Phase Relations in the Ti–Si–C System

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Abstract

For the system Ti–Si–C phase diagrams at 1373 K and at 1523 K were determined. For that purpose, several alloys and diffusion couples were equilibrated and analysed by EPMA (electron probe microanalysis) polarised light microscopy and X-ray diffraction. With EPMA the composition of the alloys could be determined accurately by measuring the titanium, silicon and carbon contents. Some differences were found with the known diagram from the literature.

Für das System Ti–Si–C wurden die Phasendiagramme bei 1373 K und bei 1523 K bestimmt. Dazu wurden mehrere Legierungen und Diffusionspaare bei den angegebenen Temperaturen ins Gleichgewicht gebracht und mit EPMA, polarisiertem Licht und Röntgenbeugung analysiert. Mit Hilfe der EPMA konnte die genaue Zusammensetzung der Legierungen durch die Analyse von Titan, Silizium und Kohlenstoff festgestellt werden. Es wurden einige Abweichungen von dem bekannten Diagramm aus der Literatur gefunden.

On a déterminé les diagrammes de phases à 1373 et 1523 K du système Ti–Si–C. A cette fin, on a porté à l'équilibre plusieurs alliages et couples de diffusion et on les a analysés par EPMA, microscopie à lumière polarisée et diffraction X. L'analyse EPMA nous a permis de déterminer avec précision la compositions des alliages par analyse des teneurs en titane, silicium et carbone. On a relevé certaines différences avec les diagrammes disponibles dans la littérature.

1 Introduction

Nowadays combinations of metals and ceramics are receiving full attention as new materials. Applic-

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ations of these new materials in e.g. cutting tools, aerospace engines, or as composite materials in the aircraft industry are very promising. In all these applications the interaction between the metal and ceramic is of crucial importance. In this laboratory the authors are studying this interaction specifically for combinations of titanium (with and without aluminium) with silicon carbide and with silicon nitride. This interaction is being investigated with the so-called diffusion-couple technique and an attempt to predict the reaction layer sequence, morphology and reaction rate according to the model developed by van Loo et al.[1] is being made. To use this model the phase diagrams of the systems Ti–Si–C and Ti–Si–N are needed, which are not reliably known up to now. In this article attention is focused upon the Ti–Si–C system. Firstly the data given in the literature will be discussed. In the second part the experiments performed to determine the isothermal cross-sections of the phase diagram will be reported, followed by a discussion of the results. Finally some conclusions are drawn.

1.1 Literature data on the Ti–Si–C system

The only experimentally determined diagram of this system in the literature to the authors' knowledge is the one determined by Bruckl[2] at 1473 K (Fig. 1). The principal features of this diagram are the ternary phase T1 with the general formula Ti_3SiC_2 and the solid solution of carbon in Ti_5Si_3 (T2). Jeitschko & Nowotny[3] determined the crystal structure of Ti_3SiC_2 to be hexagonal with lattice parameters $a = 3.06$ Å and $c = 17.66$ Å. The structure type belongs to the class of complex carbides having octahedral groups (T_6C). Carbon can be dissolved up to about 10 at.% in Ti_5Si_3. However, the diagram published by Bruckl leaves some questions.

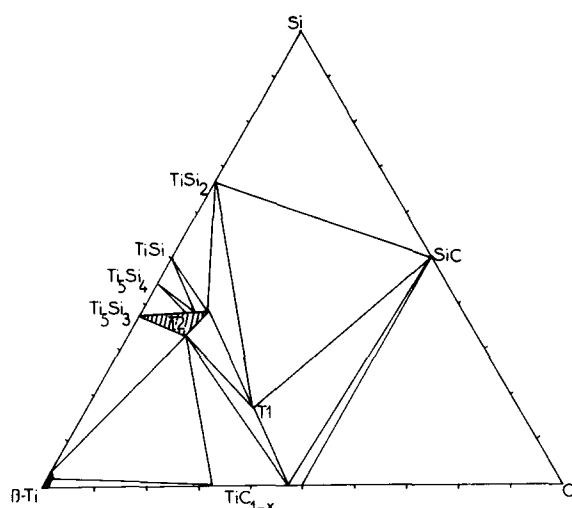Firstly, the binary Ti–Si phase diagram shows a

