Synthesis and Characterization of Cobalt Monosilicide (CoSi) with CsCl Structure Stabilized by a β-SiC Matrix

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Dedicated to Professor Rüdiger Kniep on the Occasion of his 60th Birthday

Abstract. In the Co/Si/C system a new CoSi (CsCl type) modification besides β-SiC and carbon is observed after a sintering process of the elements at a temperature of 1400 °C (4 h; vacuum). The structure of the cobalt monosilicide (CsCl type) was determined by X-ray powder diffraction methods and subsequent Rietveld refinement. CoSi (CsCl type) crystallizes in the cubic space group *Pm*$\bar{3}$*m* (no. 221) with the lattice parameters a = 281.62(2) pm (V= 22.337(7) x 10^6 pm^3). However, in the Co/Si system only the well known ε-CoSi (FeSi type) is observed at the same reaction conditions. It is supposed that β-SiC takes an important role in stabilizing the CoSi (CsCl type). Electron microscopy experiments (SEM and EDX) confirm that the cobalt monosilicide is surrounded by a β-SiC matrix containing a small amount of carbon. The thermal stability of the synthesized samples was studied. Furthermore, the density of states (DOS) was calculated.

Keywords: Cobalt monosilicide; CsCl structure; β-SiC matrix

Introduction

Silicides of iron group metals (Fe, Co, Ni) are of great research interest because of their prospect as a conductive material in many electronic applications. In particular ε-FeSi and ε-CoSi (FeSi structure) have been proposed as an important alternative to titanium silicide for electronic devices [1].

In the Co/Si system the silicides Co_2Si, CoSi, and $CoSi_2$ are formed with increasing temperature [2, 3]. Details of the formation are described elsewhere [4−6]. Cobalt monosilicide with CsCl structure could not be observed in the Co/Si system. Its existence was indeed predicted, its stability doubted however simultaneously [7]. An epitaxially stabilized CoSi with CsCl structure was firstly reported as a thin film grown on a Si(111) surface [8].

In this work the investigations in the Co/Si/C system were carried out in order to synthesize materials by solid state reactions, which may combine the conductor qualities of the cobalt silicides with the material properties of silicon carbide. The influence of carbon on the formation of the cobalt silicides should be examined at the same time.

Experimental Section

Powder of cobalt (99.8 %-wt, Alfa Aesar), was homogeneously mixed with silicon powder (99.9 %-wt, Riedel de Haën) and graphite (99.9 %-wt, Fluka). For the formation of CoSi (CsCl type) from Co, Si, and C best results in the molar ratio Co:Si:C = 1:1:1 were found. CoSi (CsCl type) is formed by using the molar ratio Co:β-SiC = 1:1 (β-SiC: 99.98 %-wt, Alfa Aesar) as well as the molar ratio Co:α-SiC = 1:1 (α-SiC: 99.98 %-wt, Alfa Aesar), respectively. The cobalt powder was also mixed with silicon powder in the molar ratio Co:Si = 1:1 to synthesize cobalt silicides for comparison. The powder samples were pressed into pellets (glove box; argon atmosphere). The pellets were heated up in sealed graphite crucibles (vacuum: $\sim 10^{-3}$ mbar) using a high temperature graphite furnace FSW 100/150-2200 LA/PS (FCT Anlagebau GmbH, Germany) at temperatures of 1200 °C, 1400 °C, 1600 °C, and 1800 °C, respectively (annealing time: 4 hours).
After cooling a part of the sintered pellets was powdered for XRD experiments. The other part was polished for SEM and EDX characterizations. The powder X-ray diffraction was conducted on a Siemens D5000 diffractometer using CuKα_1 radiation in 2 theta range of 10°−85°. Rietveld structure refinement was done by using the program GSAS [9].

Table 1 Structure parameters and selected details of the refinement of cobalt monosilicide CoSi. R_p, wR_p, and R_F refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, respectively, defined in GSAS [9].

