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Synthesis and thermal stability of nano-crystalline vanadium disilicide

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Abstract

Nano-crystalline vanadium disilicide was successfully synthesized using vanadium tetrachloride and silicon as starting materials via reduction–silication route at 650 °C in the molten salt solution of magnesium chloride and sodium chloride in an autoclave. X-ray powder diffraction patterns indicated that the product was hexagonal VSi₂ (a = 4.572 Å, c = 6.372 Å). Transmission electron microscopy images showed that the particle size of the product was in the range of 40–60 nm in diameter. There was a strong absorption peak at 271 nm in the UV-Vis absorption spectra. The oxidation of nano-crystalline VSi₂ began to proceed at the temperature of 400 °C in air. But the product had high thermal oxidation stability below 1000 °C. It can be used as an antioxidation coating material. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Due to their technologically relevant characteristics, which are high melting point, high hardness, strength, thermal stability, excellent wear and corrosion resistance, the transition metal silicides have received considerable attention in the last few decades. They, in fact, find applications in high-temperature devices [1], microelectronics (where they are commonly used as interconnects in very large scale integration applications) [2] and catalysis [3]. Among these silicides, vanadium disilicide is an important material. In addition to these common properties of metal silicides, they also have low electrical resistivity and so is used in semiconductor devices [4]. However, there have been few reports on the composition, structure and properties of nano-crystalline VSi₂. It is meaningful to synthesize nano-crystalline VSi2 as the nano-sized powders can reduce the sintering temperature [5] of bulk materials.

Traditionally, VSi₂ can be synthesized through various methods: field activated combustion synthesis [6] of vanadium disilicide by using vanadium and silicon powders

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as starting materials in a high purity argon atmosphere above 1390 °C, crystal growth of vanadium silicide [7] from high-temperature tin and copper solutions (at 1400 °C) in an argon atmosphere using vanadium metal chips and powder as starting materials, and solid-state synthesis [8] via reaction of calcium and magnesium silicide with vanadium oxides at 1000 °C. But all these methods require high temperature, and also cannot form nano-sized products.

In this paper, we have developed a molten salt route to prepare nano-crystalline vanadium disilicide via reduction–silication reaction of metallic sodium with vanadium tetrachloride and silicon at 650 °C. It can be described as follows:

 $VCl_4 + 2Si + 4Na \rightarrow VSi_2 + 4NaCl$

Reactions in molten salts provide an original method for the preparation of solids. Molten salts can accelerate the kinetics of the reaction by enhancing diffusion as the diffusion coefficients in liquid state are higher than those in solid state. Therefore, they can serve as an inorganic solvent medium to control the reaction speed and the particle size. Because vanadium tetrachloride attains gaseous state at 152 °C [9], it is necessary to carry out the whole reaction in an autoclave. The product becomes free of oxide impurities by restraining the reaction in an anaerobic environment.

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Fig. 1. XRD patterns of vanadium disilicide prepared via reduction-silication route.

2. Experimental

All the reagents used were analytically pure. All manipulations were carried out in a dry glove box filled with N₂. First, 10 g of MgCl₂ and 10 g of NaCl were added to an autoclave. Then 0.02 mol of poly-crystalline Si powder (200 meshes) was put into the autoclave followed by thorough mixing of the powder. Finally 0.01 mol of VCl₄ and 0.04 mol of Na were put into the autoclave. The autoclave was sealed and maintained at 650 °C for 10 h and then cooled to room temperature in the furnace. After that, the products were washed with 0.1 mol/l nitric acid, diluted alkali solution, distilled water and alcohol in a sequence. The final product was vacuum-dried at 60 °C for 12 h. The product obtained was a black-colored powder.

The powder-products were analyzed by powder X-ray diffraction (XRD) on an X-ray differactiometer (Rigaku rA) using Cu K α radiation (wavelength $\lambda = 1.54178$ Å), and transmission electron microscope (TEM) with a Hitachi 800 TEM. The UV-Vis absorption spectrum was recorded on a Shimadzu UV-2401PC UV-Vis spectrophotometer. The thermogravimetric analysis was performed on a thermal analyzer (Model: TA-50) below 1000 °C in air at a rate of 10 °C min⁻¹ to study the oxidation behavior of the nano-crystalline vanadium disilicide. The density of the product was found out by using a pycnometer method with toluene at 25 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared vanadium disilicide sample. All the diffraction peaks can be indexed as the hexagonal phase of vanadium disilicide. The lattice parameters were calculated to be a = 4.572 Å, c =



Fig. 2. TEM images of the vanadium disilicide prepared via reductionsilication route.

