Studying the wettability and reactivity of liquid Si-Ti eutectic alloy on glassy carbon

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Abstract

The contact heating sessile drop method was applied for a fundamental study concerning the wettability and reactivity of liquid Si-16.2at%Ti (eutectic composition) in contact with Glassy Carbon. The evolution of the contact angle behaviors and spreading kinetics were evaluated at three different temperatures. A strong temperature-dependence was found by analyzing the spreading kinetics in determining the achievement of the equilibrium at the interface. Different spreading stages with different slopes, depending on whether the diffusion of reacting phases (liquid Si and C) through the growing reaction layer (SiC), starts to be the rate-limiting factor. On the contrary, the final contact angle value seems not affected by the temperature.

The solidified Si-Ti eutectics/GC samples were examined both at the top of the drop and at the cross-section by SEM/EDS. The presence of C-pockets of dissolution and a SiC layer at the interface, confirmed the reactive nature of the interaction mechanisms. In addition, a thicker layer of SiC at the triple line was detected and most probably responsible for pinning the alloy drop and as a consequence for the final value of contact angle measured ($\theta \approx 43^\circ \pm 2$).

1. Introduction

Light, stiff, strong and highly corrosion resistant materials capable of bearing load have become increasingly valuable for the design, construction and assembling of lightweight transportation systems such as air and space crafts, satellites, drones, high-speed trains, etc [1]. In spite of the need, there are few promising new materials in current development that are suited for such kind of advanced applications [2]. It is not surprising that remarkable R&D efforts are highly focused on the development of highly performant refractory and multicomponent alloys, advanced ceramics and composites, i.e. CMC or MMC-type where the metal phase is an Al, Si, Mg or Ti-based alloy [3, 4]. MMCs and CMCs can be fabricated with different types of reinforcements which strongly influence the fabricating process, microstructure and the resulting properties. In the MMCs approach, high volume percentages of reinforcing agents are incorporated into various intermetallic matrices to carry a major portion of the load. In addition, the presence of reinforcements can facilitate either crack deflection or arrest increasing the fracture toughness of the composites. Both the constituent phases (metal matrix and reinforcement) are preliminarily considered on the basis of their chemical stability, thermo-physical and thermo-mechanical properties. MMC can be designed to have superior properties such as enhanced high-temperature performance, outstanding thermo-mechanical response, increased wear resistance than those of unreinforced metal matrix phase. On the other hand, the control of interfacial phenomena occurring between reinforcements and metal matrix during the fabrication process, high temperature consolidation or even in service, is a significant issue and should be considered in a successful composite design. Indeed, some interactions may cause interfacial instability degradation of the reinforcement properties and formation of brittle interfacial reaction compounds, with resulting detrimental thermo-mechanical properties.

Among the potential reinforcement materials, SiC is widely recognized as ideal candidate for high temperature structural applications for its low density, chemical stability, outstanding resistance at high temperatures to thermal shock, high thermal conductivity and excellent mechanical properties, unusual for a nonmetallic material [5].

A combination of SiC with metal phases compensates the poor workability and the brittleness of ceramics. In parallel, the presence of SiC incorporated in a metal matrix (as particulates or fibers) significantly increases its thermo-mechanical response [6, 7].

The design and fabrication of cost-less highly performant light-weight MMCs with SiC as reinforcement, are basically focused in selecting the proper metal matrix phase. As mentioned before, the choice is limited to few elements meeting the requirements of high thermo-mechanical response combined with low density and thermo-compatibility with SiC.

To produce such composites with desirable properties, the reactive infiltration process, belonging to spontaneous/pressure-less infiltration mechanisms, has well known advantages over other conventional and costly sintering and hot-pressing techniques i.e. lower processing temperatures, shorter times and near-net shape fabrication capabilities [8-11]. In spontaneous infiltration, the molten metal phase invades into the voids of the porous refractory material. A “compact” microstructure can be easily obtained by controlling the process parameters (temperature, total pressure, porosity etc.) promoting good wetting characteristics crucial for self-permeation.

