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An investigation of the self-propagating high-temperature synthesis of Ti(Si,Al)$_2$

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Titanium silicides have in recent years attracted interest by the aerospace industry because their high melting points and good corrosion resistance may enable them to withstand higher operating temperatures than advanced nickel-based superalloys. In addition, they have a low density, retain a high strength at temperatures in excess of 1000 °C and exhibit good creep resistance [1]. Other applications include the microelectronics industry as interconnectors and diffusion barriers for integrated circuits [1]. The main disadvantages of titanium silicides include the potential of pest corrosion and their low fracture toughness [2]. In order to overcome these drawbacks elemental additions of niobium, chromium and aluminum can be used. An additional problem to their application is the difficulty to process them. Potential manufacturing methods include mechanical alloying [3], while laser-based processes [4] and magnetron sputtering [5] have been used to prepare thin films and coatings. These processes are relatively expensive as they require high-cost equipment. Self-propagating high-temperature synthesis (SHS) is one of the processes that are under investigation for the production of titanium silicides [6, 7]. The process relies on exothermic reactions where, following ignition, the enthalpy of reaction is sufficiently high to spontaneously transform the reactants into products. The mathematical foundations of the technique were laid in the 1950s [8] and subsequently evolved by studies of Merzhanov [9]. The main attractions of the process are its potential for savings in energy utilization and time and the use of simple equipment. In spite of the significance of titanium silicides, there have been very few studies on the use of SHS for their production.

The work which is reported here investigated the use of SHS for the production of TiSi$_2$ and Ti(Si,Al)$_2$. Elemental powders of titanium, silicon and aluminum were used in the process. Samples were heated to ignition in a furnace under vacuum at a heating rate of 25 °C/min. Following ignition, the furnace was turned off and the reactions were allowed to self-propagate. The ignition temperature was measured using a thermocouple that was in contact with the top surface of the compacted powder. The products were analysed by means of X-ray diffraction (XRD) with Cu$_{K\alpha 1}$ radiation using a Philips PW1730 generator and a PW1050/25 goniometer. Scanning electron microscopy (SEM) was performed using a Camscan CS44 microscope.

A summary of the initial reactant sample compositions, the resulting phases following combustion synthesis and ignition temperature details are presented in Table I. The table also presents the expected product phases based on information from the equilibrium phase diagrams for the Ti-Si [10] and Ti-Si-Al [11] systems. A mixture of titanium and silicon powders was observed to ignite at around 1326 °C yielding TiSi$_2$ with a C-54 crystal structure. The recorded ignition temperature was very close to the two eutectic temperatures of 1332 °C that are found in the Ti-Si equilibrium phase diagram. One of the two eutectic points is at the Ti-rich end and represents the conversion of liquid to β-Ti and Ti$_5$Si$_3$, while the other one is at the Si-rich end and represents the reaction involving the liquid, TiSi$_2$ and Si. During the heating stage, silicon would be expected to start to diffuse into the titanium by means of solid-state diffusion at relatively low temperatures. Titanium–silicon diffusion couple experiments [12, 13] have shown that TiSi$_2$ and other intermediate silicides can form at relatively low temperatures and short periods of time. However, there is very little agreement as to what phases will form because all these studies have been conducted using silicon of different crystalline form and crystal orientation. On this basis it is difficult to decide which one of the two eutectic reactions would occur, leading to the ignition of the SHS reaction. According to the equilibrium phase diagram [10] during solid-state diffusion of silicon into titanium, Ti$_3$Si is expected to be the first phase to form followed by Ti$_5$Si$_3$ and then TiSi$_2$. However, Ti$_3$Si is not stable above 1170 °C as at this temperature it transforms to β-Ti and Ti$_5$Si$_3$. As observed by Trambukis and Munir [6], it appears that in the present study also, ignition of the combustion reaction initiated at the temperature where liquid-phase formation took place.

