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Solid Combustion Synthesis of Ti_3SiC_2

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Abstract

Using powders of Ti and Si and carbon black as reactants, a material composed mainly of the ternary compound Ti_3SiC_2 and of minor amounts of TiC was synthesized by the method of solid combustion. Following ignition at 1050°C, complete conversion of the reactants to the products was observed in a time of 2 to 5 s. The product obtained from the molar composition 3Ti:Si:2C has properties similar to the CVD-derived polycrystalline Ti_3SiC_2, which is a 'soft' ceramic material capable of being shaped by metal-working methods and shows a high resistance to oxidation and to aggressive environments.

Ausgehend von Titan- und Siliziumpulvern und Ruß als Reaktanden wurde durch exotherme Reaktion ein Material hergestellt, das hauptsächlich aus der ternären Verbindung Ti_3SiC_2 und geringen Gehalten von TiC besteht. Nach der Zündung bei 1050°C erfolgte die vollständige Umwandlung der Edukte zum Produkt in c. 2–5 Sekunden. Die Eigenschaften des Produkts (Zusammensetzung 3Ti:Si:2C) sind vergleichbar mit denen von CVD-synthetisiertem, polykristallinem Ti_3SiC_2, das ein 'weicher' keramischer Werkstoff ist, der durch Metallbearbeitungsmethoden geformt werden kann. Außerdem weist dieses Materials einen hohen Oxidationswiderstand auf und ist in chemisch aggressiven Umgebungen beständig.

Un matériau composé principalement de Ti_3SiC_2 et de petites quantités de TiC a été synthétisé à partir de poudres de Ti, Si et de noir de carbone par la méthode de combustion solide. Aprés amorçage à 1050°C, on observe une conversion complète au bout de 2 à 5 secondes. Le produit obtenu à partir de la composition molaire 3Ti:Si:2C présente des propriétés similaires à celles du Ti_3SiC_2 polycristallin produit par CVD, qui est une céramique 'douce', apte à être mise en forme par des méthodes métallurgiques traditionnelles et qui montre une résistance élevée à l'oxydation et aux milieux agressifs.

Introduction

According to Refs 1–5, the ternary compound Ti_3SiC_2 combines properties typical of ceramics, such as a high melting point (above 3000°C), resistance to high-temperature oxidation and resistance to aggressive environments, with mechanical properties which render it capable of being shaped by metal-working methods. Single crystals and polycrystalline Ti_3SiC_2 have been obtained by earlier authors in laboratory scale only, namely by CVD from gaseous titanium, silicon and carbon chlorides in hydrogen,[2,4,5] by reaction of gaseous TiH_2, silicon and graphite at 2000°C,[1] by heating of TiC, $TiSi_2$ and TiSi mixtures at 1400°C,[2] and by heating titanium foil with SiC at 1500°C in vacuum.[6] A development into a larger scale of these methods is difficult and the feasibility of a synthesis of Ti_3SiC_2 by solid combustion has been investigated by the present authors. In the method of solid combustion the exothermic heat of reactions is utilized to increase the temperature of reactive precursor-mixtures to a high level in a very short time, provided that the reactions are relatively strongly exothermic and that a proper preheating procedure is applied.[7–10] Due to this, the conversion to products is complete in a very short time. This energy- and time-saving method requires simple installations only and may be developed into a larger scale.

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Table 1. Characteristics of reactants

Reactant	*Source*	*Particle size*	*Content of principal element (%)*	*Main metallic impurities (mol%)*
Silicon powder	Z. A. Tarnow, Poland	10 μm	99·9	Al < 0·02 Cu < 0·02 Ni < 0·05
Titanium powder	Koch-Light Ltd, USA	150 μm	99·5	Si < 0·1 Mo ~ 0·15 Mg < 0·1 Fe < 0·1
Carbon black	Carbochem, Gliwice, Poland	20 nm	93·0[a]	Mg ~ 0·05 Fe ~ 0·05 Ca < 0·01

[a] The major impurity is oxygen.

