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PRELIMINAR RESULTS ON JOINING OF THIN $\text{SiC}_f/\text{SiC}_m$ COMPOSITES BY SILICIDES COMPOUNDS AND LOCAL HEATING

E. Jacques¹, L. Maillé¹, Y. Le Petitcorps¹, C. Lorrette^{1, 2} and C. Sauder²

¹Laboratoire des Composites ThermoStructuraux, 3 allée de la Boétie, Pessac, France

²CEA Saclay DEN/DMN/SRMA/LTMEX, Gif sur Yvette, France

ABSTRACT

The present work describes the methodology and the results for joining SiC substrates in the solid state by reactive and non reactive metallic silicides in order to use these materials as container for the Gas Fast Reactor. The operation temperatures are in the range of 1000°C but short time incursions at 1600 or 2000°C have to be anticipated. As joining material, we have chosen to study four titanium and niobium silicides: TiSi_2 and NbSi_2 (non reactive with SiC) and Ti_5Si_3 and Nb_5Si_3 (reactive with SiC) in order to modify the joint /substrate bonding. The joining between these silicides and the silicon carbide substrate was prepared by Spark Plasma Sintering in order to limit the contact time during the sintering. Post thermal treatments in the solid state performed under a control atmosphere have been performed in order to study the thermal stability of the assembly. Polished cross sections were prepared to study the interface composition, the cracking path in the vicinity of the joint/ substrate interface. In order to decrease the residual stresses within the joint, SiC particles were mixed with the silicide ones. In the case of the non reactive silicides, the SiC particles effectively reduce the cracks whereas for the reactive silicides, the SiC particles reacts with the joint leading to a thermally stable composition and the bonding to the substrate is improved. In order to prepare the joining technology, few trials of local heating have been investigated with a Laser beam. The advantage of local heating is the possibility to heat at high temperature (around 1800°C) for short time without damaging the composite structure : a CO_2 laser source has been used for this purpose. Thermal cartographies have been measured from one side to the other of the silicon carbide plate.

KEYWORDS : Brazing, Silicides, Composite Materials, Diffusion Bonding, Nuclear applications

1-INTRODUCTION

For forty years, the energy production never stopped growing to respond the demographic and industrial growth. Today, controversies concerning the use of fossil energies and the poor yield of renewable energies have made nuclear power essential. It represents 80% of the energy production in France. The ageing of nuclear power plants encourages countries all over the world to devote a part of their research programs to the Generation IV reactors. Such reactors have to meet technology goals: improve nuclear safety, minimize waste and natural resource utilization, and to decrease the cost to build and run such plants. The French institution CEA focuses its efforts on different concepts of reactors and in particular on the Gas Fast Cooled Reactor (GFR). This reactor is helium-cooled, with an outlet temperature in the range of about 500°C to 1000°C in standard situation. Several fuel forms are being considered for their potential to operate at very high temperatures and to ensure an excellent retention of fission products, examples given for ceramic matrix composite (CMC) tubes or honeycombs, advanced fuel particles, or ceramic clad elements of actinide compounds. In this study, we focused on a tube concept made of thin CMC: $\text{SiC}_f/\text{SiC}_m$ composites.

Silicon carbide ceramic matrix composites have been developed at first for applications in aeronautic such as rockets, jet engines or turbines. The temperature requirements for Generation IV reactors make them attractive also for nuclear applications. In actual nuclear reactors, metallic alloy tubes are used as fuel container but such alloys have too poor properties above 500°C. Silicon carbide (SiC) has sufficient thermal and mechanical properties : a low Coefficient of Thermal Expansion (4.10^{-6}K^{-1}), a good thermal conductivity ($300\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), a high stiffness (400GPa) and a high melting, more over, SiC is neutron transparent in order to allow good performances of the nuclear core. The structural materials are also submitted to different thermomechanical strains: thermal gradients, helium