Fig. 1. The phase diagram of Ti–Si–C at 1473 K from Bruckl.[2]

homogeneity region for Ti_5Si_3,[4] from 61 at.% up to 63·8 at.% Ti, whereas it is reported by Bruckl as a line compound without any homogeneity region. The extension of this region on addition of carbon seems unrealistic in comparison with e.g. Mo_5Si_3.[5] Furthermore, the phase field T2–Ti_5Si_4 is contradicting thermodynamic rules. Finally, it is not very likely that TiC_{1-y} is in equilibrium with only one composition of the T2 phase. No diagram was available at temperatures < 1473 K, where the Ti_3Si phase is stable.[2] Therefore it was decided to reinvestigate this diagram at 1373 K and 1523 K.

2 Experimental Procedure

The starting materials were titanium powder (99·5%, Goodfellow, UK); titanium rod (99·7%, Alpha Europe Products, Karlsruhe, FRG); silicon

powder (technical purity, No. 13733, Reidel-De Haen AG, Hannover, Germany); silicon rod (single crystal, Philips, Eindhoven, The Netherlands); carbon powder (purriss., Roth, Karlsruhe, FRG); silicon carbide (hot-pressed, without sintering additives, ESK, Munich, FRG). The alloys were made by arc-melting pre-pressed mixtures of titanium, silicon and carbon, or titanium and silicon of about 3 g total weight. This was done by using Ti and Si powder as well as rods. After melting the alloys were equilibrated at the desired temperature in an alumina tube-furnace for about two weeks. The alloys were sealed in a molybdenum capsule, which was carried out by welding a Mo lid on a Mo cylinder under 0·66 bar Argon, in a vacuum chamber which had been evacuated to 10^{-9} bar. In the tube-furnace a H_2/N_2 mixture (20/80 by volume) prevented the molybdenum capsule from oxidation. The titanium–silicon–carbon alloys were then sawn, ground and polished up to 1 μm diamond. Examination was done by optical microscopy using polarised light, electron probe microanalysis (EPMA) and X-ray diffraction.

The carbon analysis was performed by measuring the K_α intensity at 10 keV and 300 nA with Fe_3C as a carbon standard using the PROZA correction program of Bastin & Heijligers.[6,7] To prevent the build up of a carbonaceous layer at the point of impact of the electron beam (system contaminations) an air-jet was used. For measuring Ti and Si, pure Ti and Si were used as standards. For the investigation of the equilibria in the Ti–Si–C system, several diffusion couples of the type Ti_xSi_{1-x}/SiC were also annealed at 1373 K and 1523 K in a vacuum furnace ($< 10^{-9}$ bar, tungsten heating elements, shielded from the diffusion

Table 1. Alloys used to determine the phase diagrams of the Ti–Si–C system at 1373 K and 1523 K

