfacial reactions of SiC with metals, J Vac Sci Technol A. 1991; 9: 1525.

[37] Cockeram, B.V.,The diffusion bonding of silicon carbide and boron carbide using refractory metals, ASM Materials Solution 99: International Conference on Joining of Advanced and Specialty Metals and Advances in Surface Engineering; Cincinnati, OH (United States); 1999, 31(1) , 42 (1).

[38] Yaney D L, Joshi A. Reaction between niobium and silicon carbide at 1373 K J. Mater. Res. 1990; 5 (10) .

[39] Burkyna A L, Strashinskaya L V, Evtushok T M. Investigation of the interaction of silicon carbide with refractory metals and oxides Fiziko-Khimicheskaya Mekhanika Materialov. 1968; 4 (3) : 301-305.

[40] Bhanumurthy K, Schmid-Fetzer R. Interface reaction between silicon carbide and metals (Ni, Cr, Pd, Zr) Compos: Part A . 2001; 32: 569–574.

[41] Joshi A, Hu SH, Wadsworth J. Interfacial reaction of refractory metals niobium and tantalum with ceramics silicon carbide and alumina, Mat. Res. Soc. Symp. 1990; 170.

[42]Martinelli A, Drew R. Microstructural development during diffusion bonding of a silicon carbide to molybdenum. Mat Sci Eng A. 1995; 191:239–247.

[43]Triantou K I, Mergia K, Perez B, Florez S, Stefan A, Ban C, Pelin G, Ionescu G, Zuber C, Fischer W P P , BarcenaJ . Thermal shock performance of carbon-bonded carbon fiber composite and ceramic matrix composite joints for thermal protection re-entry applications. Compos Part B-Eng. 2017; 111: 270-278.

[44] Zhu Y T, Stan M, Conzone S D, Butt D P. Thermal oxidation kinetics of MoSi2-based powders. J Am Ceram Soc. 1999; 82 (10): 2785-2790.

[45]Sheikh S, Bijaksana M K, Motallebzadeh A, Shafeie S, Lozinko A, Gan L , Tsao T K , Klement U, Canadinc D, Murakami H, Guo S. Accelerated oxidation in ductile refractory high-entropy alloys, Intermetallics. 2018; 97:58-66.

[46]Chou T C, Nieh T G. Mechanism of $MoSi_2$ pest during low temperature oxidation. J Mater Res. 2016; 8 (1) : 214-226.

[47] Bruck H A, Rabin B H. Evaluation of Rule-of-Mixtures Predictions of Thermal Expansion in Powder-Processed Ni–Al2O3 Composites. J Am Ceram Soc. 1999; 82 (10): 2927-2930.

[48]Cape J, Lehman G. Temperature and finite pulse-time effects in the flash method for measuring thermal diffusivity. J Appl Phys. 1963; 34 (7): 1909-1913.

[49]Bose S, Hecht R J. Thermal properties of $MoSi_2$ and SiC whisker-reinforced $MoSi_2$. J Mater Sci.1992; 27 (10): 2749-2752.

[50] Mohamad, Ohishi Y, Muta H, Kurosaki K, Yamanaka S. Thermal and Mechanical Properties of α-MoSi2 as a High-Temperature Material. Phys Status Solidi (b), 2018. 255(4): 1700448.

[51]Ventrella A, Salvo M, Avalle M, Ferraris M. Comparison of shear strength tests on AV119 epoxy-joined ceramics (2010) J Mat Sci 45 (16), pp. 4401-4405.

[52]Ferraris M, Salvo M, Rizzo S, Casalegno V, Han S, Ventrella A, Hinoki T, Katoh Y. Torsional shear strength of silicon carbide components pressurelessly joined by a glass-ceramic. Int J Appl Ceram Tec. 2012; 9 (4): 786-794.

[53] Engstrom I, LönnbergT B. Thermal expansion studies of the group IV-VII transition-metal disilicides, J Appl Phys. 1988; 63: 4476.

[54]http://www.bettinitextile.it/ENG/2_Materials_05.htm

[55] MatWeb Material Property data, 2019.http://www.matweb.com/search/PropertySearch.aspx.