Experimental and Results

The reactants were Ti, Si and carbon black powders, the main characteristics of which are given in Table 1. The solid combustion was investigated by using several compositions which are indicated by numbers 1 to 13 in Fig. 1 on the background of the subsolidus equilibrium phase diagram of the Ti–Si–C system.[11]

Suspensions of powders of a given composition in ethanol were mechanically mixed in a ball mill and homogenized in an ultrasonic disintegrator. The suspensions were next dried to attain a content of ethanol of about 15% and shaped by uniaxial cold pressing into 10 g pellets of 20 mm diameter and 20 mm thickness. In order to initiate the synthesis the method of 'thermal explosion' was used, namely the pellets of the reactants were placed into a graphite crucible situated inside a quartz tube reactor (Fig. 2). The crucible was heated inductively first to 800°C (in order to dry the pellet completely) and next, rapidly, at a rate of 500 K/min, to 1050–1200°C. At these temperatures ignition of the reactive mixtures occurred which was followed by a rapid increase of the temperature of the mixture and a spontaneous rapid advancement of the reactions. The temperature peak following the ignition had a duration of 2 to 5 s, after which the temperature spontaneously returned to its original level. This phenomenology, similar to the one observed on solid combustion in the Si–C system,[12] was found to occur in all cases except for the binary composition corresponding to $TiSi_2$ stoichiometry. Experimentally determined ignition temperatures for the different investigated compositions are indicated in Table 2.

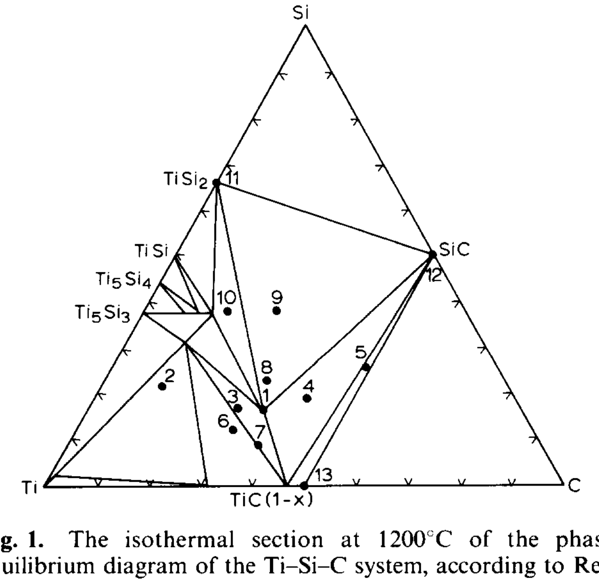

Fig. 1. The isothermal section at 1200°C of the phase equilibrium diagram of the Ti–Si–C system, according to Ref. 11. The compositions of the reactants used for solid combustion in the present work are indicated by numbers 1 to 13.

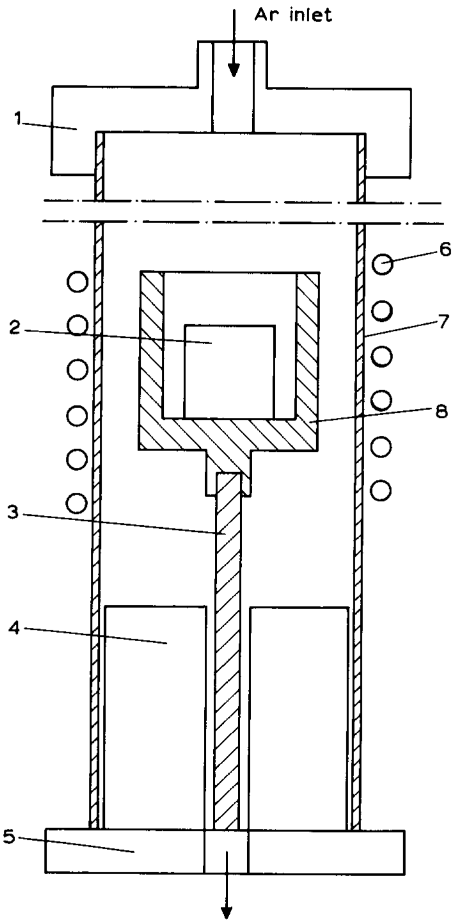

Fig. 2. The quartz reactor: 1, Teflon hood; 2, pellet of the reactive mixture; 3, graphite mandrel; 4, Al_2O_3 stool; 5, Teflon plate; 6, induction coil; 7, quartz tube; 8, graphite crucible.

