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Gas pressure combustion sintering and hot isostatic pressing in the Ti–Si–C system

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The processing of materials in the Ti–Si–C system produced by gas pressure combustion sintering (GPCS) and hot isostatic pressing (HIP) was studied. By variation of the raw material composition it was possible to produce different materials containing Ti_5Si_3, Ti_3SiC_2, $TiSi_2$, TiC, SiC and titanium. The different phase compositions of samples with the same reactants obtained by GPCS and HIP are due to the duration of each of the processes; in GPCS the equilibrium state was not achieved. The properties of the specimen are strongly related to their chemical behaviour during processing at high temperatures. Not all phases built up at the high temperatures during the GPCS and HIP processes are stable at lower temperatures, and some reactions occur during cooling, which influence densification, microstructure and properties of the bodies finally obtained.

1. Introduction

Recently, new composites with heterogeneous structure, which are called functional gradient materials (FGMs), have attracted attention in the field of advanced materials. The FGMs have a characteristic microstructure consisting of a metal phase, which increases continuously within the ceramic matrix starting from a surface layer of pure refractory ceramic. Because of their special composition, they are expected to have application as a unique high temperature material with low internal thermal stress and thermal conductivity.

The first step in designing FGMs is a comprehensive characterization of different materials to clarify a possible application for FGM. Recently, some FGMs consisting of silicides (e.g. $MoSi_2$) have been successfully produced and their design and excellent properties investigated [1]. Other possible candidates are titanium silicides, especially for materials consisting of additional carbon compounds such as titanium and silicon carbides [2]. Such compounds are also used in other applications, as reported by Gottselig *et al.* for the joining of silicon carbide to titanium layers [3]. The chemical behaviour of the Ti–Si–C system is not so simple. Depending on the titanium–silicon–carbon ratio, different titanium silicides exist, such as Ti_5Si_3, TiSi or $TiSi_2$, as well as the carbides TiC and SiC. According to some references, the ternary phase Ti_3SiC_2 can also be formed [3, 4]. In this way it should be possible to obtain materials with different phase compositions and properties.

The aim of the present study was the fabrication and characterization of materials in the Ti–Si–C system with different phase compositions, by GPCS and HIP. Finally, according to their chemical behaviour and material properties, a possible application in an FGM was examined.

2. Experimental procedure

In the present study, homogeneous composites of the Ti–Si–C system were produced by GPCS and HIP. The raw materials, titanium, silicon, carbon and SiC (Table I), were mixed by a dry mixing method. The green bodies obtained by uniaxial (150 MPa) and isostatic (250 MPa) pressing were encapsulated in Pyrex glass at 780 °C in vacuum. In order to prevent direct contact with the capsule glass, the compacts were embedded in boron nitride powder. The reaction of the raw material to the final phase composition and densification was carried out by GPCS and, in some cases, by a considerably slower post-HIP process.

GPCS is a process in which synthesis and densification occur simultaneously and rapidly by execution of self-propagating high-temperature synthesis (SHS) under high isostatic gas pressure. Many refractory non-oxide ceramics and intermetallic compounds can be sintered in a few seconds at high temperatures produced by the high exothermic character of the rapid reaction [5]. The combustion synthesis seems to be an excellent way of producing FGMs, because the rapid reaction and sintering process can limit the diffusion process and maintain the compositional configuration of the starting body. In addition, it should be possible to produce composites consisting of such different materials as metals and

TABLE I Characterization of the raw materials used

Raw material	Purity (%)	Size (μm)	Brand	Manufacturer
Ti	99.5	> 45	TSPT 350	Osaka Titanium
Si	99.9	2–3	Si 2–3	Kojundo Kagaku
C	96	0.5	SP 300	Nihon Kokuen
SiC	> 98	0.27	Betarundum	Ibiden Co. Ltd

refractory ceramics, the preparation of which is problematic with a normal sintering method, because of the different sintering behaviour of the starting materials.

In this case, the encapsulated sample was embedded in a graphite crucible with a titanium carbon powder mixture serving as ignition powder. After heating to the softening temperature of the capsule glass (780 °C) and pressurization to 100 MPa, the titanium carbon mixture was electrically ignited. The reaction to TiC produces high temperatures (approximately 3000 °C) in a very short time in which the raw materials react and densification occurs. After the reaction, the cooling process is also very fast (estimated cooling rate about 500 K min^{-1} at temperatures > 1500 °C). A more detailed description of the GPCS is given by Miyamoto *et al.* [6, 7].