	CTE [10^{-6} °C^{-1}]	% vol MSi_2/Si
$MoSi_2$/Si	3.9	33.8/66.2
$NbSi_2$/Si	3.9	29.4/70.6
$TaSi_2$/Si	6.3	61.2/38.8
$ZrSi_2$/Si	4.5	34.2/65.8
SiC	3.8 [54]	
Al_2O_3	5.5 [55]	
Mullite	5.0 [55]	
Silicon	2.5[55]	
$MoSi_2$	6.8 [53]	
$NbSi_2$	7.3[53]	
$TaSi_2$	8.7[53]	
$ZrSi_2$	8.3[53]	

Table and Figure captions:

Table 1 Coefficient of thermal expansion for the RM-wrap joining materials, calculated according to their composition, (those of the joined materials and silicides for comparison purposes); CTE values at room T, except for SiC (comprised between RT and 400°C)

Figure 1 SEM Cross-section of SiC joined by Mo-Wrap (a, b), higher magnification of the interface between $MoSi_2$/Si and SiC (c); after oxidation test: 1100 °C, 6 hours, in air (d) arrows show the interface between SiC and the *in situ* formed joining material.

Figure 2 SEM cross section of SiC joined by Nb-Wrap (a, b) and after oxidation test (c): 1100 °C, 6 hours, in air, particular of the interface between *in situ* formed $NbSi_2$/Si composite and SiC

Figure 3 SEM cross section of SiC joined by Ta-Wrap (a, b) and after oxidation test (c): 1100 °C, 6 hours, in air, particular of the interface between *in situ* formed $NbSi_2$/Si composite and SiC

Figure 4 SEM cross section of SiC joined by Zr-Wrap; the joining material shows a typical eutectic microstructure with needle-shaped Si-Zr phase within the Si matrix

Figure 5 Silicon-zirconium phase diagram with indicated the composition used for the Zr-wrap joint.

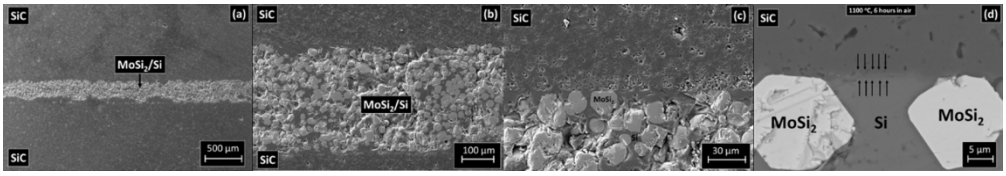
Figure 6 SEM cross-section of alumina (a) and of SiC joined to mullite by Mo-Wrap (b)

Figure 7 Thermal diffusivity (a) measured by Laser Flash Method and calculated specific heat (b) and thermal conductivity (c) versus temperature for a $MoSi_2$/Si pellet of about 11.6 mm diameter, 2.6 mm thickness

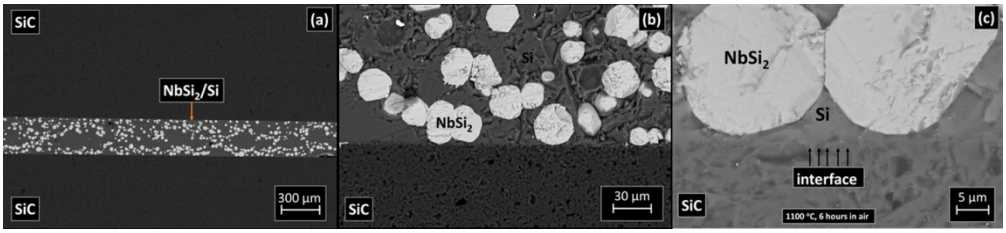
Figure 8 Torsion test on Mo-Wrap joined SiC hourglass (a), fracture surfaces after test at room temperature (b, c)

Figure 9 Mo-Wrap joined SiC tiles (35 mm x 5 mm x 4 mm) (a), machined to obtain hourglasses (b), fracture surfaces after test at room temperature (c, d)

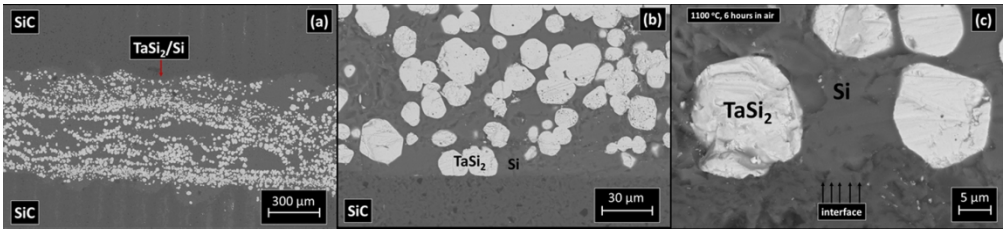
Figure 10 Summary of Wrap technology options for joining of ceramics and CMCs; RM= Refractory Metals. In the case of CMC, *coated* or *uncoated* means with or without the CVD (Chemical Vapour Deposition) SiC coating usually deposited on these materials.



