



Mechanochemical synthesis and spark plasma sintering of the cerium silicides



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ABSTRACT

The cerium silicides, Ce_5Si_3 , Ce_3Si_2 , CeSi , CeSi_{2-y} , and CeSi_{2-x} , have been prepared from the elements by mechanochemical processing in a planetary ball mill. Preparation of the cerium silicide Ce_5Si_4 was unsuccessfully attempted and potential reasons for this are discussed. Temperature and pressure of the milling vial were monitored *in situ* to gain insight into the mechanochemical reaction kinetics, which include a mechanically-induced self-propagating reaction (MSR). Some prepared powders were consolidated by spark plasma sintering to high density. Starting materials, as-milled powders, and consolidated samples were characterized by X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. The results obtained help elucidate key questions in mechanochemical processing of intermetallics, showing first phase formation similar to thin films, MSR ignition times that are composition- and milling speed-dependent, and sensitivity of stable compound formation on the impact pressure. The results demonstrate mechanochemical synthesis as a viable technique for rare earth silicides.

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1. Introduction

Rare earth silicides have been studied for many years because of their interesting electromagnetic properties, utility in semiconductor devices, refractory nature, and for the ability of some silicides to form oxidation resistant protective silica films. Cerium is well known among the rare earths for forming compounds with complicated magnetic behavior, and binary and ternary compositions near CeSi_2 have received considerable attention for their magnetic properties [1,2]. Ce_3Si_2 is isostructural with U_3Si_2 [3], and may be a potential surrogate for studies of processing techniques, oxidation, corrosion, and transport properties in this important compound. Meanwhile, CeSi , Ce_5Si_4 , and ternary compounds based on Ce_5Si_4 have been studied as magnetocaloric materials for refrigeration [4,5]. The compounds of cerium with silicon are commonly prepared by arc melting the elements, with the cast buttons used as-is or as master alloys for single crystal growth [2]. This process may dissolve oxygen or volatilize cerium or silicon as MO species, resulting in off-stoichiometric products.

Here we describe the preparation of the entire range of cerium silicides by high energy ball milling (HEBM), which is a

self-enclosed processing technique that can limit oxygen contamination and cerium or silicon loss. The HEBM technique has been used to synthesize many materials including oxide dispersion strengthened steel alloys [6] and many intermetallics [7]. The preparation of silicides by HEBM was first reported nearly thirty years ago [8,9], and the technique has since been applied to many silicide systems. Some silicides with a high enthalpy of formation, such as MoSi_2 , exhibit a sudden reaction during HEBM in a process termed mechanochemically-induced self-propagating reaction (MSR) [10]. Takacs adapted the criterion [11] for self-propagating high-temperature synthesis to predict MSR to occur in systems with an adiabatic reaction temperature >2000 K. The adiabatic temperature is given by $T_{\text{AD}} = \Delta H_f(T_{\text{rxn}})/C_p(T_{\text{rxn}})$, where ΔH_f and C_p are the respective reaction enthalpy and heat capacity of the formed compound at the temperature of the reaction. The ratio $\Delta H_f^{298}/C_p$ is assumed to be a close approximation to the high temperature value $\Delta H_f(T_{\text{rxn}})/C_p(T_{\text{rxn}})$ as high temperature properties are not well known in many systems. A similar condition requires T_{AD} to exceed the melting temperature of at least one constituent. The Ce–Si system is uncommon in the fact that all line compounds have $\Delta H/C_p > 2000$ K, as shown in Table 1, making the Ce–Si system ideal for investigating MSR-type behavior in systems with multiple intermetallic compounds.

Table 1 lists the compounds in the Ce–Si system that are relevant to the temperature range of ball milling, along with heats of formation ΔH_f^{298} [12,13], calculated adiabatic reaction temperatures T_{AD} ,

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Table 1
Thermodynamic and crystallographic data for the Ce–Si system.

Species [3]	CeSi _{2-x}	CeSi _{2-y}	CeSi	Ce ₅ Si ₄	Ce ₃ Si ₂	Ce ₅ Si ₃
Formation [3]	Peritectic	Congruent	Congruent	Peritectic	Peritectic	Peritectic
Unit cell [3]	Tetragonal	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Tetragonal
Space group [17]	I4 ₁ /amd	Imma	Pnma	P4 ₁ 2 ₁ 2	P4/mbm	I4/mcm
Prototype [17]	α-ThSi ₂	α-GdSi ₂	FeB	Zr ₅ Si ₄	U ₃ Si ₂	W ₅ Si ₃
Volume (cm ³ /mol) [17]	36.21	36.3	29.42	143.56	79.77	129.05
ΔV/V ₀ (%)	-24.4	-13.5	-12.2	-6.5	-9	-9.2
ΔH _f ²⁹⁸ (kJ/mol atom) [12,13]	-62.7	-68.1	-70.5	-65.7	-60.9	-57.2
T _{AD} = ΔH/C _p (K)	2829	3033	3017	2764	2529	2359
ΔH _f ' (kJ/mol atom)	-16.0	-16.0	-15.5	-14.8	-11.1	-9.9

effective heats of formation ΔH_f' [14], and crystallographic information [3]. Heats of formation are used rather than free energies because the product -TΔS is small for solid state reactions near room temperature and the free energy may thus be approximated by ΔH_f'. The effective heat of formation is defined as ΔH_f' = ΔH_f (x'/x) where x is the limiting reactant at the nominal composition, and x' is the limiting reactant at the composition of the lowest melting eutectic. For the crystallographic data we adopt a formalism in which CeSi_{2-x} denotes the silicon deficient α-ThSi₂ prototype compound spanning the composition range CeSi_{1.81}-CeSi₂ [2]. Likewise, CeSi_{2-y} denotes the α-GdSi₂ prototype, which melts congruently at CeSi_{1.81} but has been reported to have a greatly increased homogeneity range when equilibrated in the range 800–1100 °C [15,16].