Several examples of composite microstructures easily obtained by infiltrating liquid Si and Si-based alloys into porous SiC and C-based materials [12-15] as well as SiC-C [16-19], SiC/C_f and SiC_f/SiC [20] are reported in literature, just to name a few. In particular, depending on the preform composition and in particular on the C-content, the liquid metal infiltration evolves through Reaction Bonded Silicon Carbide (RBSC) mechanism and β -SiC is produced at the interface [8-10]. Reactive infiltration can be used also to shape and join CMCs parts.

Despite these advantages, the main drawback of these materials is the presence of unreacted Si compromising the overall mechanical performance of the composite. The partial replacement of this phase with intermetallic compounds (silicides) like MoSi₂ [21, 22], CoSi₂ [16], ZrSi₂ [17], FeSi₂ [23] was successfully obtained in the fabrication of structural ceramic matrix composites for extremely high-temperature applications by infiltrating Si-rich eutectic alloys into C-based and SiC-C preform. However, in designing light-weight composite materials, owing to their high density, the mentioned intermetallic phases are ruled out a priori.

The selection of Si-Ti system could be a viable alternative worthy to be investigated. As an example, a SiC-TiSi₂ composite material should be resulting from spontaneously infiltration of a SiC-C preform with a liquid Si-Ti alloy in the Si-rich part of the phase diagram, at a processing temperature around $T = 1330^{\circ}\text{C}$, under vacuum or inert atmosphere. The composite obtained should exhibit a density value around 3 g/cm^3 , increased thermo-mechanical properties, high inherent compatibility and increased corrosion resistance.

Despite the encouraging predictions, many aspects are not yet understood, mainly related to the interfacial phenomena occurring during reactive infiltration process. Key contributions could be coming from the know-how on the thermophysical properties of the melt phase, such as surface properties (surface tension and surface segregation), density, viscosity, [24] and in parallel, on the wetting characteristics and reactivity concerning reacting phases [25].

To our best knowledge, the only one basic study on liquid Si enriched Si-Ti alloys concerns the surface tension [26] and fundamental wetting characteristics of such alloys on SiC substrate [27].

For this reason, a systematic preliminary investigation on the wetting characteristics and reactivity at Si-Ti eutectics/C interface as a function of operating conditions was performed by contact heating sessile drop method. By evaluating wettability, spreading kinetics of the eutectic alloy and all the interfacial reactions driving the growth of SiC reaction layer at the interface, the present work aims to aid the understanding of the processes governing the kinetics of reactive infiltration and well known pore narrowing and pore closure phenomena.

2. Wetting tests: experimental procedure

2.1 Materials and sample preparation

Glassy Carbon (GC) provided by Alfa-Aesar was selected as C-substrate material and used with as received surface conditions. An average roughness (R_a) ≈ 20 nm was measured by using an optical profilometer.

The Si-16.2at%Ti alloy samples (from now Si-Ti eutectic alloy), were prepared by mixing nominal weights of high purity Si and Ti (99.98%-Goodfellow®). To limit evaporation phenomena, the alloy samples were produced by arc melting technique under an atmosphere of Ar (N60, $O_2 < 0.1$ ppm). Before the arc melting of Si-Ti alloys, the residual oxygen content inside the chamber was reduced by melting a Zr drop. To ensure the homogeneity of the alloy composition, the melting of every single Si-Ti sample (0,5 g) was repeated 3 times. No evidences of evaporation or material loss were revealed by checking the final weight.

The as produced Si-Ti eutectic microstructure and composition was checked on the cross-sectioned sample by SEM/EDS.

As it can be seen in Figure 1, the typical eutectic microstructure is detected with embedded some $TiSi_2$ precipitates. The presence of $TiSi_2$ precipitates dispersed into the eutectic matrix is due to the segregation of few layers of Si at the alloy surface during solidification.

Prior to the experiments, the alloy sample and GC-substrate were rinsed in ethanol + US and dried with compressed air.

Figure 1. BSE images at two magnifications of the cross-sectioned Si-Ti eutectic alloy sample as-produced.

2.2 Experimental device and procedure

At room temperature, the Si-Ti eutectics/GC couple was placed on a graphite sample holder, introduced into the furnace and located at the central part of the heater (see Figure 2). Once leveled the sample at horizontal plane, in order to remove any contaminant from the experimental environment, the chamber was degassed under a vacuum ($P_{tot} \leq 10^{-6}$ mbar) for two hours.