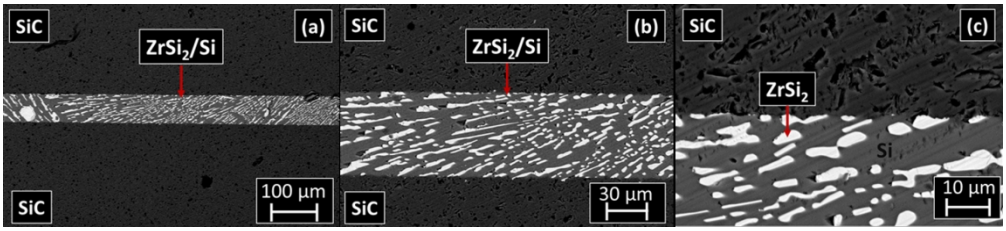
SEM Cross-section of SiC joined by Mo-Wrap (a,b), higher magnification of the interface between $MoSi_2$/Si and SiC (c); after oxidation test: 1100 °C, 6 hours, in air (d) arrows show the interface between SiC and the in situ formed joining material.



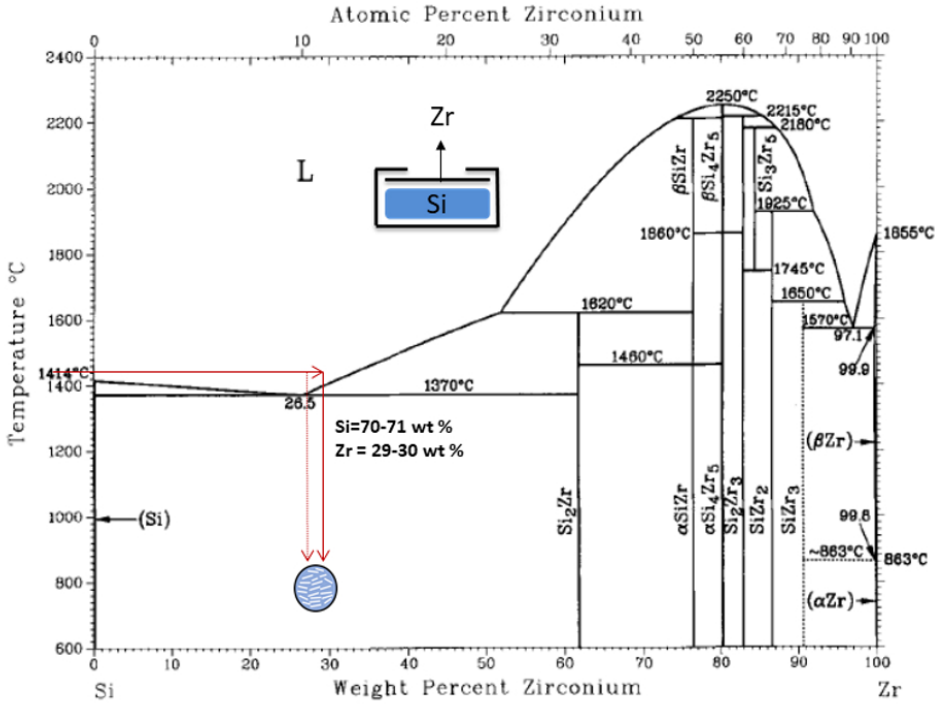
SEM cross section of SiC joined by Nb-Wrap (a, b) and after oxidation test (c): 1100 °C, 6 hours, in air, particular of the interface between in situ formed $NbSi_2$/Si composite and SiC



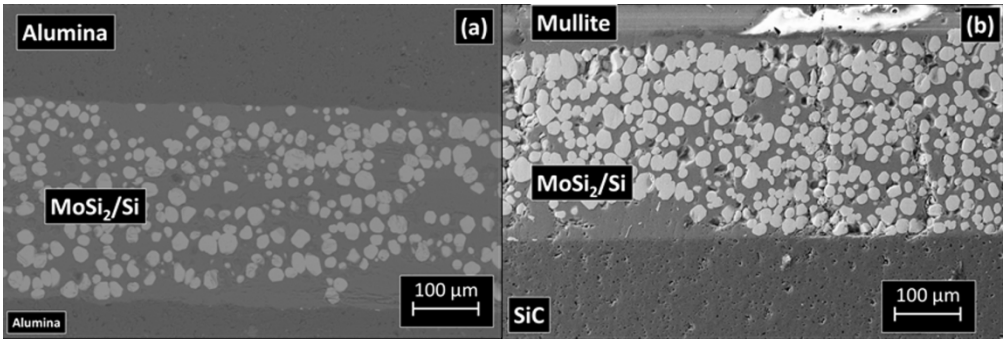
SEM cross section of SiC joined by Ta-Wrap (a, b) and after oxidation test (c) : 1100 °C, 6 hours, in air, particular of the interface between in situ formed $TaSi_2$/Si composite and SiC



