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Note

Influence of Gas Environment on Synthesis of Silicon Carbide through Reaction between Silicon and Amorphous Carbon in a Solar Furnace at P.S.A. (Plataforma Solar de Almería)

アルメリア太陽エネルギー実験施設（P.S.A.）の太陽炉を使ったケイ素と無定形炭素からの炭化ケイ素（SiC）合成反応への気相雰囲気の影響

Jorge CRUZ FERNANDES, Luís GUERRA ROSA, Diego MARTÍNEZ*, José RODRIGUEZ* and Nobumitsu SHOHOJI**

Departamento de Engenharia de Materiais, Instituto Superior Tecnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal
**Plataforma Solar de Almería, Centro Europeo de Ensayos de Energía Solar, Centro de Investigaciones Energeticas Medioambientales y Tecnologicas, P.O.Box 22, 04200 Tabernas, Spain*
***Departamento de Tecnologias de Produção, Instituto de Materiais e Tecnologias de Produção, Instituto Nacional de Engenharia e Tecnologia Industrial, Estrada do Paço do Lumiar, 1699 Lisboa Codex, Portugal*

Silicon carbide (SiC) was synthesized from compacted pellet composed of Si powders and amorphous carbon powders through heating in solar furnace under controlled atmosphere (Ar or N_2). Under irradiation of the solar energy flux 1350 kW/m² (ca. 1650°C in terms of measured temperature) for 30 min, Si was completely converted to SiC in Ar atmosphere while the conversion was incomplete in N_2.

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1. Introduction

Carbon (C) might exist in variety of allotropic forms like graphite, diamond and amorphous carbon. Graphite is in the reference state of C and activity a(C) of graphite is 1. Activity a(C) of other allotropic forms of carbon, like amorphous carbon, is greater than that of graphite and accordingly, by employment of amorphous carbon as a medium for carburising, carbon content higher than the one achieved by carburizing through reaction with graphite might be realized for synthesis of metal carbide MC_x with certain extent of non-stoichiometric homogeneity range or for synthesis of carbonitride MC_xN_{1-x}.[1)-5)] Besides this equilibrium merit of amorphous carbon yielding carbide or carbonitride with comparatively high C content, there is also kinetic merit of using amorphous carbon as a carburization medium. That is, the carburization reaction with active carbon completes faster than that with graphite.

However, active carbon tends to be graphitized when exposed to temperature T higher than 1500°C for prolonged duration and thence, if the graphitization process of the amorphous carbon is completed before the completion of the carburization reaction, equilibrium merit of amorphous carbon to produce carbide with higher C content would not be gained. Thus, it is an advantage to use a furnace with very quick heating capacity and with massive heat capacitance in order to gain full equilibrium and kinetic merits of carburization reaction with amorphous carbon.

Solar furnace is one of such means of heating. In this report, preliminary results obtained from reaction between Si and amorphous carbon in a solar furnace (SF) in Plataforma Solar de Amería (P.S.A.) are summarized.

2. Experimental

SF (solar furnace) in PSA (Plataforma Solar de Amería) is capable of intensifying the solar light flux by factor 15000 with the parabolic concentrator composed of segmented concave mirrors. In the present work, 5-cm diameter spot of the peak flux 1350 kW/m² was gained from the natural solar irradiance 800 W/m².

Figure 1 depicts schematic constitution of the reaction chamber set in the SF. This chamber is connected to evacuation system and to gas feed line and the reaction in this chamber might be carried out in either vacuum or other arbitrary gas atmosphere. We call this reaction chamber Mini Vac.

Starting material was compacted powder mixture composed of Si (>99.9% pure, −100 mesh; Ventron, Karlsruhe, Germany) and amorphous carbon (Aktivkohl (50 μm) of E. Merck AG, Darmstadt, Germany) cold-pressed with pressure around 400 MPa into a pellet of diameter around 1 cm and height 0.5 cm. Proportion of amorphous carbon was set to be 1.5 times the molar ratio of Si to ensure that the prepared SiC was in equilibrium with the residual free carbon. Unlike mixture of graphite with Si or other metals, mixture of amorphous carbon and Si did not consolidate readily in as-mixed condition and thence, prior to the compacting, liquefied paraffin heated above its melting point was desired to be added to the powder mixture as the binder. It was ensured experimentally[1)-3)] that