pressured at 70 bars in the reactor...) and then need to have good damage tolerance, thermal shock resistance and a limited brittleness. Mechanical properties of unreinforced silicon carbide are noticeable with a Young's modulus twice as much as steel at room temperature but its brittleness is important. Using SiC fiber reinforcement in a SiC matrix permits to increase the damage tolerance (typically 0.6% of tensile deformation before break at room temperature) thanks to a damage mechanism. SiC_f/SiC_m ceramic composites are then good candidates to answer all these specifications. Nevertheless, there are some technological issues to overcome such as the difficulty to accomplish complex geometries. Then, a suitable method of joining SiC_f/SiC_m components is required. Riveting and bolting are not considered for ceramics and the key issue seems to reside in joining pieces by brazing, soldering (but not possible on very refractive materials such as silicon carbide) or solid state diffusion bonding. The joining material should have the same thermomechanical properties as the composite and have to keep these properties at very high temperature. Several other joining methods have been developed for the assembly of ceramics such as mechanical fastening, plasma spray or physical and chemical vapor deposition. Brazing is used extensively due to its simplicity, low cost investment and potential to be a mass production process. In recent years, joining SiC with Ag-Cu or Cu-based braze has been reported but their utilization is restricted to 500°C. Other authors have developed eutectic brazes from metals but the presence of free silicon doesn't enable their use beyond 1400°C. Many studies have been carried out on Ti-Si-C and Cr-Si-C systems on eutectic compositions: Si-22%wtTi (TiSi₂ and Si), Si-18%atCr (CrSi₂ and Si) and Si-44%atCr (CrSi and CrSi₂).

The aim of this study is to find relevant compositions and processing routes for joining SiC_f/SiC_m tube composite. The requirements for the brazing composition can be describe as follow : The brazing has to be adherent to the silicon carbide substrate with a limited reaction zone in order to avoid the damaging of the SiC, the brazing must not be cracked in order to avoid any leaks, the assembly must withstand for short durations temperatures around 1600°C. Taking into account these requirements, 4 silicides have been selected (TiSi₂, Ti₅Si₃, NbSi₂, Nb₅Si₃), these silicides have a higher CTE and a lower Young's modulus than SiC. These silicides are available in a powder shape. In order to reduce the strain mismatch, few amount of SiC powders have been had to the brazing composition. More over, M₅Si₃ silicides are reactive to SiC, in order to limit the reaction with the silicon carbide substrate, few amount of SiC powders or metallic disilicides powders (MSi₂) have also been had to the brazing composition. The joining of two the silicon carbide substrates was prepared by Spark Plasma Sintering in order to limit the contact time during the sintering. Post thermal treatments in the solid state performed under a control atmosphere have been performed in order to study the thermal stability of the assembly. Polished cross sections were prepared to study the interface composition, the cracking path in the vicinity of the joint/ substrate interface.

2- MATERIALS AND METHOD :

2-1 : Selection of the constituents :

The study of ternary phase diagrams (M, Si, C) shows a chemical stability of some metal-based silicides or carbides with silicon carbide, whereas other silicides of the same metal are unstable and forms a metallic carbide (Figures1a-c). By considering the matches of the properties between SiC and the joining material, MSi₂, M₅Si₃ and MC (M=Ti or Nb) can be considered as potential joining compounds (Table1).

Figure 1. : Ternary diagram of the systems M-Si-C

(a) Ti-Si-C at 1227°C, (b) Ti-Si-C at 1727°C, (c) Nb-Si-C at 1727°C

	SiC	TiC	NbC	Ti ₃ SiC ₂ (T1)	TiSi ₂	Ti ₅ Si ₃	NbSi ₂	Nb ₅ Si ₃
Tf (°C)	2700	3140			1540	2120	1930	2480
α (10^{-6} K^{-1})	4.5	7.6			10.4	11	8.4	7.3
E (GPa)	410	450			260	-	-	-

Table 1. Physical properties of compounds of interest

The ternary phase diagrams of Ti-Si-C and Nb-Si-C show the thermodynamic stability of disilicides with the silicon carbide. On the contrary, with silicides such as Ti₅Si₃ or Nb₅Si₃, a reaction zone should be observed due to the absence of equilibrium. Different diffusion paths can be considered :

Ti₅Si₃ → TiC → SiC

Ti₅Si₃ → TiC → T1 → SiC

Nb₅Si₃ → NbC → NbSi₂ → SiC

Nb₅Si₃ → NbC → SiC

The main advantage of using chemically stable silicides as joining material is the chemical stability in time of the assembly. But with this lack a chemical reaction, a weak bonding between the elements can be expected. On the other hand, a strong bonding can be expected with the M₅Si₃ silicides but to the prejudice of a chemical damage of the SiC substrate. A compromise has to be found among adhesion, mechanical behavior against cracks and chemical reactivity with silicon carbide.