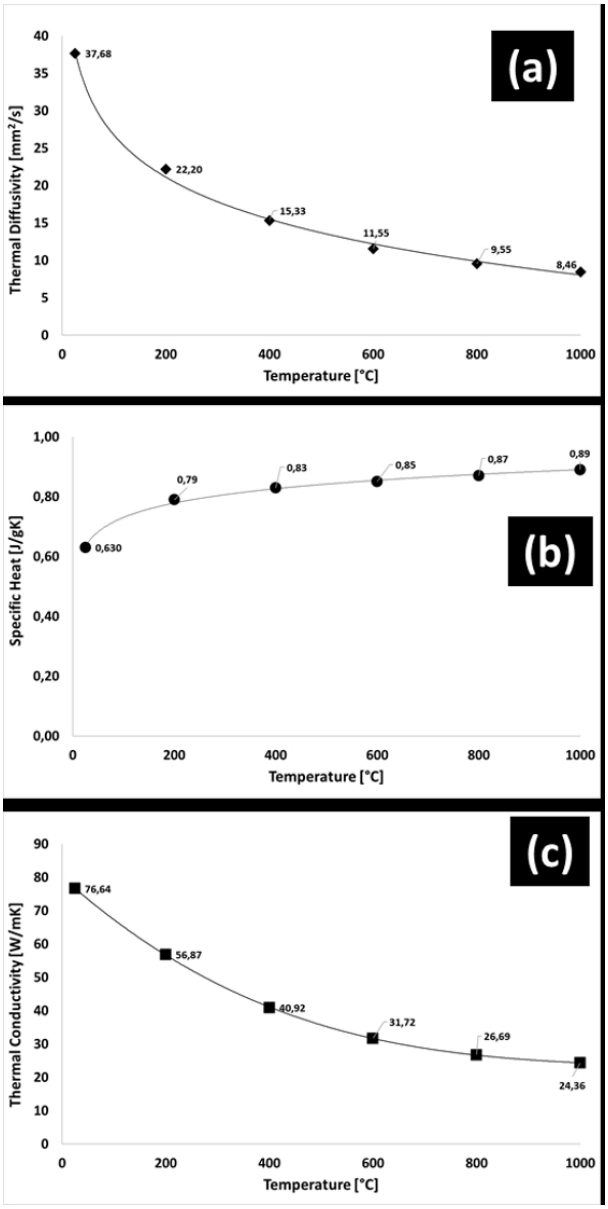
SEM cross section of SiC joined by Zr-Wrap; the joining material shows a typical eutectic microstructure with needle-shaped Si-Zr phase within the Si matrix



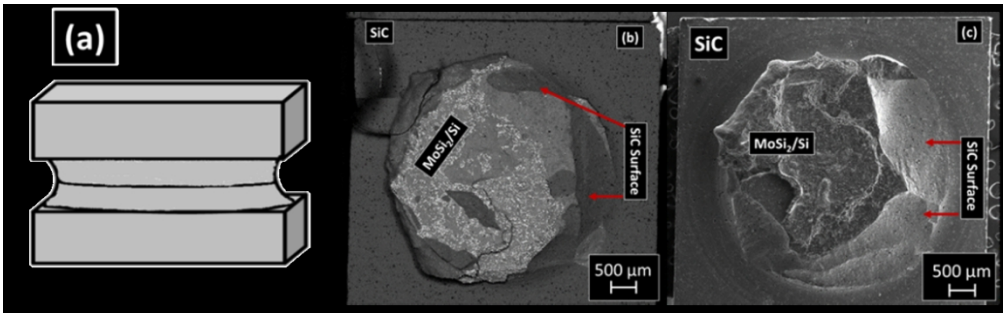
Silicon-zirconium phase diagram with indicated the composition used for the Zr-wrap joint.