The HIP process, as a post-HIP process of the samples after GPCS, was carried out in a boron nitride powder bed at approximately 1800 °C under an isostatic argon pressure between 160 and 180 MPa.

After decapsulation, the samples obtained were characterized by their density, using Archimedes' method and phase content, using X-ray diffractometry (XRD) with CuK_α radiation.

Information about the microstructure was obtained by observing the polished surface of the samples using an optical microscope.

Some mechanical properties, such as Vickers' hardness, fracture toughness and bending strength, were also evaluated. Fracture toughness was measured by the indentation microfracture method (IM) by applying a load of 49 N for 15 s. The values were obtained from measurement of the crack length using the equation given by Niihara *et al.* [8]. In the case of ceramic–metal composites it was not possible to use this method because of a more plastic behaviour. These data were obtained by using a chevron-notch method described by Munz [9]. The bending strength was measured in three-point bending geometry with a span of 15 mm on specimens 3 mm × 4 mm × 20 mm in dimensions. The tensile surface were polished and the edge removed prior to testing.

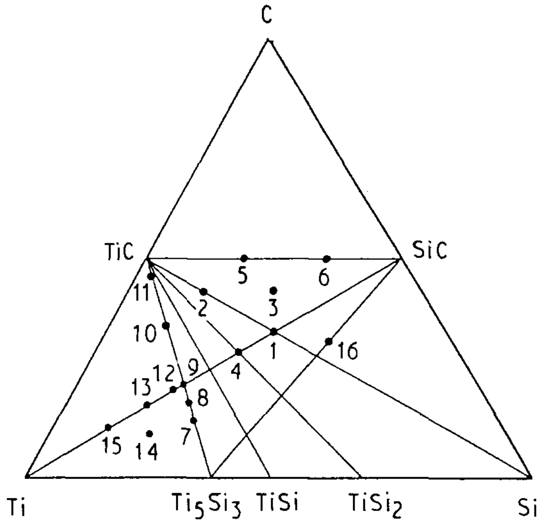

Figure 1 Map of the starting composition in the Ti–Si–C system.

3. Results and discussion

3.1. Chemical behaviour in the Ti–Si–C system

Fig. 1 shows the map of starting compositions in the Ti–Si–C system. Depending on the raw material composition, different titanium silicides, Ti_5Si_3, TiSi and $TiSi_2$, should be produced. The final composition is also influenced by the carbon content in the material. In the titanium-rich corner, limited by the Ti_5Si_3–TiC line, only Ti_5Si_3, TiC and titanium were detected; the final phase composition, however, became more complicated with increasing silicon content. TiSi was not detected by XRD in the investigated samples. Probably it combines with TiC to form the more stable Ti_3SiC_2 (Equation 1) which was found according to the XRD data given by Goto and Hirai [4]

$$TiSi + 2TiC \rightleftharpoons Ti_3SiC_2 \tag{1}$$

In this area of the phase diagram, the phase composition of samples with the same raw materials was different after GPCS and HIP. One possible reason for these results could be diffusion problems related to the very short reaction time during the combustion process but, on the other hand, the influence of diffusion at such high temperatures should be small. In addition, no different phase compositions after GPCS and HIP were found for samples in the titanium-rich corner of the system. Fig. 2 shows the XRD patterns of Sample 1 after GPCS and post-HIP. After HIP treatment a higher amount of $TiSi_2$ was found; meanwhile the titanium-rich phase, Ti_3SiC_2, disappeared. A similar tendency was obtained for other samples, e.g. Samples 2, 3 or 4. After HIP, the phase content of the titanium-rich silicides became smaller, but a higher amount of the silicon-rich silicides was found. It is supposed that during the combustion process the titanium-rich silicides are built up first. Depending on the cooling time, these compounds produced at very high temperatures will convert to the thermodynamically more stable ones at lower temperatures. This assumption is supported by comparing the phase compositions of samples with the raw material composition 5, produced by combustion and HIP.