By considering the thermomechanical behavior, the mismatch between the physical properties of SiC and the silicides shows that after cooling, the SiC is in a compression state, whereas the silicides are in tension. Due to the lack of room temperature ductility of the silicides, the brazing will be cracked. In order to decrease the CTE and to increase the stiffness of the brazing, 0 to 30% in Vo. of SiC were added to the all silicides. In the case of the M₅Si₃ silicides, the chemical reaction with SiC will transform the joint composition into a more stable one as described before.

The different compositions of the joint are recapped in table 2.

	Reasons of choice	Expected behavior after sintering	Expected behavior after a post-thermal treatment
MSi_2	Chemical stability	Cracking with in the joint	Better sintering
$\text{MSi}_2 + \% \text{SiC}_{\text{powders}}$ Vo. : 0-20%	Decrease in the residual stresses	Less cracking according to the volume fraction of reaction zone	Stable
M_5Si_3	Increase of the bonding with the SiC	Better bonding and reaction zone with SiC	Stable composition but with a damaging of SiC
$\text{M}_5\text{Si}_3 + \% \text{SiC}_{\text{powders}}$ Vo. : 0-20%	Limit the reaction zone with the SiC	Better bonding and lower reaction zone with SiC	Stable composition with a controlled reaction of SiC
$\text{MSi}_2 + \text{M}_5\text{Si}_3 + \text{SiC}_p$ (40-40-20)% in Vo.	Limit the reaction zone with the SiC and decrease in the residual stresses	Better bonding, lower reaction zone with SiC, no cracks in the joint	Stable composition with a controlled reaction of SiC

Table 2 : Compositions of interest for the joint (M=Ti or Nb)

2-2 : Preparation of the samples :

Détailler la taille des poudres, les épaisseurs des joints, la nature des différents mélanges, la preparation des mélanges de poudres, les conditions de frittage SPS, les moyens de caractérisation, les différents traitements thermiques...Schéma des échantillons oui

All the samples have been prepared with a Spark Plasma Sintering equipment. This device permits the sintering of ceramics in a very short time. Limiting thus the grain growth or the reaction zone with the substrate. The singularity of this technique is the application of a uniaxial pression on the sample during the process combined with an alternative or DC current. The samples are pressed within a graphite die and the pressure in the chamber is around 5Pa. The sintering temperature is always 200°C below the melting temperature of the compound in order to maintain a solid state reaction. The temperature rising rate is 100°C/min and a pressure of 50MPa is applied since the sintering temperature is reached.

3- RESULTS AND DISCUSSION

3-1 : Non reactive silicides (MSi_2 or $\text{MSi}_2 + \text{SiC}$)

We have first studied the sintering of the chemically stable silicides TiSi_2 and NbSi_2 . The good adhesion of the two is relevant but cracks are observed in both cases (Figure 2a). Those cracks are very harmful while they are crossing grains and even within the SiC substrate. To minimize this effect, we introduced a certain amount of SiC fine powders. For TiSi_2 , the SEM images confirm the hypothesis while the higher the amount of SiC fine powders is the smaller density of cracks is observed (Figures 2a-c). No thermal treatment has been carried out on TiSi_2 as its melting temperature is below 1600°C.

Figure 2. SEM micrographes of as-pressed materials : (a) TiSi_2 , (b) $\text{TiSi}_2 + 10\%_{(\text{vol})} \text{SiC}$, (c) $\text{TiSi}_2 + 20\%_{(\text{vol})} \text{SiC}$, with the joint, the silicon particles are the grey spots

A good adhesion is observed for $\text{NbSi}_2 + 10\% \text{SiC}$ but a worsening is noted after 3 hours at 1600°C (Figure 3).