The major crystalline phases in the products of solid combustion were determined on the basis of powder X-ray diffraction patterns registered by using a TUR M62 apparatus (GDR) equipped with a horizontal goniometer (HZG4) and a Co lamp with Fe filters. The identification of the phases were based on data for Ti_3SiC_2 published in Refs 1 and 5,

Table 2. Characteristics of products

Composition number	*Elemental composition of reactants (mol%)*			*Ignition temperature (°C)*	*Major crystalline phases in products*
	Ti	*Si*	*C*		
1	50	16·7	33·3	1 050	Ti_3SiC_2, TiC
2	67	22	11	1 000	Ti, TiC
3	55	18	27	1 050	TiC, Ti_3SiC_2
4	40	20	40	1 050	Ti_3SiC_2, TiC, $TiSi_2$
5	25	25	50	1 050	TiC, β-SiC
6	57	14	29	1 100	TiC
7	55	9	36	1 080	TiC, Ti_3SiC_2, β-SiC
8	46	23	31	1 020	Ti_3SiC_2, β-SiC, $TiSi_2$, TiC
9	36	38	26	1 010	$TiSi_2$, TiC, β-SiC
10	45	38	17	1 010	$TiSi_2$, TiC
11	33·3	66·6	—	no ign.	$TiSi_2$
12	—	50	50	1 180	β-SiC
13	50	—	50	1 100	TiC

and on JCPDS Powder Diffraction File for the other compounds.[13] The results are given in Table 2. In case of composition 1, corresponding to stoichiometric Ti_3SiC_2, the product was additionally HF treated in order to remove any residual Ti and Ti-silicides if present (Ti_3SiC_2 and TiC are resistant to action of the hydrofluoric acid). There was no change of mass after such a treatment, which indicates that Ti and Ti-silicides do not accompany here the major phases.

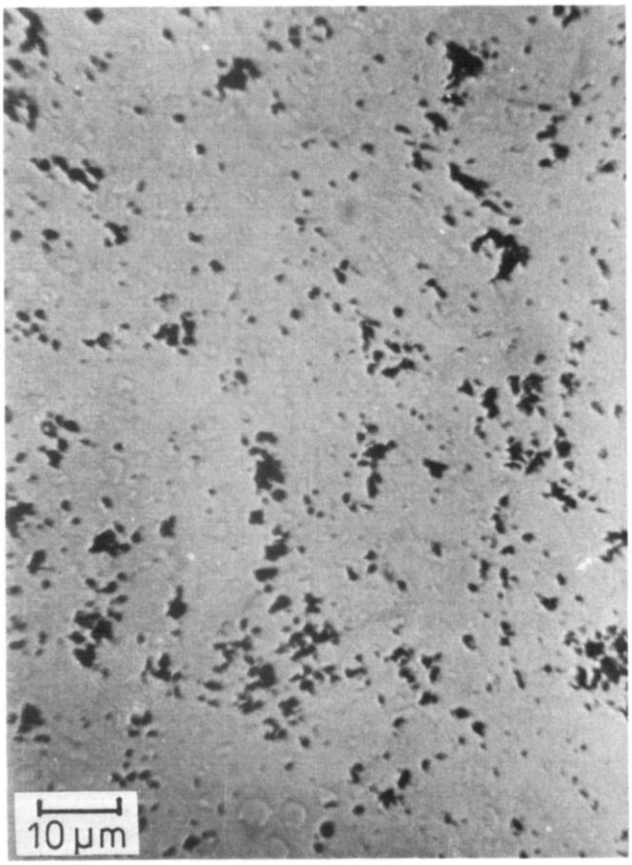

Fig. 3. Photomicrograph of a polished section of the Ti_3SiC_2-based material synthesized by solid combustion from mixtures of molar composition 3Ti:Si:2C.