The metal sample/substrate couple was heated under a Ar ($O_2 < 0.1$ ppm) atmosphere by a 800 kHz high frequency generator coupled to a graphite susceptor, extensively described elsewhere [28]. The experiments were performed under an inert atmosphere in order to avoid evaporation phenomena which typically occur during measurements of such liquid Si-based alloys [29]. In addition, the presence of graphite as a heater ensures an experimental surrounding atmosphere with a residual oxygen content of $PO_2 < 10^{-8}$ mbar.

Withing the wetting experiments, the temperature was continuously monitored by a pyrometer (Minolta-CYCLOPS52), previously calibrated by detecting the melting temperature of high purity metals (Sn, Al, Au, Cu, Si and Ni).

The wetting experiments were performed by contact heating sessile drop method and the isothermal conditions were achieved with a heating rate of $5^\circ\text{C}/\text{sec}$. The selected temperature was kept constant for 15 minutes, then the sample was “quenched” (cooling rate $10^\circ/\text{sec}$) to preserve the new formed interfaces and interface microstructure.

The evolution of contact angles was monitored in real-time and recorded (10 frames/sec) by a high resolution camera connected to a computer. Every single frame was processed by an image analysis software ad hoc-developed (ASTRAVIEW®) [30], which allows the automatic acquisition of contact angles and drop geometric variables (R-base radius and H-drop height). By analyzing the experimental method used and all the possible affecting factors, the accuracy of the contact angle value is estimated around $\pm 2^\circ$ [31].

2.3. Microstructural characterization

After wetting tests the Si-Ti eutectic/GC samples were embedded in epoxy-resin, cross-sectioned and polished using standard metallographic procedure (800-4000 grinding SiC papers and $1\ \mu\text{m}$ polishing diamond past) and prepared for the microstructural characterization. In order to analyze the microstructure and reaction products, both at the top and at the cross-sectioned solidified drop, a Optical Microscope (OM-Keyence VHX-700F) and a Scanning Electron Microscopy (SEM-Hitachi TM3000) equipped with an energy dispersive X-Ray detectors (EDS) were used.

Figure 2. Schematic layout of the experimental set-up used during contact heating sessile drop tests.

3. Results and discussion

As it can be seen in Figure 3, where the images sequence of spreading at $T = 1350^\circ\text{C}$ is shown, the complete melting of the Si-Ti eutectic alloy drop is achieved after 30 s. Although, as reported by [32], the isothermal temperature is 20°C higher than the melting temperature of Si-16.2at%Ti eutectic composition ($T_m = 1330^\circ\text{C}$), the delay in the melting could be due to the presence at the surface of 1)

SiO₂ as native oxide, 2) pure Si-segregated and 3) TiSi₂ precipitates embedded into the eutectic matrix (Figure 1).

The layer of native oxide is decomposed by its reaction with the underlying Si, forming the volatile Si monoxide [33]:

Figure 3. Time sequence images of spreading of Si-Ti eutectics/GC couple at T = 1350°C.

As shown in Figure 4, after the complete melting revealed at $t = t_1$, the alloy starts to interact with GC exhibiting a linear spreading kinetics (spreading rate $U_{\text{spr}} \approx 16.1 \mu\text{m/s}$) and in 30 s the transition between no-wetting to wetting behavior at Si-Ti/GC interface occurs. Indeed, the contact angle value rapidly decreases from $\theta \approx 120^\circ$ to $\theta \approx 48^\circ$ within the time range of $t_1 < t < t_2$. The contact angle continues to decrease linearly ($t_2 < t < t_3$) as a function of time with a sharp change in the slope (spreading rate $U_{\text{spr}} \approx 1.1 \mu\text{m/s}$). In general, linear spreading rates are associated to reactive wetting [34].

Despite the affinity of both the alloy constituents for carbon [35], at this temperature and for a Ti-content in the alloy of 16.2at%, the reaction of liquid Si to produce SiC at the interface, is thermodynamically more favored respect to the production of TiC or ternary carbides [36].

Figure 4. Contact angle values (■) and normalized R-Base radius of Si-Ti eutectics/GC at T = 1350°C (■).

