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Nanocrystalline chromium disilicide synthesized by a fast Chlorine-Transfer-Reaction

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Abstract

Pure nanocrystalline chromium disilicide (CrSi₂) were synthesized for the first time by a fast Chlorine-Transfer-Reaction between chromium chloride and silicon with the support of thermodynamics calculation. The use of sodium and lithium chloride diluent enables to decrease the aggregates size from ~2000 nm to ~500 nm and to reach a nanocrystallite size ranging from 50 – 200nm suitable for new applications.

Keywords: Nanocrystalline materials; Microstructure; Metallurgy; Thermodynamics and kinetics of processes in materials

1. Introduction

Chromium disilicide is studied since several years for its thermoelectric properties [1] and for electrical transportation [2, 3]. It is a p-type semiconductor with a bandgap of about 0.35 eV, its power factor, $\alpha^2\sigma$ (with α the Seebeck coefficient and σ the electrical conductivity), is similar to the best industrial thermoelectric (TE) materials [4]. However its figure of merit ZT is 0.25 [4], while it is about 1 for the best industrial TE materials. This low value is mainly related to its relatively high thermal conductivity κ which is about 10 W/mK at 300 K. Different routes have been investigated in the past years to decrease κ : doping with heavy elements, insertion of point defects or even by decreasing the dimensionality. This last point could be promising, however additional efforts are still needed in the synthesis of nanomaterials. In this study we will focus on the synthesis of CrSi₂ in the shape of nanocrystals. Nanostructuring of chromium disilicide has been investigated in the past few years by top-down approach such as

mechanical alloying/milling [5-7] and by bottom-up approach by Physical Vapor Transportation (PVT) which enables the growth of CrSi₂ nanostructures in the shape of nanowires or 2D nanostructured objects [1-3, 8-11].

In this study we will focus on the synthesis of nanostructured CrSi₂ by Chlorine-Transfer-Reaction (CTR) by adapting the protocol described by Trentler et al. [12] on MoSi₂ with the support of thermodynamic calculations. We also report the effect of an inert diluent into the reaction mixture to control the size of the aggregates and thereby enable the formation of nanocrystalline powders.

2. Materials and methods

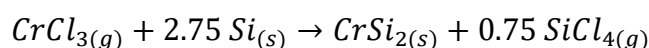
CrCl₃ (flakes, 3N), Si (1 – 5 μ m, 5N), NaCl (powders, 4N) and LiCl (powders, 2N) from Alfa Aesar were used as raw materials. In a glovebox, the mixtures (1CrCl₃ : 2.75Si, with different amount of LiCl or NaCl) are grinded and are transferred into a sealed fused silica tube under Argon (5N, Air product). This tube consists of two zones (13mm \emptyset , 100mm length each): a reaction zone which is located into the furnace and a by-product collection zone which is located outside of the furnace. The reaction is conducted in a tubular furnace possessing a 30 mm temperature homogeneous zone. The quartz vessel is connected to an argon gas flow (2L/min) equipped with a bubbler to prevent a pressure build up and to catch SiCl₄ gaseous species which could leave the by-product collection zone. The mixture is heated up to 600°C, 700°C or 800°C with a ramp rate of 500°C/h and maintained to this temperature for 5 minutes. The reaction tube is quenched under air by removing the fused silica tube from the furnace in order to prevent grain coarsening and sintering. The mixture is cleaned 5 times with deionized water and centrifugated. The powders are then dispersed in absolute ethanol with an ultrasonic bath (90 minutes, 25 kHz) and extracted after centrifugation. The samples are characterized by powder X-Ray Diffraction (Philips X'PERT). Rietveld refinement with Fullprof software is used for structural analysis of each sample [13]. Dynamic Light Scattering (DLS) measurements are performed with a Vasco Particle Size Analyzer DL135 (Cordouan Technologies, $\lambda = 657 \text{ nm}$, autocorrelation function modelled by Pade Laplace algorithm). SEM analysis is conducted using a Zeiss Ultra55.

Thermodynamic analysis of the gaseous phase chemistry is made using Factsage thermodynamic software. The thermodynamic database SGTE is completed with the

thermodynamic data of the gaseous compounds in the Si-Cl-H system [14] and the thermodynamic data of the stoichiometric compound CrSi [15].