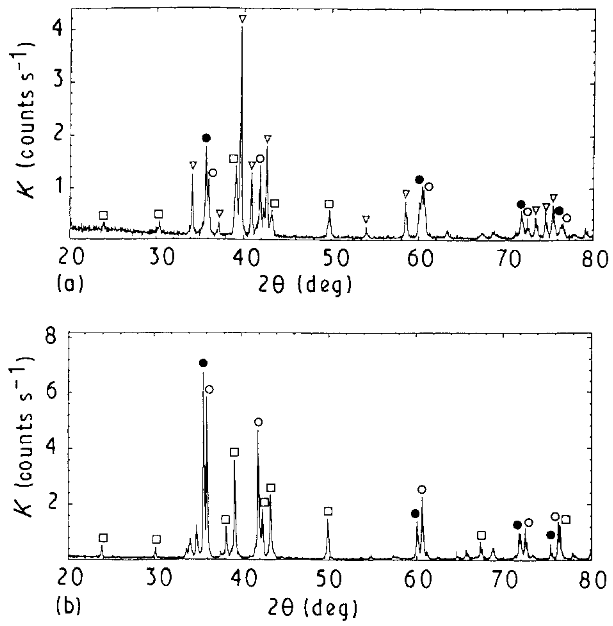

Figure 2 XRD pattern of samples with the raw material ratio 2: (a) after GPCS, (b) after post-HIP. (●) SiC, (○) TiC, (▽) Ti_3SiC_2, (□) $TiSi_2$.

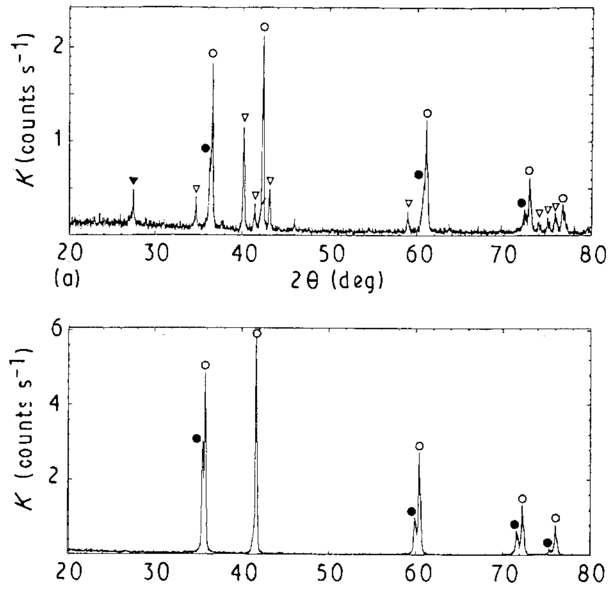

Figure 3 XRD pattern of samples with the raw material ratio 3: (a) after GPCS, (b) after post-HIP. (●) SiC, (○) TiC, (▽) Ti_3SiC_2, (▼) C.

Although according to the raw material ratio, only TiC and SiC should be produced, Ti_3SiC_2 and carbon were found in the sample after GPCS (Fig. 3). After the HIP process, which required much more time, these phases disappeared and only TiC and SiC remained.

Information about the dependence of the stability of the compounds in this system on temperature, are obtained by thermodynamic calculation. From the thermodynamic point of view, the titanium-rich silicides and SiC are stable at high temperatures, but the silicon-rich silicides and TiC became the stable phases at lower temperatures. As an example, the free energy of the reaction between Ti_5Si_3 and SiC, according to Equation 2, is plotted as a function of temperature in Fig. 4.

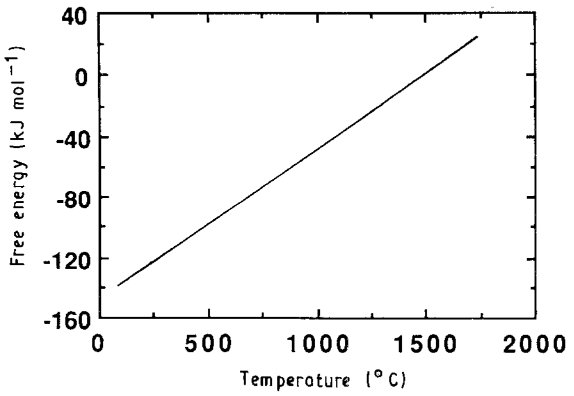

Figure 4 Temperature dependence of free energy for Equation 2.

$$3\,Ti_5Si_3 + 7\,SiC \rightleftharpoons 8\,TiSi_2 + 7\,TiC \qquad (2)$$

During cooling, the direction of this equilibrium changes from the high-temperature phases Ti_5Si_3 and SiC, to $TiSi_2$ and TiC, stable at temperatures below 1475 °C. This behaviour, which is in agreement with the above results, was confirmed in an experiment where the phase content of a sample with $3Ti_5Si_3$ and 7SiC converted completely to 8 $TiSi_2$ and 7 TiC after HIP at 1800 °C. Such reactions are supposed to be the main reason for the different phase compositions after GPCS and HIP. In contrast to the HIP process after GPCS, the samples were quenched in a very rapid cooling process. So the equilibrium state was not achieved and a higher content of the high-temperature stable phases was found.