As shown in Figure 5, the presence of SiC as unique reaction product at the Si-Ti eutectic/GC interface was confirmed by SEM/EDS analysis, randomly distributed at the center of the Si-Ti/GC interface as epitaxial SiC-crystals with a size of 5 μm . On the contrary, a quite compact thick SiC-layer (3-10 μm) was found at the triple line. At the triple line, during the spreading, the liquid alloy remains in contact with a non-reacted C, thus the growth rate of SiC parallel to the interface results at the end much higher than the growth rate at the interface behind the triple line where the interaction between the reactants is limited by the diffusion through the thin SiC layer produced [33, 35, 37]. The limited diffusion between the substrate and the liquid alloy by the epitaxial growing SiC layer and the SiC-thickening at the triple line, can explain the decrease in the spreading rate observed after $t = 200 \text{ s}$ where the equilibrium at the interface was achieved with a final contact angle of $\theta = 44^\circ$. The contact angle values measured at Si-Ti eutectics/GC are in agreement with the values reported for Si-85at%Ti/SiC measured at T = 1415°C [27] and in general with the contact angle values observed at Si-based alloys/SiC interfaces as reviewed by [38]. It is a further confirmation that Si-Ti

strongly reacts with GC but does not wet the substrate. The contact angle values observed at the equilibrium are in real between liquid Si-Ti eutectic alloy and SiC.

Figure 5. BSE image at the Si-Ti eutectics/GC after wetting test performed at $T = 1350^{\circ}\text{C}$.

Figure 6 shows the contact angle behaviors as a function of time for Si-Ti eutectic alloy on GC at different temperatures. As it can be seen, by increasing the temperature at $T \geq 1400^{\circ}\text{C}$, the equilibrium at the Si-Ti/GC interface is faster achieved than at $T = 1350^{\circ}\text{C}$. In particular, under equilibrium the same final contact angle value of $\theta = 43^{\circ}$ was measured at Si-Ti eutectic alloy/GC after $t = 40$ s and $t = 30$ s, at $T = 1400^{\circ}\text{C}$ and $T = 1450^{\circ}\text{C}$, respectively. Moreover, by analyzing the spreading kinetics without considering the melting stage at $T = 1350^{\circ}\text{C}$, is evident that $U_{\text{spr}}(1350^{\circ}\text{C}) < U_{\text{spr}}(1400^{\circ}\text{C}) < U_{\text{spr}}(1450^{\circ}\text{C})$.

As discussed before, in the wetting experiments performed by contact heating sessile drop method on highly reactive systems, the early-stage of spreading can start within the melting stage. In addition, the presence of native oxide layer at the interface represents a competitive factor to be taken into account as well as a not homogenous starting composition of the melting phase.

Figure 6. Evolution of contact angle values of Si-Ti eutectics/GC at different temperatures.

At higher temperatures, all the kinetics and transport phenomena are enhanced. Firstly, the increased kinetics of SiO_2 -decomposition by the reaction (1) contributes to achieve faster the complete melting of the alloy drop. Secondly, at higher temperatures, Si-evaporation/condensation phenomena are more favored, as shown in Figure 7.

As it can be seen, the area of evaporation adjacent to the triple line of Si-Ti/GC couple at $T = 1350^{\circ}\text{C}$ consists of a continuous thin layer of SiC with a width of $20\text{ }\mu\text{m}$. Moving far from the triple line, unreacted regions of GC appear with circular small areas of SiC-thin layer. Such phenomenon results typically from evaporation and condensation of highly reactive micro-droplets. As a consequence of condensation, the Si micro-droplets react with C to produce SiC. As suggested by [25], Si-evaporation might be also favored by the Si-segregation at the surface of the molten drop owing to the higher tensioactive effect of liquid Si respect to liquid Ti [24].

At the triple line of Si-Ti/GC couple, a shadow surrounding the drop perimeter resulting in a larger uniform SiC-layer around the drop, is revealed at $T = 1450^{\circ}\text{C}$. In this case, larger and more neighboring circular areas of SiC are produced. As it can be seen, close to triple line of both Si-Ti eutectic alloy/GC couples, a crack is generated most probably during the fast cooling of the sample.

It is due to the mismatch in the thermal expansion coefficients and to the strong adherence of Si-Ti alloy at the layer of SiC.

Figure 7. SEM/EDS analyses at the top of the solidified Si-Ti eutectic alloy/GC samples after wetting tests performed a) at $T = 1350^{\circ}\text{C}$ and b) at $T = 1450^{\circ}\text{C}$.