3. Results and discussion

From the thermodynamic calculations, the heating of CrCl_{3(s)} in an atmosphere of argon mainly leads to the formation of CrCl_{3(g)} between 500°C and 1000°C. In lower amount, CrCl_{4(g)}, CrCl_{2(g)}, Cl_(g) and Cl_{2(g)} are also produced (Figure 1a). Then, CrCl_{3(g)} reacts with Si_(s) to form solid chromium silicides and gaseous species. Thermodynamic calculations show that the nature of solid silicides is strongly influenced by the initial CrCl_{3(s)}:Si_(s) ratio (not given here). For the experimental ratio of 1:2.75, calculations indicate the formation of solid CrSi₂ at more than 99 mol% (the other solid is Cr₅Si₃) between 500°C and 1000°C. The gaseous phase is mainly composed of SiCl_{4(g)} together with a small amount of Si₂Cl_{6(g)}, SiCl_{3(g)} and CrCl_{3(g)}, the latter probably coming from the re-sublimation of CrSi_{2(s)} at high temperatures (Figure 1b). The Chlorine-Transfer Reaction can therefore be summarized by the equation:



Experimentally, dark gray powders have been obtained in the reaction zone together with the formation of SiCl₄, condensed in the collection zone of the tube. From Figure 2, Rietveld analysis shows the presence of three solids: unreacted silicon and two silicides, CrSi₂ and Cr₅Si₃. The quantity of CrSi₂ increases from 52 to >94 wt. % for respectively 600 °C and 800°C, while on the same temperature range, the quantity of impurities, Si and Cr₅Si₃, decrease respectively from 20 to <1 wt. % and from 30 to <5 wt. %. These amounts are below the sensibility limit of XRD and agree with the thermodynamic results which indicate the formation of 99 wt. % pure CrSi₂ from 500°C to 1000°C. The presence of Cr₅Si₃ and Si in the experiments at 600°C and 700°C can be explained by the local inhomogeneity of composition due to the remaining CrCl_{3(s)} in the mixture at these temperatures. Below 750°C, thermodynamic calculations show that 66% of CrCl₃ stay in its solid form while above 750°C, all the CrCl_{3(s)} is converted into chromium chloride gaseous species (Figure 1a). Therefore, a compromise is found experimentally at 800°C to ensure an almost complete reaction between CrCl₃ and Si without favoring a grain coarsening mechanism at higher temperatures. From Rietveld analysis, the peaks are thin and shows that CrSi₂ is well crystallized at 800°C. The CrSi₂ powder obtained

consists of aggregates with a mean size of about 2 μm , as measured by DLS and SEM, a value similar to the initial silicon powder (Table 1). Rietveld's refinement followed by a microstructural analysis (Figure 3) shows that the aggregated are composed of crystallites with sizes ranging from 50 nm to 200 nm.

We have also investigated the role of LiCl and NaCl on the synthesis of chromium silicides by the Chlorine-Transfer Reaction. The Rietveld analysis show that CrSi_2 is obtained with a purity >94 wt. % with Si and Cr_5Si_3 as the main impurities. In Figure 3, it is observed that the use of NaCl and LiCl lead to refined microstructures. Additionally, we observe a strong influence of the diluent on the average Particle Size Distribution (\overline{PSD}) either with LiCl or NaCl diluent. The \overline{PSD} falls to respectively 970 and 670 nm in volume for 10 mol.% NaCl and 10 mol.% LiCl, it is slightly lower in number with respectively 420 and 440 nm. We also have observed that after 1h decantation, the \overline{PSD} in volume decreases to about 410 nm which would permit to prepare nanometric powder in two steps. The possible reason could be the formation of a liquid phase assisting the synthesis of CrSi_2 that could modify the growth mechanisms from vapor-solid mechanisms (without diluent) to vapor-liquid-solid mechanisms when a diluent is added (NaCl or LiCl). Indeed, LiCl is already liquid from $\sim 605^\circ\text{C}$ and the binary NaCl- CrCl_3 presents a liquid region for the conditions investigated [16]. The refined microstructure obtained with LiCl diluent compared to NaCl diluent confirm this assumption.

4. Conclusion

We have demonstrated that CrSi_2 nanopowders with crystallite size about 50 to 200 nm and mean volume particle size distribution down to about 670 nm in volume and about 420 nm in number can be obtained through Chlorine-Transfer-Reaction followed by sonication. It has been demonstrated that the use of diluent is needed and permit to decrease the PSD of CrSi_2 by a factor ~ 4 .