Composition of alloy	Temperature (K)	Equilibrium phases
$Ti_{0.74}Si_{0.26}$ (powder)	1 373	β-Ti, Ti_5Si_3
$Ti_{0.74}Si_{0.26}$ (rod)	1 373	Ti_3Si
$Ti_{0.67}Si_{0.13}C_{0.20}$	1 373	β-Ti, $Ti_{0.62}Si_{0.35}C_{0.03}$, TiC_{1-y}
$Ti_{0.44}Si_{0.53}C_{0.03}$	1 373	$Ti_{0.56}Si_{0.35}C_{0.09}$, $TiSi_2$, TiSi
$Ti_{0.45}Si_{0.39}C_{0.16}$	1 373	$Ti_{0.55}Si_{0.34}C_{0.11}$, $TiSi_2$, $Ti_{0.50}Si_{0.17}C_{0.33}$
$Ti_{0.67}Si_{0.29}C_{0.04}$	1 373	$Ti_{0.63}Si_{0.35}C_{0.02}$, β-Ti
$Ti_{0.37}Si_{0.20}C_{0.43}$	1 373	TiC, SiC, $Ti_{0.50}Si_{0.15}C_{0.35}$
$Ti_{0.53}Si_{0.14}C_{0.33}$	1 373	$Ti_5Si_3C_x$, TiC_{1-y}
$Ti_{0.28}Si_{0.45}C_{0.27}$	1 373	$Ti_{0.49}Si_{0.17}C_{0.34}$, SiC, $TiSi_2$
$Ti_{0.52}Si_{0.17}C_{0.31}$	1 373	$Ti_{0.57}Si_{0.32}C_{0.11}$, $Ti_{0.51}Si_{0.16}C_{0.33}$, TiC_{1-y}
$Ti_{0.84}Si_{0.07}C_{0.09}$	1 373	$Ti_{0.62}Si_{0.35}C_{0.03}$, β-Ti, TiC_{1-y}
$Ti_{0.52}Si_{0.45}C_{0.03}$	1 373	$Ti_5Si_3C_x$, Ti_5Si_4, TiSi
$Ti_{0.57}Si_{0.40}C_{0.03}$	1 373	$Ti_5Si_3C_x$, Ti_5Si_4
$Ti_{0.74}Si_{0.26}$	1 523	β-Ti, Ti_5Si_3
$Ti_{0.66}Si_{0.14}C_{0.20}$	1 523	β-Ti, TiC_{1-y}, $Ti_{0.63}Si_{0.34}C_{0.03}$
$Ti_{0.44}Si_{0.53}C_{0.04}$	1 523	$Ti_{0.54}Si_{0.35}C_{0.10}$, $TiSi_2$, TiSi
$Ti_{0.46}Si_{0.39}C_{0.15}$	1 523	$Ti_{0.53}Si_{0.36}C_{0.11}$, $Ti_{0.49}Si_{0.16}C_{0.36}$, $TiSi_2$
$Ti_{0.67}Si_{0.28}C_{0.05}$	1 523	β-Ti, $Ti_{0.63}Si_{0.34}C_{0.03}$, TiC_{1-y}
$Ti_{0.52}Si_{0.17}C_{0.31}$	1 523	$Ti_{0.55}Si_{0.34}C_{0.11}$, $Ti_{0.49}Si_{0.16}C_{0.35}$, TiC_{1-y}

Table 2. Various diffusion couples annealed during 100 h at the given temperatures

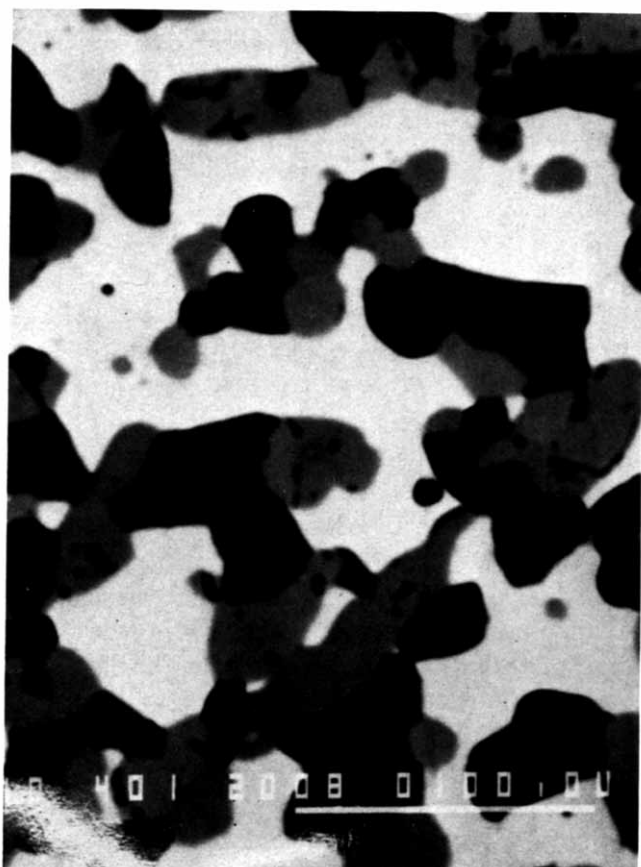| Couple type	Temperature (K)	Phases in equilibrium
Ti(foil)–SiC	1 499	$(TiSi_2 + Ti_3SiC_2)/SiC$
TiSi–SiC	1 523, 1 373	$TiSi/Ti_5Si_3C_x/TiSi_2/Ti_3SiC_2/SiC$
Ti$_5$Si$_3$–SiC	1 523, 1 373	$Ti_5Si_3C_x/TiSi_2/Ti_3SiC_2/SiC$
Ti–SiC	1 523, 1 373	$Ti(C, Si)/Ti_5Si_3C_x/Ti_5Si_3C_x + TiC_{1-y}/Ti_3SiC_2/SiC$

$/$ = Interface with phases on both sides in equilibrium.