6.372 Å, which are in good agreement with the values (a = 4.572 Å, c = 6.373 Å) found in the Powder Diffraction File.¹ No evidence of impurities such as V, Si, V₂O₃, V₂O₅ and SiO₂, can be found in the XRD patterns. The crystallite size is estimated to be about 50 nm in diameter, according to the reflections by the Debye–Scherrer equation with a shape factor of 0.9. The density using a pycnometer method with toluene at 25 °C is 4.550 g cm⁻³, which is close to the reported result (D_x : 4.624 g cm⁻³).

A TEM image is shown in Fig. 2. The material exhibits slightly agglomerated particle morphology. The primary par-

¹ See Powder Diffraction File No. 38-1419, International Center for Diffraction Data, New town Square, PA, USA.



Fig. 3. Room temperature UV-Vis absorption spectra of the vanadium disilicide prepared via reduction-silication route.

ticle size is estimated to be in the range 40–60 nm in diameter, which is in agreement with the value calculated from the Debye–Scherrer equation.

The UV-Vis absorption spectra of the VSi₂ nano-crystallites, which were ultrasonically dispersed in absolute ethanol, are shown in Fig. 3. It can be seen that there is only a strong absorption peak at 271 nm. The onset of the absorption appears at about 350 nm. We have not found any information about the UV-Vis absorption records of VSi₂ in literatures. The width of the absorption band [10] is associated with the dispersion of the particle size. So we can see that the quantum dimension effect of nano-crystalline vanadium silicide results in the broadening of the band.

The oxidation process of nano-crystalline VSi₂ was studied at temperatures below $1000 \,^{\circ}$ C by TGA, as shown in Fig. 4. The weight of the product does not increase significantly below $400 \,^{\circ}$ C but increase gradually by about 28% from 400 to $1000 \,^{\circ}$ C. But when the temperature is above 600 $\,^{\circ}$ C, the increase in weight becomes even bigger. That is to say the oxidation begins at a relatively low temperature



Fig. 4. TGA curves heated in flowing air for vanadium disilicide prepared via reduction-silication route.



Fig. 5. The XRD patterns of the oxidation product of TGA testing.

of 400 °C and takes place slowly only on the surface of the particles. Theoretically, the increment in weight is about 106.7% according to the calculation when VSi₂ was oxidized thoroughly. This result is not in agreement with the result obtained in [7], who reported that the oxidation of VSi₂ crystals began to proceed at a measurable rate in the temperature range of about 515 °C and yielded the final oxidation product V_2O_5 . This is because the VSi₂ prepared using the method shown in this paper is nano-crystalline and has a high surface energy. So the oxidation occurs at a lower temperature.

The XRD patterns of the oxidation product obtained after TGA testing are shown in Fig. 5. All the peaks in the XRD patterns are indexed as the hexagonal VSi₂ is the majority phase, while the orthorhombic V_2O_5 , is the minority phase. There are no SiO₂ peaks in the patterns, due to the fact that SiO₂ is amorphous. As the temperature rises, oxidation begins at the surfaces of the particles, gradually forming vanadium oxide and silicon dioxide. The newly-formed vanadium oxide and silicon dioxide, becomes a protective layer, and cannot evaporate from the surfaces of the particles and they have the power to diminish a further oxidation process. The final product is mainly vanadium silicide. Because the oxides (V₂O₅ and SiO₂) were formed on the surfaces of the particles, the as-prepared nano-crystalline vanadium disilicide exhibits high thermal stability.

4. Conclusion

As a summary we conclude that nano-crystalline hexagonal vanadium disilicide has been successfully prepared via a reduction–silication route by the reaction of metallic sodium with vanadium tetrachloride and silicon at $650 \,^{\circ}$ C in a molten salt solution using magnesium chloride and sodium chloride in an autoclave. The molten salts serve as reaction-medium to control the reaction rate and particle size. The particle size is estimated to be in the range of 40–60 nm in diameter. The oxidation in air begins to proceed at the temperature of 400 °C. The formed oxides on the surfaces can diminish further oxidation below 1000 °C.

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