Formula	CoSi	profile range	$10^\circ \leq 2\theta \leq 85^\circ$
formula weight	87.02	no. data points	3990
crystal system	cubic	no. reflections	22
space group	*Pm*$\bar{3}$*m* (No. 221)	displacement factors	2
radiation (λ / pm)	CuKα_1 (154.06)	profile parameters	25
lattice parameter a /pm	281.62(2)	wR_p	0.007
volume / $\cdot 10^6$ pm^3	22.337(7)	R_p	0.005
Z	1	R_F	0.093

The synchrotron experiments were performed in Debye-Scherrer mode at the high-resolution powder diffractometer beam line B2 at HASYLAB, Hamburg, using two different wavelengths of 70.994 pm and 90.785 pm, respectively. The samples were filled in

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0.3 mm quartz capillaries without dilution. Monochromatic photons were selected from the white beam of a bending magnet by a Ge(111) double-crystal monochromator. Full patterns were collected in the 2 theta range 10°−90° with a step width of 0.004° using the image plate detector. A subsequent Rietveld refinement was performed with the "Fullprof" program.

Qualitative and quantitative electron microscopic analysis was performed using a Hitachi S-2700, Japan. The oxygen content of the products was controlled by hot gas extraction (Leco ET/TC-300, Germany). In order to determine the electronic qualities of the CoSi (CsCl-type) the density of states (DOS) was estimated by GGA calculations [10].

Results and Discussion

The reaction products (annealing temperature: 1200 °C) in the Co/Si/C (Co/β/SiC or Co/α-SiC) system are not single-phased but consist of cobalt silicides, β-SiC, carbon, and cobalt. Cobalt evaporates under the vacuum conditions at higher annealing temperatures. The formation of cobalt carbide or a ternary Co/Si/C compound was not observed by XRD analysis. The results of the hot gas extraction indicates no oxygen content of the reaction products. Depending on the temperature (reaction time: 4 h; atmosphere: vacuum), different cobalt silicides are produced (figure 1).

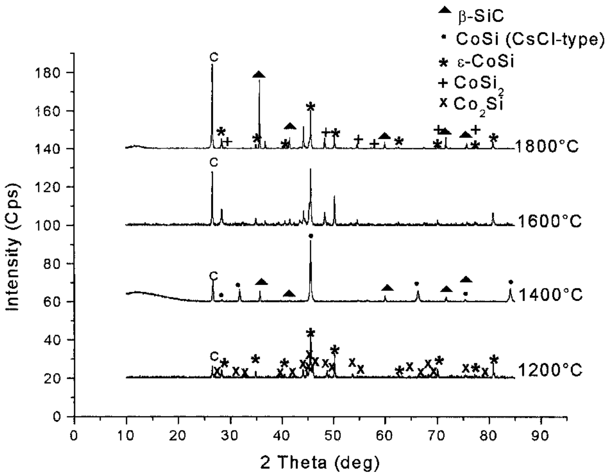

Fig. 1 X-ray diffraction pattern of Co/Si/C reaction products (basic materials: cobalt, silicon and graphite in the molar ratio 1:1:1) after sintering (4 h; vacuum) at temperatures of 1200 °C, 1400 °C, 1600 °C, and 1800 °C. (Only the reflections of the cobalt silicides, β-SiC, and graphite are marked.) The reflections of CoSi (CsCl type) are observed after sintering at a temperature of 1400 °C.

Orthorhombic cobalt silicide Co_2Si (a = 491.8 pm, b = 710.9 pm, c = 373.8 pm; space group *Pnam* (no. 62) [11]) and cobalt monosilicide (a = 443.0 pm; space group $P2_13$ (no. 198) [12]) with FeSi-type structure well known as ε-CoSi is produced at a reaction temperature of 1200 °C.

Unknown reflections (in addition to β-SiC and carbon) in the X-ray powder diffraction diagram occur in the case of 1400 °C.

ε-CoSi as well as cubic cobalt silicide $CoSi_2$ with CaF_2-type structure (a = 536.4 pm [13]) is observed after sintering at 1600 °C.

$CoSi_2$ is formed after sintering at 1800 °C.

The formation of the respective cobalt silicide is independent of the basic materials. In such a way, both mixtures of cobalt, silicon and carbon and mixtures of cobalt and silicon carbide reacted under identical conditions to the same cobalt silicides (figure 2).