Acknowledgment

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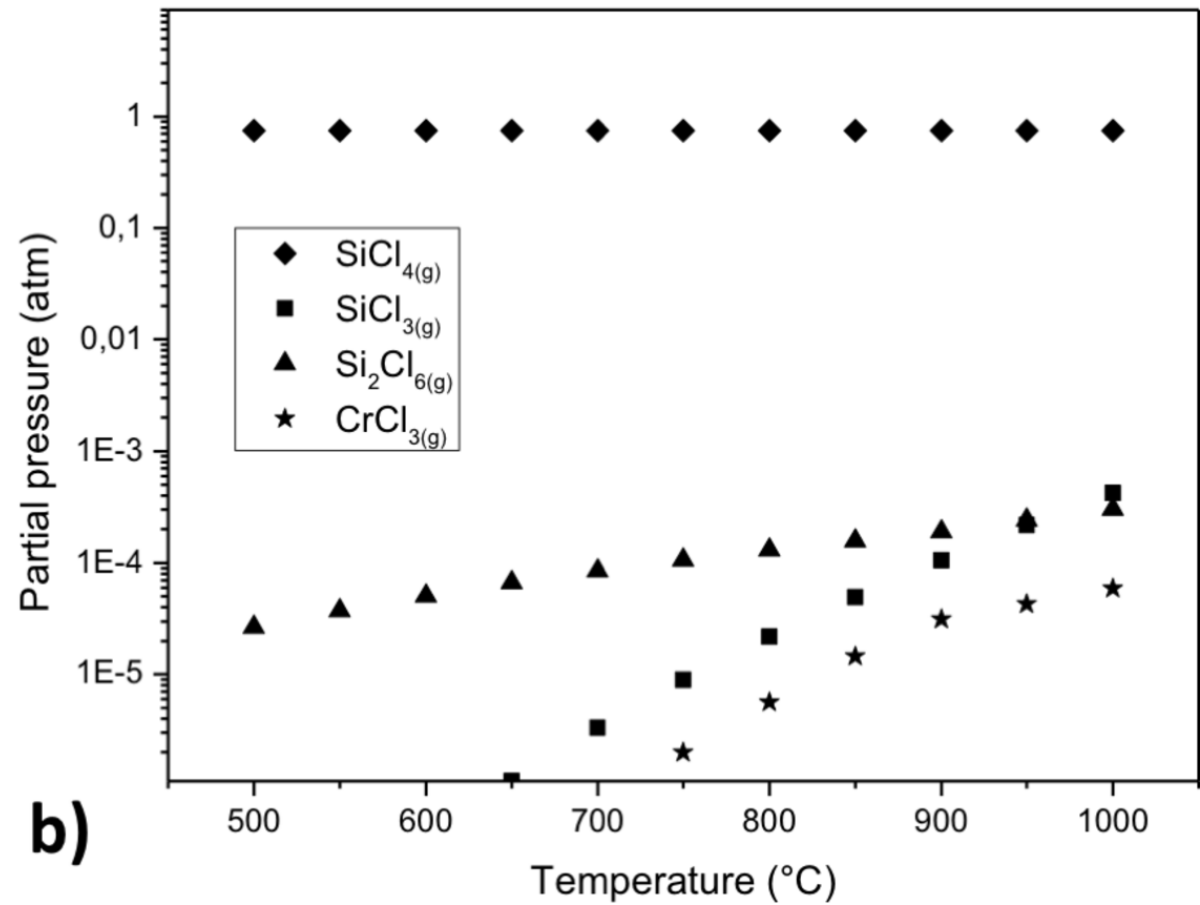
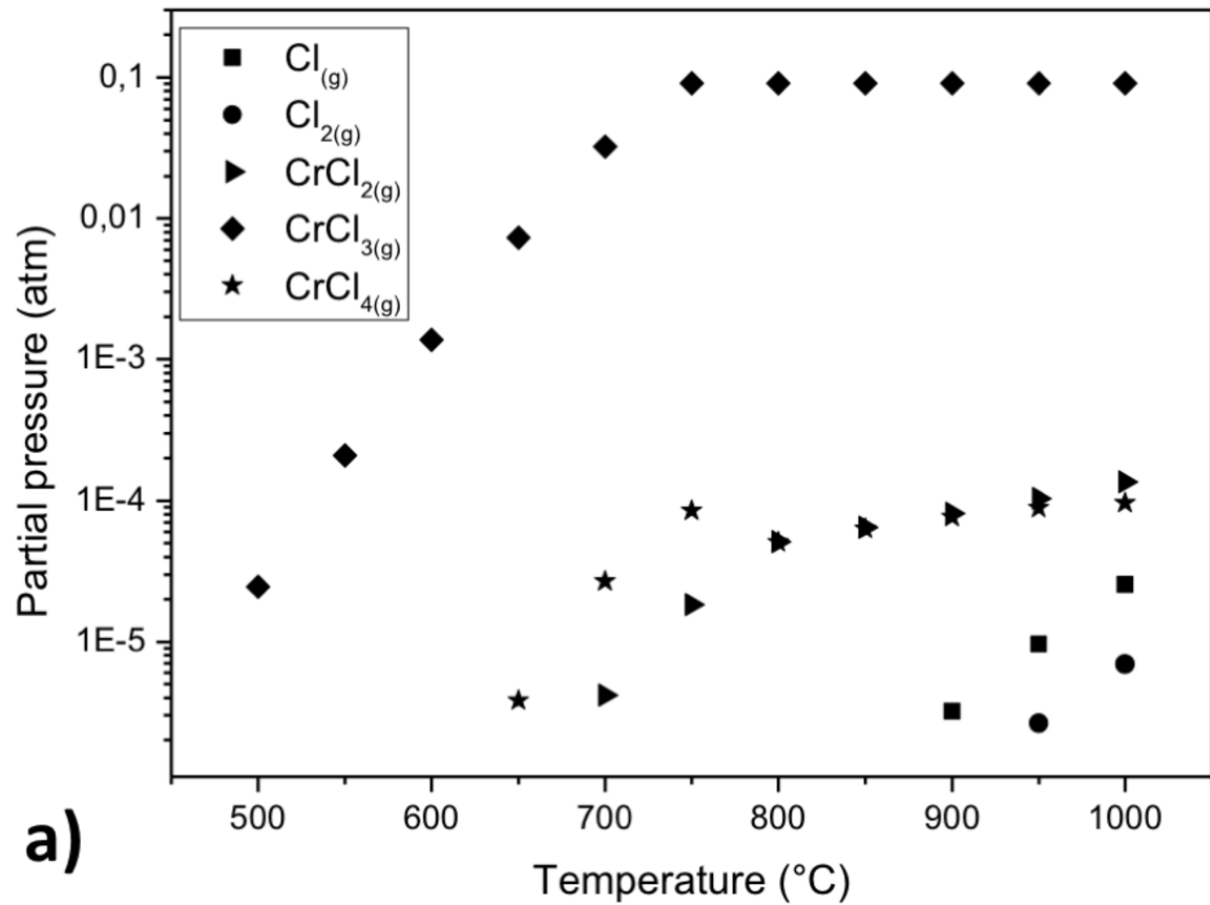
Captions