2. Materials and methods

The starting materials were cerium filings (99.9%, ESPI Metals, USA) and silicon powder (1–20 μm, 99.9995%, Alfa Aesar, USA). The cerium filings were supplied at -40 mesh, and were further graded to +60 (corresponding to screened particle sizes of 420–250 μm) before conducting experiments. X-ray diffraction (XRD) analyses showed the cerium to be phase pure to within the detection limit of the XRD, while the silicon was phase pure with a low amorphous background. All experiments were performed with a planetary ball mill (Retsch PM100, Germany) with a 250 mL hardened steel milling vessel and ceria-stabilized zirconia milling (CSZ) media of 5 and 10 mm diameter. Before beginning experiments, the volume of the milling vessel after sealing the attached lid was calculated to be 274 mL by measuring the amount of deionized water required to completely fill the assembly. The pressure and temperature within the vessel during milling were monitored *in situ* by sensors mounted in the milling vessel lid. The pressure sampling rate was 2 s⁻¹ and temperature sampling rate was 1 s⁻¹. The ambient pressure and temperature near the mill was sampled by a benchtop datalogger at 10 min intervals in order to separate any effect of the ambient conditions on the data collected *in situ* during milling.

After each milling run in which pressure and temperature were monitored, the vessel was allowed to cool to ambient temperature. The milling run was then repeated without opening the jar to allow for the separation of the effects of chemical reaction(s) from that of mechanical heating of the milling jar. Milled silicides with higher cerium contents than that of CeSi tended to adhere to the milling vessel walls. To clean the vessel when changing from one nominal composition to another, the milling vessel volume was filled 2/3 full with CSZ media and 20 mL isopropyl alcohol and milled for 5 min at 500 rpm. This treatment was sufficient to remove gross deposits of silicide. Media were cleaned of adhered silicide between milling experiments of identical compositions by another 5 min milling in isopropyl alcohol, and fresh media were substituted when changing compositions. As-milled powders were screened to -120 mesh and stored in an argon-atmosphere glovebox. Some as-milled powder was consolidated into dense pellets by spark plasma sintering (SPS) (Dr. Sinter SPS-550, Fuji Corp., Japan) for further experiments and microstructural characterization of the monolithic product.

3. Experimental procedures

In a typical milling experiment, 5 g of the elemental starting materials were weighed and added to the milling vessel along with fifteen 10 mm and ten 5 mm media in an argon atmosphere glovebox with P_{O2} < 30 ppm, resulting in a ball-to-powder ratio of approximately 10:1. Different sized media were used in order to randomize milling media trajectories and help ensure that no portion of the vessel contained unmilled material. Milling was conducted at 500 rpm for between 5 min and 8 h. At least two

experiments were conducted at the nominal composition of each line compound in Table 1, as well as at the nominal compositions identified as the middle eutectic (55% Si, CeSi_{1.23}) and near the Si-poor boundary of the CeSi_{2-y} phase (61% Si, CeSi_{1.56}).

In a typical SPS experiment, 4 g of milled powder was loaded into a graphite die (I-85, Electrodes Inc, USA) in a nitrogen atmosphere glovebox with P_{O2} < 200 ppm. Samples were cold pressed at 5 kN in the die and then transported to the SPS in a polyethylene bag. The graphite dies had a 21 mm bore and 15 mm thick wall and were lined with grafoil (99.8%, Alfa Aesar, USA). Samples were heated at 100 °C/min to 1000–1300 °C with a 5–15 min hold. Process temperature was controlled by a pyrometer focused in a 5 mm bore hole drilled to within 5 mm of the sample. Samples were pre-loaded at 5 kN in the SPS apparatus and held at 5 kN throughout the temperature ramp until cooldown. Sintered samples of CeSi_{2-x}, CeSi, and Ce₃Si₂ were prepared in this manner.

The crystallite size and phase of starting materials, as-milled powder, and sintered pellets were characterized by XRD in Bragg–Brentano geometry (Rigaku Miniflex, Japan). To avoid excessive oxidation, powder samples were mixed with a small amount of vacuum grease under argon before loading the XRD sample holder. A single peak was noted at 28.1° 2θ when characterizing a blank slide containing only vacuum grease. Phase identification was performed by comparison to the Inorganic Crystal Structure Database [17]. Microstructure and morphology were investigated by scanning electron microscopy and stoichiometry by energy dispersive spectroscopy (Hitachi 3400-N, Japan). EDS spectra were collected with an accelerating voltage of 10 kV to improve surface selectivity and sensitivity to silicon content.

4. Results

4.1. Pressure and temperature monitoring results

The *in situ* monitoring of temperature and pressure revealed a small spike in pressure between 30 min and 150 min of milling at 500 rpm. The exact location depended on the composition, and the occurrence, height, and timing of the spike was repeatable to within 10% relative error from run to run. Representative data for four different compositions are shown in Fig. 1, with details of the ΔT calculation given in Section 5. The inset shows a very nearly linear dependence of milling time before reaction on milling speed for the CeSi composition.

4.2. Milling results

All of the line compounds in the Ce–Si system except Ce₅Si₄ were successfully synthesized by high-energy ball milling at 500 rpm. Representative diffraction plots for the each composition are shown in Fig. 2. XRD analysis of CeSi₂ showed a small amount of unreacted cerium, which was determined to be a consequence of a small amount of material that became trapped in the vessel lid seal during milling. No impurity phase was detected in XRD of

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