As a consequence of the increased temperature, the reactivity between Si-Ti alloy and C-substrate is enhanced as well as the rate of SiC-grow at the interface. Comparing the Si-Ti/GC interfaces obtained at $T = 1350^{\circ}\text{C}$ and $T = 1450^{\circ}\text{C}$, the strong temperature-dependence on the interfacial microstructure development is evident. In Figure 8a, at $T = 1350^{\circ}\text{C}$ the presence of C-dissolution pockets is revealed under the starting Si-Ti/GC interface. The growth of few SiC-crystals over the starting interface is detected. On the contrary, owing to the increased reactivity at $T = 1450^{\circ}\text{C}$, the C-dissolution pockets are completely transformed in a rougher and thicker SiC reaction layer (see Figure 8b).

Although the more pronounced evaporation observed at higher temperatures, the consequent formation of a thin reaction layer beyond the triple line, does not allow the further advancement of contact angle as observed for Si-Co eutectic alloy/GC at the same temperature [25]. It can be justified by the different molten phase. Si-Ti eutectics and TiSi_2 silicide phase exhibit a lower density than Si-Co eutectics and CoSi_2 . In addition, the surface tension of Si-Ti is little bit higher than Si-Co. The lower density combined with a higher surface tension of the molten phase could allow a more stability of the molten alloy on the GC substrate.

Figure 8. BSE/EDS analyses at the cross-sectioned Si-Ti eutectic alloy/GC samples after wetting tests performed a) at $T = 1350^{\circ}\text{C}$ and b) at $T = 1450^{\circ}\text{C}$.

4. Conclusions

For the first time, wettability and reactivity studies of liquid Si-16.2at%Ti eutectic composition in contact with Glassy Carbon were performed successfully by contact heating sessile drop method as a function of temperature. Wettability in terms of spreading kinetics and interfacial microstructure are strongly dependent by the temperature. In particular, within the melting stage, competitive phenomena such as the presence at the surface of alloy drop before the melting of SiO_2 as native oxide as well as a layer of Si-atoms segregated evidently affect the spreading kinetics mainly at lower temperatures. On the contrary, the temperature does not influence the final contact angle values even considering the more pronounced evaporation/condensation phenomena observed at higher temperatures.

Clear evidences were obtained and confirmation that the wettability and in particular the spreading kinetics are controlled by the formation and thickening of SiC at the interface and at the triple line.

The results obtained can be helpful to identify the key parameters affecting the manufacture of SiC/TiSi₂ composite materials. Nevertheless, the reactivity of liquid Si-Ti alloys on C should be extended by estimating the influence of Si-content and isothermal time on the SiC growth which is mainly responsible for the pore closure/narrowing phenomena affecting the kinetics of infiltration. In addition, the observed infiltration kinetics could be well-interpreted by using as inputs for modelling, still lacking reliable data on the thermo-physical properties.

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Fig. 1. BSE images at two magnifications of the cross-sectioned Si-Ti eutectic alloy sample as-produced.

59x22mm (300 x 300 DPI)

Fig. 2. Schematic layout of the experimental set-up used during contact heating sessile drop tests.
49x28mm (300 x 300 DPI)

Fig. 3. Time sequence images of spreading of Si-Ti eutectics/GC couple at $T = 1350^{\circ}\text{C}$.

16x57mm (300 x 300 DPI)

Fig. 4. Contact angle values ($\square$) and normalized R-Base radius of Si-Ti eutectics/GC at $T = 1350^{\circ}\text{C}$ ($\square$).
82x53mm (300 x 300 DPI)

Fig. 5. BSE image at the Si-Ti eutectics/GC after wetting test performed at $T = 1350^{\circ}\text{C}$.

43x32mm (300 x 300 DPI)

Fig. 6. Evolution of contact angle values of Si-Ti eutectics/GC at different temperatures.

82x53mm (300 x 300 DPI)

Fig. 7. SEM/EDS analyses at the top of the solidified Si-Ti eutectic alloy/GC samples after wetting tests performed a) at $T = 1350^{\circ}\text{C}$ and b) at $T = 1450^{\circ}\text{C}$.

86x32mm (300 x 300 DPI)