Figure 3. $\text{NbSi}_2 + 10\% \text{SiC}$ (a) as pressed and (b) after 3h at 1600°C

To conclude on these compositions, $\text{MSi}_2 + 20\% \text{SiC}_{\text{particles}}$ are interesting materials on a physico-chemical point of view even after thermal treatments (1500°C for TiSi_2 or 1600°C for NbSi_2). In order to improve the joint morphology, it would be better to use smaller silicides powders (similar to SiC ones), this would permits also to reduce the joint thickness. The assembly was done under pressure, it would be interesting to study the bonding without any pressure during the sintering.

3-2 : Reactive silicides (MSi_2 or $\text{MSi}_2 + \text{SiC}$)

The same experiments have been carried out with the reactive silicides Ti_5Si_3 and Nb_5Si_3 (Figure 4).

Figure 4. SEM micrographes of as-pressed materials : (a) Ti_5Si_3 , (b) $\text{Ti}_5\text{Si}_3 + 10\%_{(\text{vol})} \text{SiC}$, (c) $\text{Ti}_5\text{Si}_3 + 20\%_{(\text{vol})} \text{SiC}$

The presence of a reaction zone between the joint and the SiC substrate is observed when the joint contains less than 10% of SiC_p (Figure 4a,b). As expected, there is a chemical reaction at the interface with the silicon carbide substrate. For higher content of SiC_p (20 or 30%), the reaction occurs at the interface but also within the joint itself (Figure 4c). The chemical transformation of the joint seems to be correlated to the amount of SiC powder incorporated. With 0 to 10% of SiC , less than 5% of the joint thickness has reacted, 20% are transformed with 20% of SiC_p and nearly 35% are transformed with 30% of SiC_p . (Pour faire ce calcul, j'ai considéré que la zone de reaction faisait le double de ce qui est indiqué dans le tableau cad des 2 côtés du substrat et que l'épaisseur totale du joint faisait $500\mu\text{m}$). The EDS analysis of this reacted zone reveals the presence of titanium carbide (TiC_x) against

the SiC substrate where as no TiSi_2 is observed. The presence of TiC_x is interesting for at less two reasons, TiC has a Young's modulus and a CTE close to SiC and TiC_x is in equilibrium with SiC and Ti_5Si_3 (Figure 1, Table 1).

Figure 5. SEM micrographes after 3h at 1600°C heat treatment : (a) Ti_5Si_3 , (b) $\text{Ti}_5\text{Si}_3 + 10\%_{(\text{vol})}$ SiC, (c) $\text{Ti}_5\text{Si}_3 + 20\%_{(\text{vol})}$ SiC

After thermal treatment, a large debonding and a strong reaction with the SiC substrate is noticeable (Figure 5 a-b) for the low content of SiC_p . These results emphasize the role played by the SiC powders mixed to the silicide (Figure 5c). An EDS analysis has revealed that the thermal treatment leads to the formation of the Ti_3SiC_2 , TiC within a Ti_5Si_3 matrix and is coherent with the ternary phase diagram (Figure 1a). The presence of the pseudo-ductile Ti_3SiC_2 is interesting for mechanical purpose of the assembly. After 3h hours of diffusion time, the joint is still composed 65% of unreacted Ti_5Si_3 in the middle of the joint thickness. The TiC formed at the joint/ silicon carbide interface plays the role of a diffusion barrier.

In the case of Nb_5Si_3 with a large amount of SiC_p , a good behavior is also observed before and after a thermal treatment (Figure 6a-b). Within the joint, The thickness of the reaction zone is limited by comparison with Ti_5Si_3 whereas the substrate is strongly chemically attacked (Figure 6a-b). The EDS analysis leads to the formation of niobium carbide (NbC_x). The chemical composition of Nb_5Si_3 after thermal treatment remains the same with the presence of the NbC_x interface between SiC and Nb_5Si_3 . Whereas NbC_x and TiC_x are very similar with a vacancy in carbon, the difference of chemical reaction between the two silicides with SiC can be explain by the presence of the T1 compound (in the Si,C, Ti) phase diagram which can play the role of a diffusion barrier. As a consequence even that Nb_5Si_3 has a higher melting point than Ti_5Si_3 , it is less interesting for this application. After the thermal treatment at 1600°C, some un-reacted Ti_5Si_3 is still present in the joint and the composition of the blend ($\text{SiC}+\text{Ti}_5\text{Si}_3$) has to be tuned.