Table 1: \overline{PSD} in volume (number) of CrSi₂ aggregates after sonication in function of LiCl and NaCl dopant ratio.

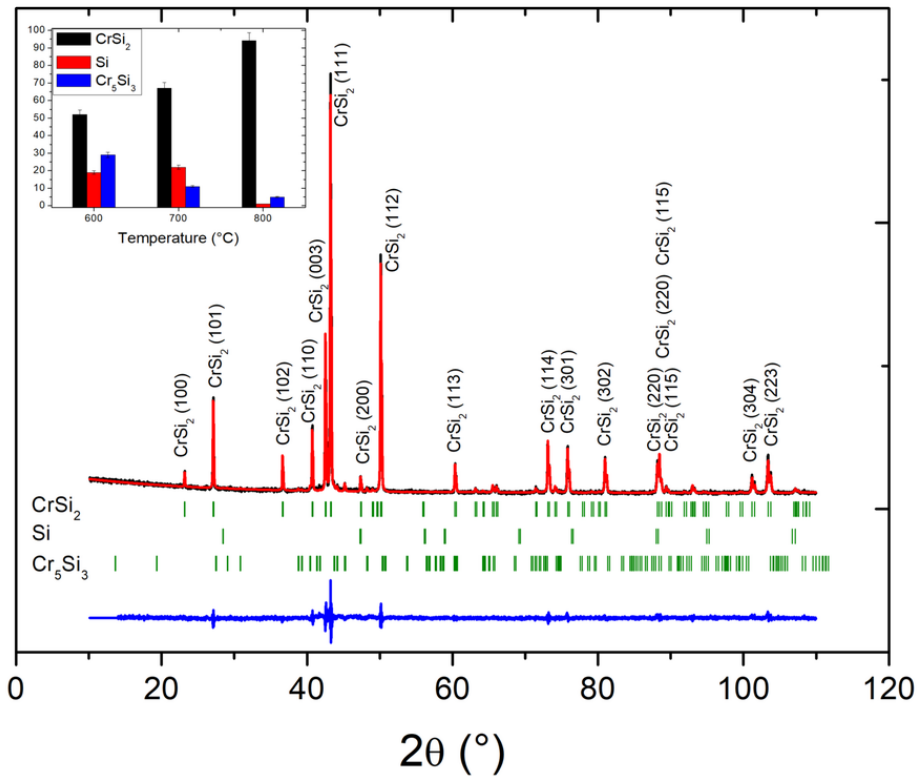
Figure 1: Calculated partial pressures of Cl_x and CrCl_x gaseous species as a function of the temperature for the initial mixtures: a) 1 CrCl₃(s) + 10 Ar(g). b) 1 CrCl₃(s) + 2.75 Si(s)+10 Ar(g). Total pressure: 1 atm.

Figure 2: Observed (black), calculated (red) and difference (blue) XRD profiles for the Rietveld refinement of CrSi₂ after Chlorine-Transfer-Reaction (800°C, Ar, 5 min, no diluent). The Bragg peaks of the most intense peak are also given. The amount (w%) of the phases at different temperature is given in the inset.

Figure 3: SEM Secondary-Electron images of CrSi₂ aggregates: a-b) no diluent, c-d) 5% NaCl, e-f) 5% LiCl, g-h) magnification of typical aggregates.



Intensity (a.u.)



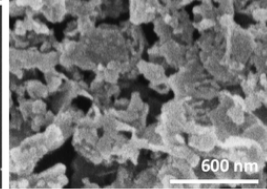
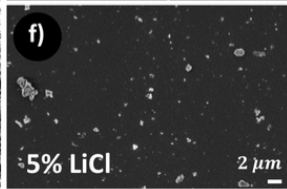
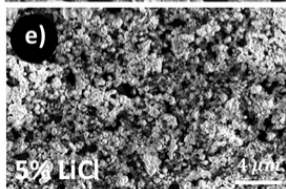
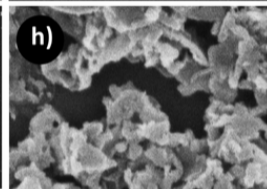
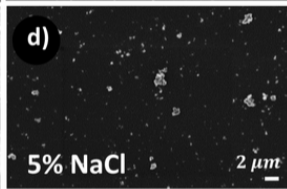
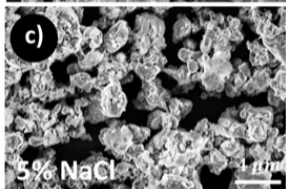
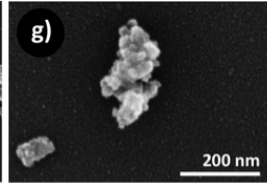
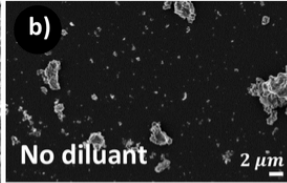
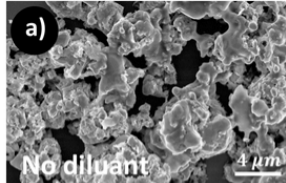


Table 1

Diluent (molar ratio)	No diluent	0.5 LiCl	5 LiCl	10 LiCl	0.5 NaCl	5 NaCl	10 NaCl
<i>PSD</i> (nm) volume (number)	2100 (1750)	1340 (1250)	1040 (870)	670 (440)	1700 (880)	1010 (940)	970 (420)

Tube furnace