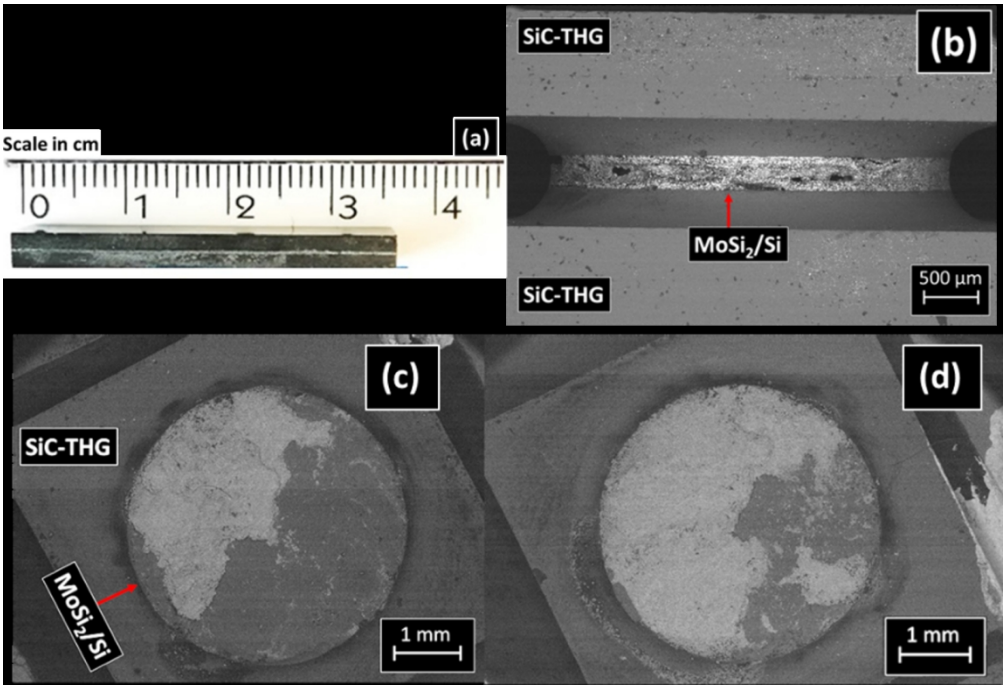
SEM cross-section of alumina (a) and of SiC joined to mullite by Mo-Wrap (b)



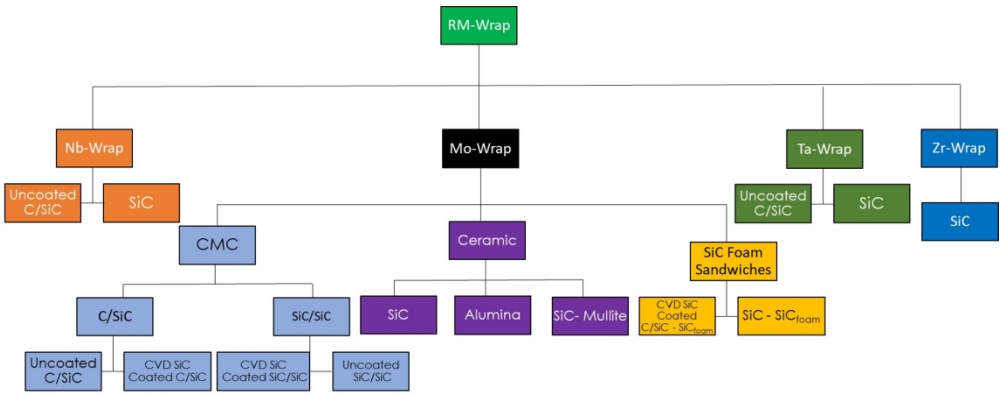
Thermal diffusivity (a) measured by Laser Flash Method and calculated specific heat (b) and thermal conductivity (c) versus temperature for a $MoSi_2$/Si pellet of about 11.6 mm diameter, 2.6 mm thickness



Torsion test on Mo-Wrap joined SiC hourglass (a), fracture surfaces after test at room temperature (b,c)



Mo-Wrap joined SiC tiles (35 mm x 5 mm x 4 mm) (a), machined to obtain hourglasses (b), fracture surfaces after test at room temperature (c, d)



Summary of Wrap technology options for joining of ceramics and CMCs; RM= Refractory Metals. In the case of CMC, coated or uncoated means with or without the CVD (Chemical Vapour Deposition) SiC coating usually deposited on these materials.

336x131mm (149 x 149 DPI)