Figure 6. SEM micrographes of $\text{Nb}_5\text{Si}_3+20\%\text{SiC}$ joint composition (a) as-pressed, (b) after 3h at 1600°C heat treatment

3-3 : Non reactive and reactive silicides ($\text{MSi}_2 + \text{MSi}_2 + \text{SiC}$ (40/40/20% in Vo.

In order to get rid of the drawbacks of reactive and non reactive silicides and above all to minimize the presence of the reaction zone, we have blended them in a certain quantity and observed the behavior of the joints (Figure 7).

Figure 7. SEM micrographes of 40 MSi_2 /40 M_5Si_3 -20 SiC (% Vo.) (M= Ti or Nb)/ SiC interfaces

(a) $\text{TiSi}_2 + \text{Ti}_5\text{Si}_3 + \text{SiC}$ after 3h at 1600°C heat treatment (**je ne comprends pas TiSi_2 aurait du fondre ou alors c'est le matériau avant traitement thermique?**), (b) as-pressed $\text{NbSi}_2 + \text{Nb}_5\text{Si}_3 + \text{SiC}$, (c) $\text{NbSi}_2 + \text{Nb}_5\text{Si}_3 + \text{SiC}$ after 3h at 1600°C heat treatment

For $\text{TiSi}_2 + \text{Ti}_5\text{Si}_3 + \text{SiC}$ composition, a lack of reaction zone is relevant even after a severe heat treatment, few cracks are however present and are crossing the joint from the SiC substrate showing a good bonding. The stability of the joint even after a thermal treatment is of interest. The ternary phase diagram of the Ti-Si-C system shows that TiSi_2 and Ti_5Si_3 are not stable and should form TiSi (Figure 1). We don't observe the formation of this phase but the presence of TiC at the interface of Ti_5Si_3 grains and the presence of a dominant phase of TiSi_2 is noted. Then, we assume that Ti_5Si_3 reacts with the SiC fine powder more easily than with the disilicides to form TiC_x and probably Ti_3SiC_2 . The initial powder sizes of TiSi_2 and Ti_5Si_3 have to be decreased in order to have a thinner joint. Moreover, by decreasing the size of the powders, will make easy the sintering.

For $\text{NbSi}_2 + \text{Nb}_5\text{Si}_3 + \text{SiC}$ composition, we observe the formation of a reaction zone between the joint and the substrate but it is considerably thinner than in the case Nb_5Si_3 alone $25\mu\text{m}$ against $5\mu\text{m}$ in that case (Figures 6a and 7b). However, the thermal treatment leads very large and damageable cracks in the joint and at the interface between the substrate and the joint where the NbC_x is present (Figure 7c).

3-4 : Local heating with a CO_2 Laser beam

4- CONCLUSION

What ever the composition of the silicide is, it is necessary to blend with the silicide powder with fine SiC particles ($1\mu\text{m}$). The amount of SiC has not been adjusted but at least 20% in volume are necessary. A compromise has to be find, in order to minimize the residual stresses a maximum of SiC is required but with a high amount of SiC_p , the sintering and the solid state diffusion to the substrate will be more difficult. For all the composition, in order to facilitate the sintering and to decrease the thickness of the joint, the initial powder sizes of the silicides have to be decrease. Three types of composition were found to be of interest : (1) The first one is a $\text{TiSi}_2 + \text{SiC}$, the stability is limited to the melting temperature of the disilicide (1540°C) but this composition can be sintered at a low temperature, (2) the second one $\text{Ti}_5\text{Si}_3 + \text{SiC}$ is unstable, TiC_x and Ti_3SiC_2 are formed at the substrate

interface allowing the bonding without damaging the substrate, the amount of the Ti_5Si_3 has to be tuned in order to have a stable joint in time, (3) Finally, the 3rd composition $\text{TiSi}_2+\text{Ti}_5\text{Si}_3+\text{SiC}$ is of interest because the presence of TiSi_2 limits the quantity of Ti_5Si_3 which can react with the silicon carbide substrate. The operating temperature is however limited to the melting temperature of the disilicide. (j'ai suppose que sur la photo 7a, il n' y a pas eu de traitement thermique) The adhesion of these composition has now to be tested by a mechanical test.

5- REFERENCES