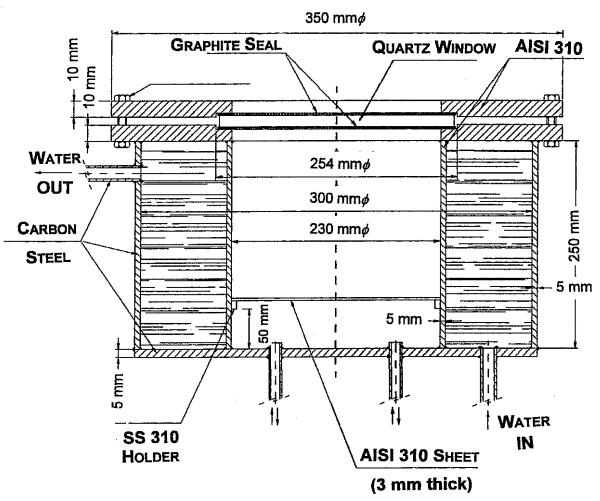

Fig. 1. Schematic cross section of the reaction chamber (MiniVac) for the solar furnace.

paraffin does not exert any noticeable influence on the reaction between carbon and metal because it evaporates before the reaction temperature between the carbon and the metal is reached.

The compacted pellet of the powder mixture composed of Si, amorphous carbon and paraffin held in a graphite crucible was placed in the reaction chamber as depicted in Fig. 1 and exposed to flux of concentrated solar light in the focused spot of the SF. Atmosphere in the chamber was either 99.9% pure Ar (specimen A) or 99.8% pure N_2 (specimen B). In both cases, the maximum temperature (1620°C for A and 1650°C for B) was reached within 3 min and the specimen was kept at the maximum temperature for 30 min. Thereafter, the shutter of the SF was closed and the specimen was cooled in the furnace. It took 5 min to close the shutter completely.

3. Results and discussion

The X-ray diffraction (XRD) patterns for the reaction products are summarized in Fig. 2 and identification of peaks for these specimens are summarized in Table 1 (specimen C: the unreacted reference specimen composed of Si, amorphous carbon and paraffin). Line identification for Si was made with reference to JCPDS (Joint Committee on Powder Diffraction Standards) diffraction data card 27-1402 (cubic $Fd3m$) and that for SiC with reference to JCPDS 29-1129 (cubic $F\bar{4}3m$; polytype 3C). The results summarized in Table 1 show that Si in the specimen A reacted in inert Ar gas was completely converted to SiC while Si in the specimen B reacted in N_2 gas was not completely converted to SiC. Probable explanation for the retarded SiC formation process in N_2 environment (sample B) might be ascribable to the driving force to form silicon nitride Si_3N_4 in N_2 environment which competed against the SiC formation reaction. In fact, it is well known (e.g., Ref. 6) that high-temperature oxidation behaviour of metallic materials in pure O_2 (or O_2 diluted with inert Ar) is distinguishable from that of the same material in N_2-containing environment (air, for example).

Table 1. X-ray Diffraction Analysis Results Obtained with Cu Kα Radiation (45 kV, 20 mA; Scan. Speed 2°/min)

Identification	Specimen A		Specimen B		Specimen C	
	2θ / °	Intensity	2θ / °	Intensity	2θ / °	Intensity
C (002)	26.20	34	26.60	34	26.75	35
Si (111)			28.50	430	28.57	2749
SiC (111)	**35.71**	**2868**	**35.74**	**1727**		
SiC (200)	**41.44**	**310**	**41.49**	**203**		
Si (220)			47.35	405	47.42	1346
Si (311)			56.18	270	56.25	1068
SiC (220)	**60.04**	**1072**	**60.12**	**582**		
Si (400)			69.21	70	69.25	111
SiC (311)	**71.82**	**749**	**71.89**	**377**		
SiC (222)	**75.54**	**93**	**75.66**	**53**		
Si (331)			76.44	70	76.48	252
Si (422)			88.08	76	88.17	591
SiC (400)	**90.00**	**91**	**90.48**	**22**		
Si (511)			95.05	51	95.04	165
SiC (331)	**100.79**	**212**	**100.97**	**103**		
SiC (420)	**104.47**	**144**	**104.64**	**66**		
Si (440)			106.79	26	106.79	111
Si (531)			114.16	30	114.20	210