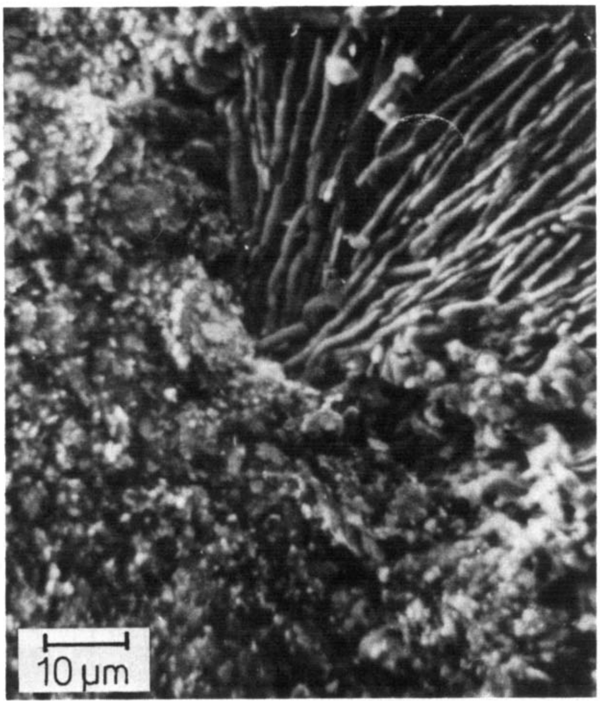

Fig. 4. Morphology of the same material as in Fig. 3 (SEM).

A comparison of the data in Table 2 with the equilibrium phase diagram of the Ti–Si–C system (Fig. 1) shows that except for the presence of small amounts of additional TiC the major phases found in all products of solid combustion are the ones predicted by the equilibrium diagram. The reasons for the occurrence of some amounts of additional TiC are not clear.

As expected from the equilibrium diagram, Ti_3SiC_2 was found to be the major constituent in the material obtained by solid combustion of compositions having the molar composition 3Ti:Si:2C. The product looked dense and showed a silvery, metallic gloss. Photomicrographs revealed, however, that it contains pores which are unevenly distributed (Fig. 3). Besides the predominating morphology of equiaxed grains of a size of 1–5 μm, larger columnar and platelike grains occurred (Fig. 4).

In order to compare the mechanical properties of this material with those of the ductile polycrystalline Ti_3SiC_2 derived from CVD, Vickers microhardness determinations were made. A Hanemann microhardness tester of type mhp 100 (GDR) was used, which enables an application of measuring indenter loads up to 100 g. The indenter load was applied to the material for 30 s and the indentation measured at a magnification of 480×. The indentations were made in dense zones on non-etched sections of the materials. Figure 5 shows the relation between the indenter load and the mean value of the diagonal of the indentation obtained, while Fig. 6 illustrates the changes of the Vickers microhardness calculated from the previous values versus the indenter load.

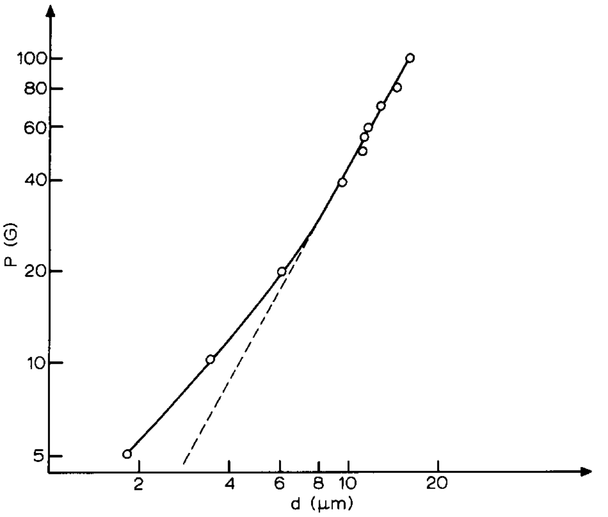

Fig. 5. Indenter load versus length of diagonal of indentation observed with the Ti_3SiC_2-based material shown in Fig. 3.