The presence of aluminum in subsequently ignited Ti-Si powder mixtures led to a significant reduction in the ignition temperature to between 575 °C and 590 °C. These values coincide with the eutectic temperature of around 577 °C exhibited by the Al–Si equilibrium phase relationship [14]. This observation confirmed that the ignition temperature for the reacting mixtures was indeed determined by the formation of a liquid phase

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TABLE I The composition, expected product, observed product and ignition temperature for a selection of samples

Sample no.	Reactant composition (Ti:Si:Al atomic ratio)	Expected product phases	Observed product phases	Ignition temperature (°C)
1	1:2:0	$TiSi_2$(C-54)	$TiSi_2$(C-54)	1326
2	1:1.94:0.06	$TiSi_2$(C-54) $TiSi_2$(C-49)	$TiSi_2$(C-54) $TiSi_2$(C-49)	590
3	1:1.88:0.12	$TiSi_2$(C-49)	$TiSi_2$(C-49) Small amounts of $TiSi_2$(C-54) and Ti(Si,Al)	577
4	1:1.82:0.18	$TiSi_2$(C-49)	$TiSi_2$(C-49) Small amounts of $TiSi_2$(C-54), Ti(Si,Al) and $Ti(Si,Al)_3$	575

Figure 1 Photograph of pellet of sample 4 following the SHS reaction showing significant deformation of the pellet.

during the heating process. In contrast to Ti–Si pellets, Ti–Si–Al pellets suffered significant deformation as a result of the combustion reaction as shown in Fig. 1. It was also evident that almost spherical globules formed at the surface of the pellets of all the aluminum-containing mixtures. These features implied that the reaction was violent by nature and led to substantial melting within the sample.

The microstructure obtained from the SHS reaction of sample 2 is presented in Fig. 2. SEM examination revealed the presence of two phases. The light grey phase contained 1.80 at.% Al, while the aluminum content of the dark phase was higher at 8.01 at.%. The higher amount of aluminum in the dark phase was achieved at the expense of silicon, while the amount of titanium in these phases remained almost constant. On the basis of XRD analysis, the two phases were identified as C-54 and C-49 $Ti(Si,Al)_2$, the latter of the two containing a higher amount of aluminum than the former. According to the Ti–Si–Al equilibrium ternary phase diagram [11], the starting composition for this sample lies within the C-54 and C-49 $Ti(Si,Al)_2$ phase field and therefore yielded the expected equilibrium phases.

The combustion synthesis for a Ti–Si–Al mixture that lied entirely within the C-49 $Ti(Si,Al)_2$ phase field (sample 3) of the phase diagram [11] yielded mainly the C-49 phase with traces of both the C-54 phase and Ti(Si,Al). SEM examination indicated that the C-49 phase was not uniform exhibiting regions with variation in both the aluminum and silicon content. This observation is displayed in Fig. 3, where the darker parts of the matrix contain up to 18 at.% aluminum at the expense of silicon. According to the Ti–Si–Al phase relationship, this figure is close to the maximum amount of 20 at.% Al that the C-49 phase can accommodate. The lighter parts of the matrix in Fig. 3 contained about 9.4 at.% Al, a value which is also in good agreement with the phase diagram and representing the lowest amount of aluminum that the C-49 phase can exhibit. Near one end of the pellet, small particles of C-54 $Ti(Si,Al)_2$ were also detected. This may have occurred due to poor mixing of the reactant powders in that area during sample preparation. In addition to this, Ti(Si,Al) was also observed to form within some of the pores of the product. In combustion products from compositions within the C-49 phase field but with higher amounts of aluminum, there

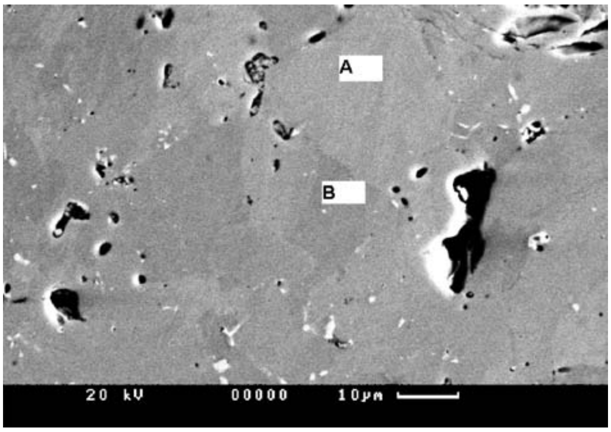

Figure 2 Microstructure of sample 2 showing the C-54 $Ti(Si,Al)_2$ phase (light grey areas marked A) and the C-49 $Ti(Si,Al)_2$ phase (darker areas marked B).