Intensity: as-counted in cps (counts per second) unit

C(002) peak was broad for any specimen examined

Specimen A: 1620°C for 30 min in Ar at 1.5 bar
Specimen B: 1650°C for 30 min in N_2 at 2 bar
Specimen C: unreacted reference

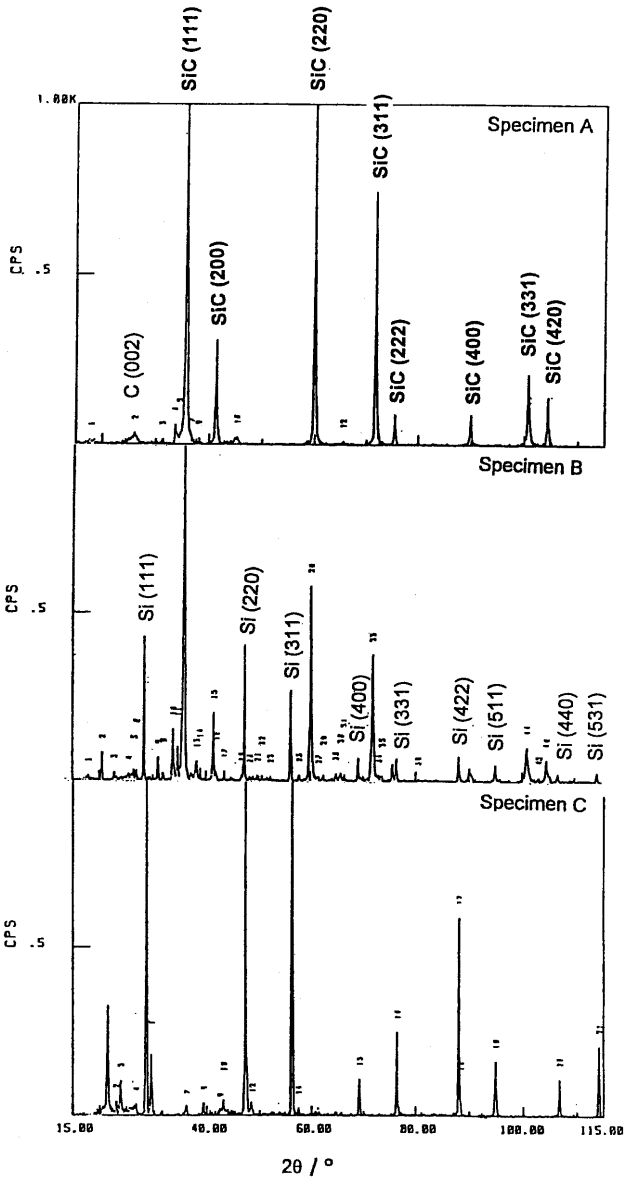

Fig. 2. X-ray diffraction analysis results obtained with Cu Kα radiation (45 kV, 20 mA; scan. speed 2°/min).

Another important aspect noticed in the obtained XRD patterns is that C(002) peak remained broad after the reaction. This evidence implied that the graphitization of the amorphous carbon did not proceed during the reaction. Peak position of C(002) of graphite is $2\theta=26.50°$ but C(002) peak position and breadth might vary depending on the degree of deviation of crystallinity of the non-graphitic carbon from that of graphite.[7),8)]

4. Conclusions

Following conclusions were drawn from the present carbide synthesis experiment using the solar furnace at PSA.

(1) Solar furnace is a useful material processing apparatus allowing very rapid heating (a few minutes to raise the temperature up to around 1600°C from room temperature) for massive amount of specimen material (homogeneous temperature spot diameter about 5 cm). Noting intense energy flux of concentrated solar beam (peak flux as high as 1350 kW/m² from natural solar irradiance 800 W/m²), instantaneous homogeneous heating might be realized for quite thick specimen which is not attainable with other laboratory furnace like IR (infra-red) gold image furnace.

(2) Due to very rapid heating rate to considerably high temperature achievable in the solar furnace, preparation of

carbide with comparatively high C content using amorphous carbon in place of graphite might be undertaken in the solar furnace without problem of graphitization of the amorphous carbon. Spectrum of solar beam did not promote the graphitization of amorphous carbon either in spite of our concern whether it might happen due to certain photo-chemical reaction.

(3) If the metal to be carburized is also a strong nitride former, carbide preparation reaction should be undertaken in inert Ar atmosphere rather than in N_2 gas.

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