The product of the well reproducible sintering process in the case of 1400 °C is of special interest. The phase causing the unknown reflections observed in the X-ray diffraction

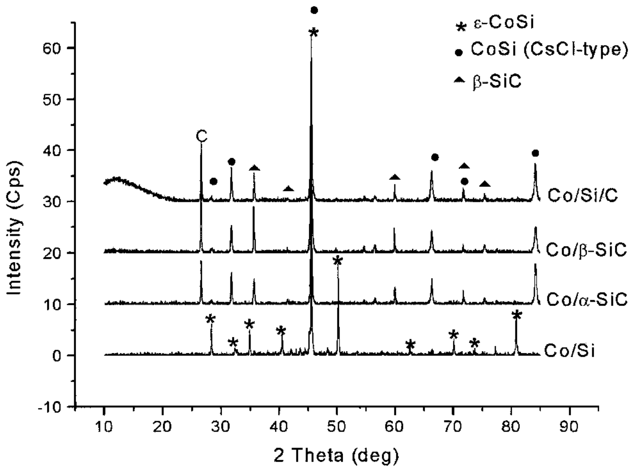

Fig. 2 X-ray diffraction pattern of Co/Si/C reaction products after sintering at 1400 °C (4 h; vacuum). Basic materials: Cobalt, silicon and graphite (the upper one); cobalt and silicon carbide (the two middle); cobalt and silicon (the lower one).

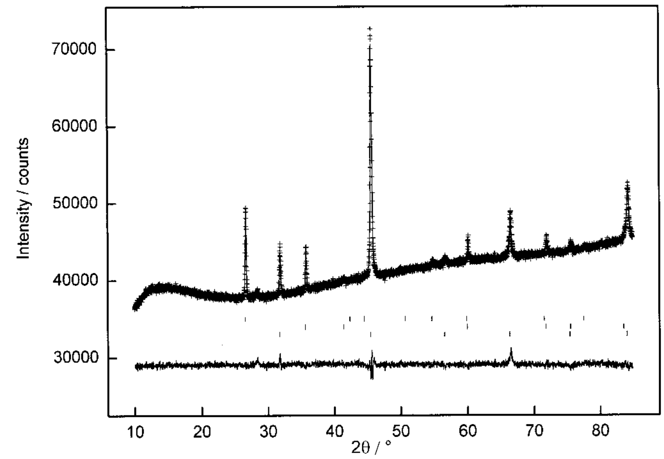

Fig. 3 Scattered X-ray intensities for a sample of cobalt, silicium, and carbon after sintering at 1400 °C (4 h; vacuum) as a function of diffraction angle 2 theta. Shown are the observed patterns (crosses), the best Rietveld-fit profiles (line) and the difference curve between observed and calculated profiles (line below). The wavelength was λ = 154.06 pm. The lower row of vertical lines indicate possible peak positions of CoSi (CsCl type), the middle row β-SiC, and the upper row graphite.

pattern, could be identified as CoSi with CsCl structure (figure 3). It crystallizes in the cubic space group $Pm\bar{3}m$ (no. 221) with the lattice parameters of a = 281.62(2) pm (V= 22.337(7) · 10^6 pm^3). Synchrotron radiation diffraction experiments and subsequent Rietveld refinement using the program Fullprof confirmed the crystal structure (a = 281.334(2) pm) [14].

However, in the Co/Si system only the well known ε-CoSi (FeSi type) is observed under the same reaction conditions. It is supposed that β-SiC plays an important role in stabilizing the CoSi (CsCl type). Scanning electron microscopy (SEM) shows that the product after sintering at 1400 °C consists of two areas (figure 4). An EDX analysis of the darker area results in a ratio of composition cobalt to silicon = 50.9:49.1 At-%. This corresponds to the formula CoSi. The brighter area consists of silicon carbide and carbon (EDX analysis: ≤ 5 At-%). In such a way, the sample can be described also as insular areas of CoSi (CsCl type) embedded in a β-SiC matrix containing a small amount of carbon. The CoSi (CsCl type) areas have a mean radius of ~15 µm.