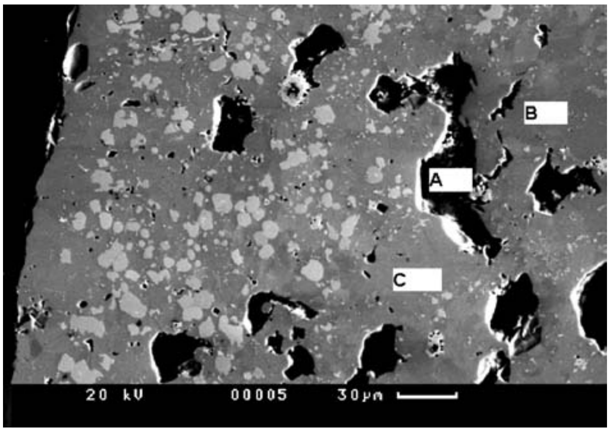

Figure 3 Microstructure of sample 3 showing: A: porosity; B: C-49 $Ti(Si,Al)_2$ phase containing a higher amount of aluminum; C: C-49 $Ti(Si,Al)_2$ containing a low amount of aluminum; bright particles: C-54 $Ti(Si,Al)_2$.

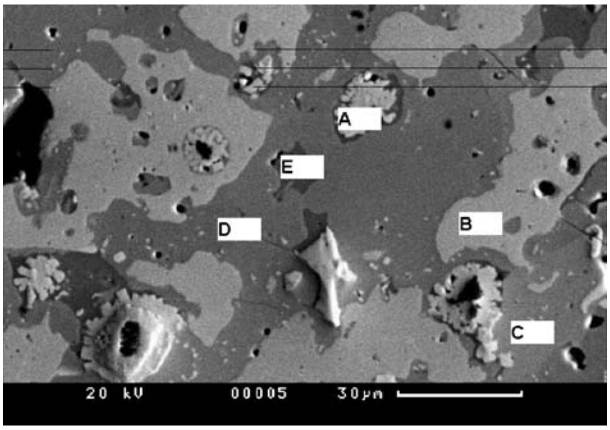

Figure 4 Microstructure of sample 4 showing: A: Ti(Si,Al) formation within pores; B: C-54 $Ti(Si,Al)_2$; C: C-49 $Ti(Si,Al)_2$ containing a low amount of aluminum; D: C-49 $Ti(Si,Al)_2$ phase containing a higher amount of aluminum; E: dark regions of $Ti(Si,Al)_3$ forming within pores.

was increasing evidence of Ti(Si,Al) formation within the pores as shown in Fig. 4. In addition, formation of $Ti(Al,Si)_3$ within some pores was also observed. The morphology of these phases that formed within the pores and particularly that of Ti(Si,Al) differed significantly from that of the other product phases. This, coupled with the fact that the two phases were observed to form only within the pores implied that Ti(Si,Al) and $Ti(Al,Si)_3$ followed a different mechanism of formation. The most likely reaction mechanism for these products was formation via the vapour phase and specifically via the vapour-liquid-solid mechanism. The combustion temperature for the sample shown in Fig. 3 was experimentally measured to be 2032 °C. Using thermodynamic data compiled by Turkdogan [15], the partial pressures of titanium, silicon and aluminum at the combustion temperature were calculated to be 4.0×10^{-4} atm, 7.2×10^{-4} atm and 6.5×10^{-2} atm respectively. These values are relatively high and therefore some volatilisation of the three reactant elements would be expected to take place during the reaction process. At the combustion temperature, the three elements would be expected to be in the molten state, while solid $Ti(Si,Al)_2$ was being formed. During this process, the vapour became trapped within the pores and as cooling progressed the vapour phases became supersaturated. The supersaturation ratio, S.R., may be calculated using the equation,

$$\text{S.R.} = \frac{(p - p_o)}{p_o}$$

where p is the vapour pressure of the of the condensed phase and p_o represents the equilibrium partial pressure at ambient temperature. It appears that as cooling of the samples proceeded, the elemental vapours reacted together condensing solid Ti(Si,Al) and $Ti(Al,Si)_3$. The product phases from reaction of the elemental vapours were not the phases predicted to form by the thermodynamics of the system, but were dictated by the vapour composition within the pores. The high supersaturation ratio of the elemental vapours as the samples cooled provided the driving force for Ti(Si,Al) and $Ti(Al,Si)_3$ to form within the porous regions. The partial volatilisation of the reactant elements also probably contributed to the deformation of the product pellets and the ejection of molten globules to the pellet surface.

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