3.2. Properties of the materials produced

The properties of the samples obtained by both GPCS and HIP are strongly related to their chemical behaviour. It was not possible to achieve fully densified samples in all cases. In the combustion process, one reason for this is the insufficient sintering time which is not long enough for complete densification of more refractory materials to occur. As an example, the achieved density of Ti_5Si_3/TiC samples, where no reactions occur during cooling, with increasing TiC content is shown in Fig. 5. At a TiC content as high as 50 mol%, fully densified samples were still not obtained by GPCS with a titanium–carbon mixture as the ignition powder. These materials were, however, fully densified using the HIP process (1800 °C/170 MPa, 1 h). With further investigation of the processing of GPCS, especially in optimizing the temperature–time dependence of different ignition powders, it should be possible to improve the capability of this method too.

This may be only one of the reasons for the incomplete densification of the samples in the Ti–Si–C system. The phenomenon of densification is very complex and is also influenced by the chemical behaviour of the material. It is supposed that because of the reactions occurring during cooling, the microstructure of the material also changes. Furthermore, reactions such as

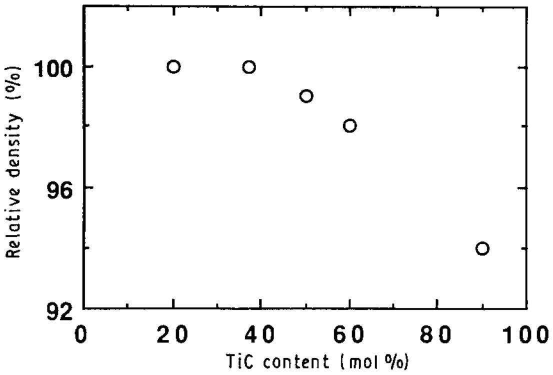

Figure 5 Density of Ti_5Si_3/TiC samples produced by GPCS with different TiC contents.

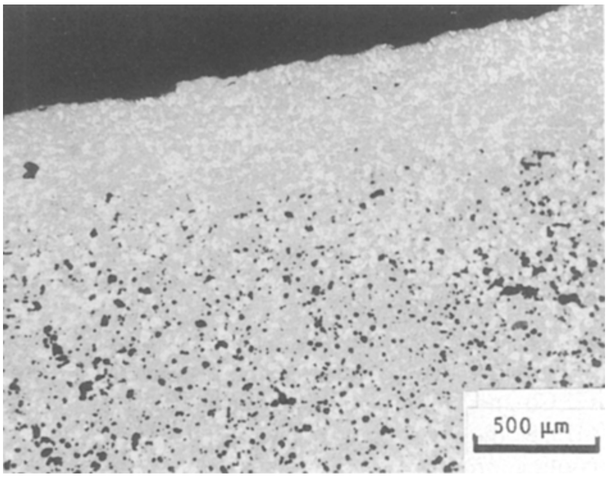

Figure 6 Microstructure of Sample 16 after GPCS.

that shown in Equation 2, produce TiC which has a higher density than the other components. In this case, the calculated density of the mixture $3Ti_5Si_3 + 7SiC$ is 4.00 g cm^{-3} and increases after changing to $8TiSi_2 + 7TiC$ to 4.30 g cm^{-3}. In this way the volume phase of the products becomes smaller and pores can be produced. Fig. 6 shows the microstructure of the polished surface of Sample 16 produced by GPCS. Although a large amount of low-melting phase ($TiSi_2$, $F = 1540$ °C) was present, this material was porous. Only at the edge of the sample was the material fully densified. The conversion to $TiSi_2$ and TiC occurred first at this area due to the temperature gradient during cooling. The applied gas pressure was sufficient to densify this region of the sample. When the process moved to the centre, the edges were already stable and inhibited a complete densification.