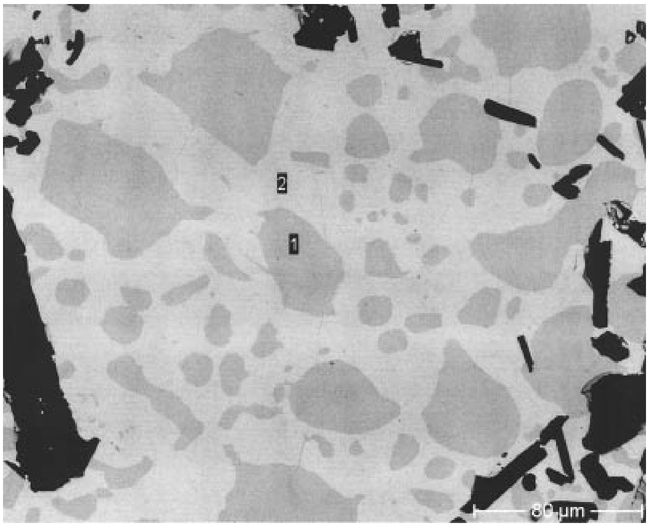

Fig. 4 SEM picture of a Co/Si/C reaction product (basic materials: cobalt, silicon and graphite in the molar ratio 1:1:1) after sintering (4 h; vacuum) at a temperature of 1400 °C. The darker areas (area 1) consist of CoSi (CsCl type). The brighter areas (area 2) consist of β-SiC and carbon. (Black areas: holes).

In order to check the stability of the reaction product in air, a thermogravimetric measurement (TG) was carried out from room temperature up to 1150 °C. By means of the mass loss it could be shown that the free carbon of the sample burned completly at ~560 °C. After cooling the sample was studied again by XRD. Only the reflections of carbon had disappeared, not however, the reflections of CoSi (CsCl type) and β-SiC.

To study the effect of the β-SiC matrix on the stabilization of CoSi (CsCl type), the sample became fine-ground in a ball mill for 20 hours in order to break down a part of the β-SiC matrix surrounding the cobalt monosilicide. Tribochemistry effects through the milling could not be proved. The well known composition of the sample (CoSi (CsCl type), β-SiC, and carbon) could be confirmed by a subsequent XRD analysis.

High temperature XRD experiments show that CoSi (CsCl type) is stable up to ~750 °C and then converts into ε-CoSi (FeSi type). In such a way, the CoSi (CsCl type) shows a high thermal stability without complete cover through the β-SiC matrix. Cobalt monosilicide (CsCl type) can not be formed without presence of silicon carbide. It is insignificant whether silicon carbide is first produced of carbon and silicon or silicon carbide is used as basic material.

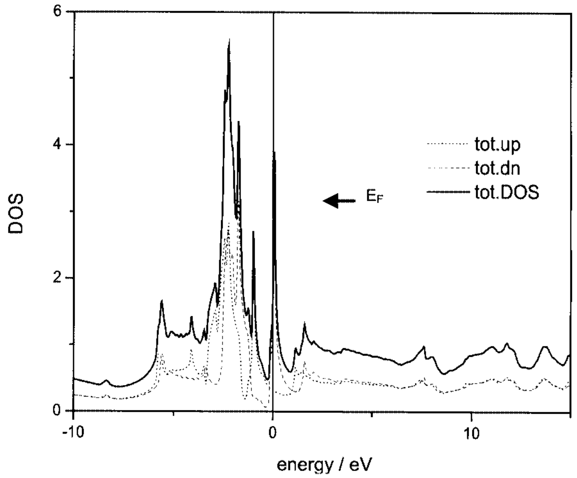

Fig. 5 Calculated density of states (DOS) of CoSi (CsCl type).

In order to receive first notes on the electronic qualities of the CoSi (CsCl-type) the density of states (DOS) was calculated (figure 5). A comparison of the density of states between CoSi (CsCl type) and ε-CoSi previously reported [15] explains the different electronic qualities of both cobalt monosilicide modifications. According to the calculations CoSi (CsCl type) is metallic.

The result of our study is the successful synthesis of a material which combines the qualities of a metallic conductor with the properties of a structural ceramic [16].

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