Fig. 2. A SEM micrograph of a Ti–Si–C alloy equilibrated at 1523 K with white phase = β-Ti, grey phase = $Ti_5Si_3C_x$ and black phase = TiC_{1-y}.

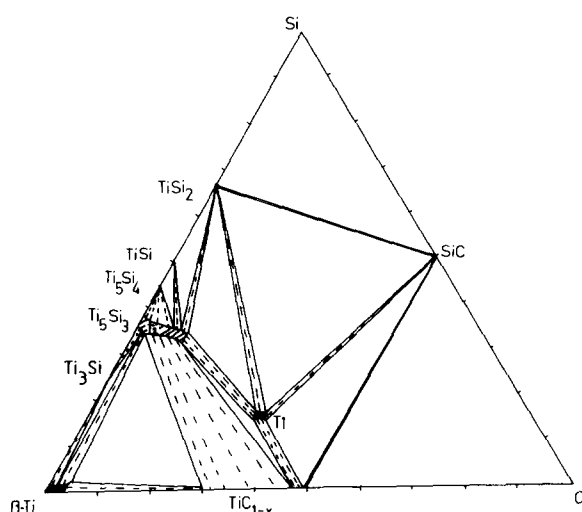**Fig. 3.** The phase diagram of Ti–Si–C at 1373 K determined in this work. T1 = Ti_3SiC_2 and T2 = $Ti_5Si_3C_x$.

couple). Before annealing the couple halves were ground and polished up to 3 μm diamond and ultrasonically cleaned in acetone. After annealing for 100 h, the couples were sawn with a low-speed diamond saw perpendicular to the interface between the couple halves. Next, these cross-sections were ground and polished up to 1 μm, again using diamond paste, and after polishing were ultrasonically cleaned in acetone. The reaction products formed between the two original couple halves are analysed by optical microscopy and EPMA. The equilibria at the phase interfaces should be the same as those given in the phase diagram.[8]

3 Results and Evaluation

Table 1 shows the composition of the alloys that were used to determine the phase diagram. The three analysing methods which were used gave consistent results. With microprobe analyses the composition of the different phases in the Ti–Si–C alloy in equilibrium was accurately determined. Figure 2 shows an example of an alloy with the phases β-Ti, $Ti_5Si_3C_x$ and TiC_{1-y} as identified by EPMA. Table 2 gives the different diffusion couples that were annealed, giving the reaction products in equilibrium with each other.

3.1 Ti–Si–C alloys

Figures 3 and 4 show the phase diagrams determined at 1373 K and 1523 K. The ternary compound T1 has at 1373 K a clear homogeneity region, contrary to the line compound suggested by Bruckl[2] at 1473 K. At 1523 K a narrower homogeneity range is found. Also, the homogeneity range of the T2 phase and its compositions which are in equilibrium with TiC_{1-y} are different from Bruckl's diagram. The Ti_3Si phase is present at 1373 K and decomposes into T2 and β-Ti when only very little carbon is added to the system. A similar behaviour can be seen in the case where a small amount of oxygen is present as a third compound. This probably explains why many authors do not find this phase in their experiments. In line with other authors[9] it is believed
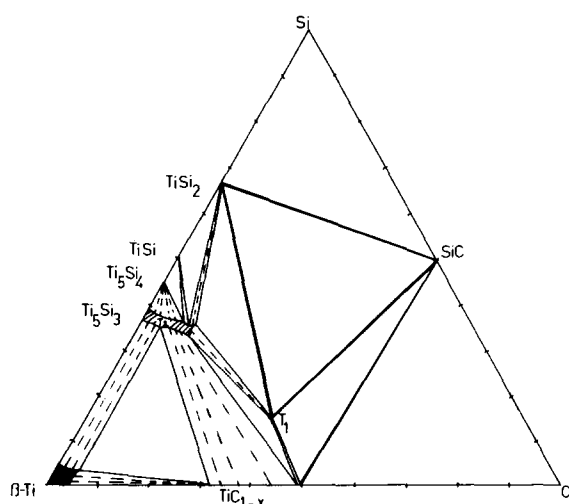
Fig. 4. The phase diagram of Ti–Si–C at 1523 K determined in this work. T1 = Ti_3SiC_2 and T2 = $Ti_5Si_3C_x$.