The complex character of densification in this system is shown as an example for Material 3. During the HIP process at approximately 1800 °C, a considerable change in microstructure was found. Probably very good conditions exist for crystal growth of SiC at these temperatures. Fig. 7 shows the microstructure of samples with Composition 3 after treatment under different HIP conditions, which are shown schematically in Fig. 8. In particular, at the edge of the SiC particles, pores were found which were the result of the reactions during cooling. Because of the steric effect of the large SiC particles, the densification became much more difficult compared with the material in Fig. 7b where no hold time at 1800 °C was applied to avoid crystal growth. Fig. 7c shows the material from Fig. 7b after an additional post-HIP treatment under the conditions of Fig. 7a. As a result of the hold time at 1800 °C, large SiC particles appeared which again produced more pores. The small differences obtained in the density of these three samples showed the same

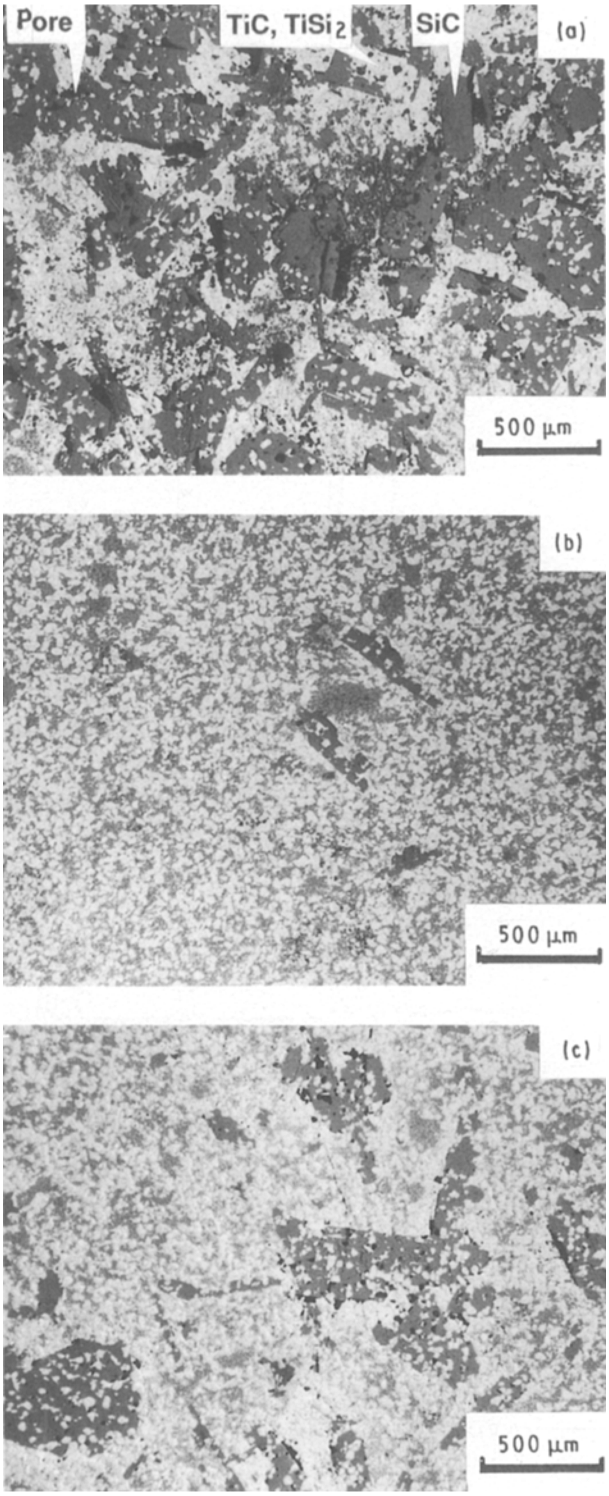

Figure 7 Microstructure of Sample 3 after different HIP processes. (a) Cycle 1, with hold time at 1800 °C of 60 min, (b) cycle 2, with hold time at 1800 °C of 10 min, (c) post-HIP of Sample (b) with cycle 1.

TABLE II Mechanical properties of samples from the Ti–Si–C system produced by GPCS and HIP (by estimation of the phase content, the formation of nonstoichiometric TiC was neglected)

Production method	Phase composition (vol%)					ρ	σ	k_{1c}	H_V	E
	Ti$_5$	Si$_3$	TiC	SiC	Ti	(g cm^{-3})	(MPa)	(MPa m$^{1/2}$)	(GPa)	(GPa)
GPCS	7	81	19	–	–	4.52	350	4.23	12.40	275
	8	74	26	–	–	4.52	350	4.10	12.88	279
	9	67	33	–	–	4.52	355	3.45	13.32	282
	12	63	32	–	5	4.52	350	3.94	12.28	284
	13	49	23	–	28	4.49	580	6.05	11.05	207
	14	56	13	–	31	4.47	770	7.04	9.80	211
	15	31	15	–	54	4.49	1115	10.01	6.04	178
Post-HIP	5	–	62	38	–	4.27	260	5.04	30.39	386
	6	–	29	71	–	3.72	350	3.99	25.15	358
	10	39	61	–	–	4.67	345	3.72	25.73	268
	11	11	89	–	–	4.84	340	3.57	32.70	406