Table 3. Vickers microhardness of Ti_3SiC_2-based and of some ceramic materials

Material	*Indenter load (g)*	*HVM (kg/mm²)*
Si polycrystals	40	1 600[a]
Steatite	80	733[a]
α-Al_2O_3 polycrystals	80	1 750
β-SiC polycrystals	100	3 150
Ti_3SiC_2–TiC (solid combustion)	40	750
Ti_3SiC_2 (CVD) polycrystals	100	600
Ti_3SiC_2 single crystals (Ref. 2)	—	300–400[b] 1 200–1 500[c]

[a] Data kindly furnished by Dr J. Piekarczyk.
[b] Measured parallel to the TiC-like layers.
[c] Measured perpendicular to the TiC-like layers.

The error bars in Fig. 6 were calculated at a probability level of $\alpha = 0{\cdot}05$. As shown in Fig. 6, at indenter loads below 0·392 N (40 g) a continuous decrease of microhardness is observed with an increase of the load, while at loads above 0·392 N the microhardness becomes stabilized at a level of 7·355 GPa (750 kg/mm²). These changes are similar to the ones observed by Goto and Hirai[5] for the ductile polycrystalline Ti_3SiC_2 obtained by chemical vapour deposition. They found a decrease of the measured Vickers microhardness from 1000 to a stabilized value of 600 kg/mm² when the indenter load increased up to 100 g. The Vickers microhardness of the Ti_3SiC_2-based materials and of some other ceramic materials is given in Table 3. It may be seen from the table that the microhardness both of the CVD-derived and of the solid combustion-derived Ti_3SiC_2-based materials lies within the limiting values of 300–400 and 1200–1500 kg/mm² found for single crystals of Ti_3SiC_2 by Nikl *et al.*,[2] respectively, in the directions perpendicular and parallel to the Ti–C layers of the Ti_3SiC_2 structure. The somewhat higher microhardness of the solid combustion-derived material in comparison with the one found for the CVD-derived Ti_3SiC_2 may be due to dispersion hardening by TiC inclusions, the microhardness of which is of the order of 2400–3000 kg/mm².[14] It may be seen further from Table 3 that the microhardness of the solid combustion-derived Ti_3SiC_2-based material is three to four times lower than the microhardness of Si. Among the other compounds forming in the Ti–Si–C system a microhardness comparable to that of Ti_3SiC_2 is shown by $TiSi_2$ and TiSi, where the values of 620–760 and 760 kg/mm², respectively, were found. The microhardness of Ti_5Si_3 is 1200 kg/mm².[3] All these data have been obtained by measuring the Knoop hardness, which furnishes similar values as the Vickers method used in the present work.

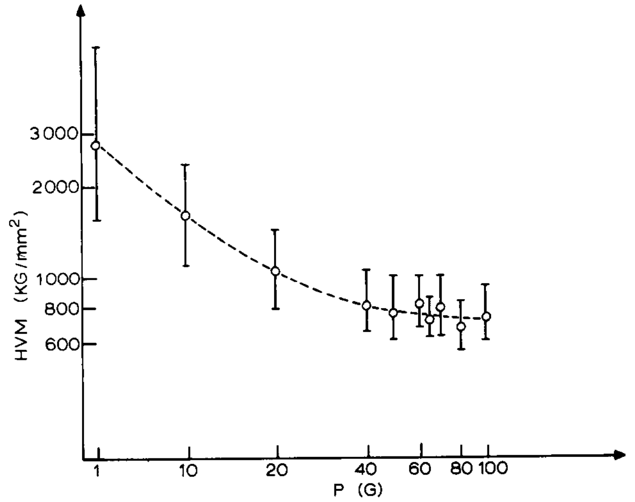

Fig. 6. Vickers microhardness versus the indenter load observed with the Ti_3SiC_2-based material shown in Fig. 3.

Conclusions

The synthesis of a Ti_3SiC_2-based material containing some TiC by solid combustion and the microhardness measurements on this material indicate that (i) at room temperature it has mechanical properties which are similar to those of pure Ti_3SiC_2 obtained by chemical vapour deposition, the properties of the latter being similar to those of steel[5] (until now it has been claimed that such properties can be found with CVD-derived Ti_3SiC_2 only); and (ii) because solid combustion permits, in contrast to CVD, large-scale fabrication, this opens the way for utilization of the unique mechanical properties of this 'soft' ceramic which are combined with a high resistance to oxidation and aggressive environments, typical of ceramics.

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