that Ti_3Si is destabilised by oxygen. Therefore experiments were performed to make Ti_3Si from titanium rod and silicon single crystal and also from the respective powders. In the latter case the presence of adsorbed oxygen could surely be expected. Indeed Ti_3Si was found in the first case and not in the alloy made from powders. In the latter case about 1 at.% oxygen was measured in Ti_5Si_3. The present diagram fits well with the diagram calculated by Touanen et al.[10] for 1500 K.

3.2 Diffusion couples

When two different materials are put together at high temperature diffusion will take place. After a sufficiently long time there will be equilibrium at the interfaces of the reaction products. In Fig. 5 a micrograph is shown of a reaction layer in a diffusion couple, taken by means of a scanning electron microscope. In this micrograph the phases that are in thermodynamic equilibrium with each
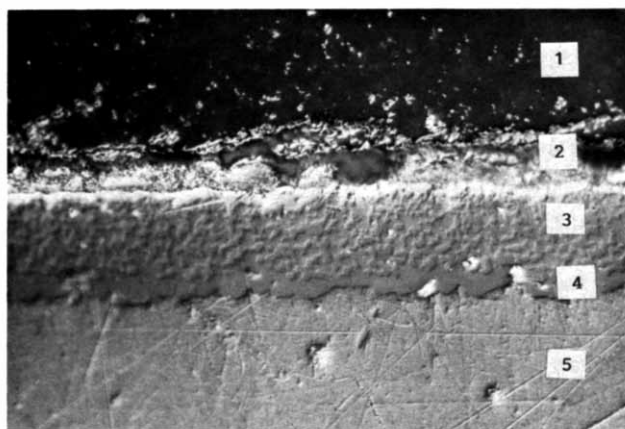

Fig. 5. Optical micrograph of a diffusion reaction layer between titanium and silicon carbide annealed for 100 h at 1373 K. The total layer thickness is 45 μm. 1 = HipSiC, 2 = Ti_3SiC_2, 3 = $Ti_5Si_3C_x$ + TiC_{1-y}, 4 = $Ti_5Si_3C_x$, 5 = β-Ti.

other at the interfaces can be seen. The phases are identified with help of EPMA and shown in Table 2.

In the semi-infinite couple between thick pieces of Ti and SiC equilibria between $Ti_5Si_3C_x$ and TiC_{1-y}, between Ti_3SiC_2 and $Ti_5Si_3C_x$, and between $Ti_5Si_3C_x$ and the solid solution of carbon and silicon in titanium are found. In the case of the titanium foil between two pieces of silicon carbide, the metal has reacted completely. No initial titanium was left. As is expected from the phase diagram, the reaction products are $TiSi_2$ and Ti_3SiC_2, which are situated as a mixture between the two pieces of SiC. Finally, from the TiSi/SiC couples an equilibrium between $Ti_5Si_3C_x$ and $TiSi_2$ and between Ti_3SiC_2 and $TiSi_2$ was found.

4 Conclusion

The phase diagrams of Ti–Si–C are now accurately determined at 1373 K and 1523 K and show some differences with the diagram known up to now. At 1373 K the ternary T1 phase has a homogeneity range (about 1 at.% in C, 0·7 at.% in Si and 1·2 at.% in Ti) and seems to become a line compound at 1523 K. Also the shape of the homogeneity range of the T2 phase is different. It is clear that this phase is a solid solution of carbon in Ti_5Si_3 without a change in the Ti/Si ratio. The stability of the Ti_3Si phase is obviously strongly influenced by the presence of impurities like carbon and oxygen. With the help of diffusion couples it is possible to determine a great part of the equilibria between the phases in an isothermal cross-section of the phase diagram.

Acknowledgement

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