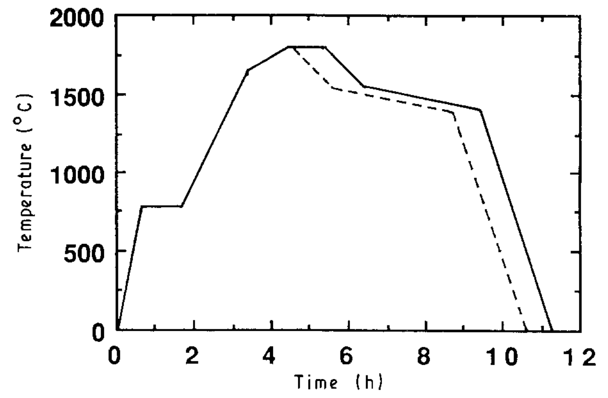

Figure 8 Schematic temperature–time dependence of the post-HIP processes. (—) Cycle 1 (- - -) cycle 2.

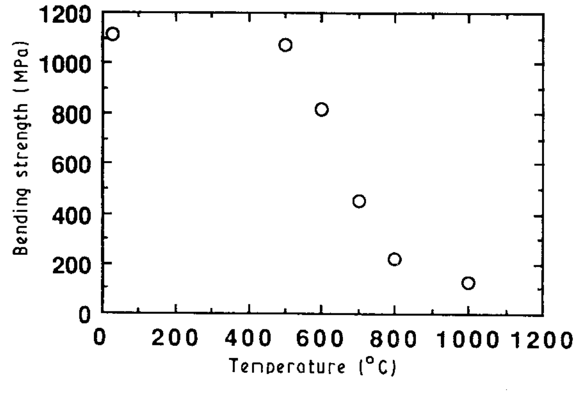

Figure 9 Results of bending-strength test as a function of temperature for Sample 15 after GPCS (three-point bending, crosshead speed 0.5 mm min^{-1}).

tendency. The highest density was obtained for the material in Fig. 7b with 4.08 g cm^{-3}, compared with those of the materials in (a) of 4.01 g cm^{-3} and in (c) of 4.03 g cm^{-3}. No noticeable difference in the phase composition of these three materials was found.

As described, the densification in this system is not only a question of the refractory character of the materials, it is also influenced by changes in the microstructure due to chemical reactions and grain growth.

This behaviour also influences the mechanical properties of the samples obtained. The changed microstructure due to chemical reactions and grain growth produced defects and residual stresses in the material which are responsible for the poor properties, especially in strength. Some properties of fully densified samples obtained by GPCS and HIP are given in Table II.

In the case of the Ti–Ti$_5$Si$_3$–TiC composites, superior properties were found. With increasing metal content, an improved behaviour in bending strength and fracture toughness was obtained: the material showed a more plastic behaviour. At high temperatures, in particular, a plastic deformation of the specimen occurred during the test, related to a considerable degradation in strength, as shown in Fig. 9.

Owing to the chemistry in the Ti–Si–C system, the processing in both GPCS and HIP processes was difficult. With the exception of the ceramic–metal composites and materials containing Ti$_5$Si$_3$/TiC or TiC/SiC, the densification was influenced by changes in the phase composition and microstructure. Because of the high chemical reactivity of the materials in this system, any application at high temperatures would be difficult.

4. Conclusion

The processing of materials in the system Ti–Si–C by GPCS and HIP was studied. In the titanium-rich corner, limited by the line between Ti$_5$Si$_3$ and TiC, only Ti$_5$Si$_3$, TiC and titanium were found, the phase composition becoming much more complicated with increasing silicon content. The titanium-rich silicides built up at high temperatures were converted during cooling to silicon-rich silicides and TiC which were stable at lower temperatures. This and the very short reaction time should be the main reasons for the different phase compositions obtained by GPCS and HIP. During the GPCS process, the equilibrium state was not achieved.

The properties of the materials produced were strongly related to their chemical behaviour. Changes in phase composition and microstructure during processing at higher temperatures influence the densification and finally the mechanical properties of the samples. For this reason and their high chemical reactivity at high temperatures, any application of these materials at high temperatures could be problematical.

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