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Facile and scalable synthesis of Ti_5Si_3 nanoparticles via solid-state route in an autoclave

A novel method of the synthesis of titanium silicide nanoparticles via solid-state route in an autoclave at 700 ℃ is reported. The reaction of titanium silicide could be described briefly as: $5TiO_2 + 3Si + 20Li = Ti_5Si_3 + 10Li_2O$. XRD pattern indicated that the product was hexagonal Ti_5Si_3. The Ti_5Si_3 particle size (about 20–40 nm) is confirmed by the TEM images. Furthermore, the thermal stability and oxidation resistance of the titanium silicide nanoparticles were also investigated.

Keywords: *titanium alloys, nanocrystalline materials, X-ray diffraction (XRD).*

INTRODUCTION

In recent years, alloys systems have attracted widespread attention from researchers home and abroad, because of their excellent physical and chemical properties [1–3]. Metal silicides are a broad family of refractory intermetallic compounds between transition metals and silicon. Titanium silicide (Ti_5Si_3) has attracted considerable attention due to its outstanding properties including high melting temperature (2122 °C), low density (4.32 g/cm^3) and high hardness, as well as excellent strength at elevated temperature and high oxidation resistance, which consequently promote Ti_5Si_3 as a promising material for high-temperature structural applications [4–7].

Simple and scalable synthesis of Ti_5Si_3 nanomaterials will be vital for their technological applications [8, 9]. Generally, titanium-silicon alloy is prepared through conventional methods, such as combustion synthesis [10, 11], self-propagating high temperature synthesis (SHS) [12], ball-milling method [13], molten salt rod [14], reaction hot pressing [15], chloride-generated route [16], mechanical alloying (MA) [17], chemical vapour deposition [18, 19], electro-pressure sintering [20]. It is difficult now to obtain the Ti_5Si_3 nanomaterials. So far, Ti_5Si_3 nanopaticles have only been prepared in molten salts system at 700 °C [21].

In this work, a solid-state route in an autoclave for preparation of Ti_5Si_3 nanomaterials at low temperature was reported for the first time, with process being described by the following equation: $5TiO_2 + 3Si + 20Li \rightarrow Ti_5Si_3 + 10Li_2O$. The approach to synthesize Ti_5Si_3 nanoparticles in an autoclave is favorable and could be exploited for practical industrial Ti_5Si_3 nanomaterials production.

EXPERIMENTAL

Preparation of Ti_5Si_3 nanomaterials

All the chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The synthesis was carried out in a stainless steel autoclave (20 mL), in which 0.8 g of titanium dioxide, 0.168 g of silicon powders and 1.5 g of Lithium powders were added. The temperature of the stove was raised from room temperature to 700 °C with a heating ramp rate of 5 °C/min and maintained at the target temperature for 10 h, and then it was cooled to room temperature naturally. The precipitates in the autoclave were collected and washed with absolute ethanol, dilute hydrochloric acid, and distilled water several times to remove the impurity. The final products were dried in vacuum at 60 °C for 6 h.

Characterization

The XRD measurements were carried out with a Philips X-ray diffractometer. TEM images, high-resolution transmission electron microscopy (HRTEM) images, and the corresponding selected-area electron diffraction (SAED) patterns were taken on a JEOL-2000 transmission electron microscope with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) profile was collected with a Shimadzu-50 thermoanalyzer apparatus under flowing of air.

RESULTS AND DISCUSSION

The Powder X-ray diffraction (XRD) pattern of the sample prepared at 600 °C is shown in Fig. 1, *a*. The diffraction peaks (200), (111), (002), (210), (211), (300), (112), (221), (311), (400), (222), (410), (213), (402) and (322) in the figure are completely consistent with the standard card of hexagonal Ti_5Si_3 (JCPDS PDF No. 29-1362; space group P63/mcm, a = 7.444 Å, c = 5.143 Å.). The EDS spectrum (see Fig. 1, *b*) reveals the presence of Ti and Si elements at a Ti/Si atomic ratio of 1.67:1, indicating the formation of Ti_5Si_3 (the signals of Cu came from the copper grid used for the EDS observation). Both XRD pattern and EDS spectrum confirm that the sample is Ti_5Si_3.

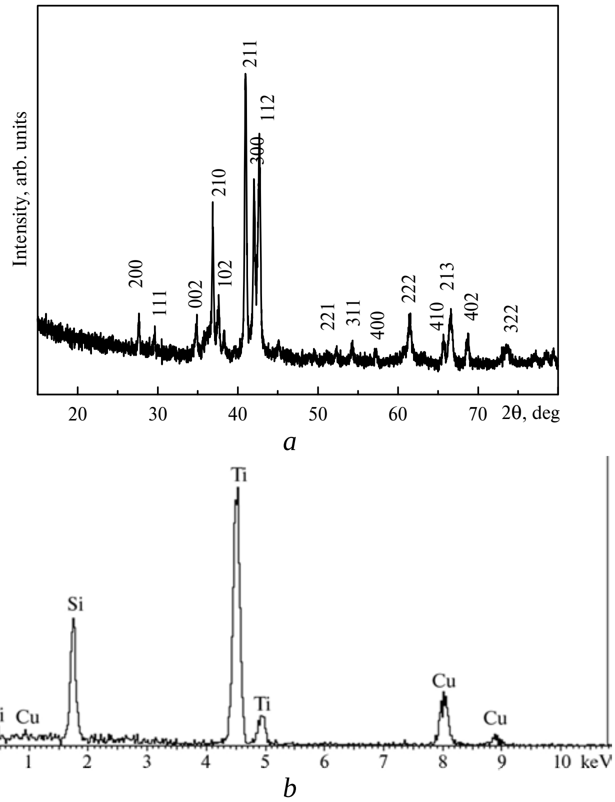

Fig. 1. XRD pattern (*a*) and EDS spectrum (*b*) of Ti_5Si_3 nanoparticles.

Representative Ti_5Si_3 nanocrystals are compiled in Fig. 2. Scanning electron microscopy (SEM) images of the Ti_5Si_3 nanoparticles reveal that the as-prepared NPs are homogeneous, with particle size clearly at the nanoscale (see Fig. 2, *a*). Transmission electron microscopy (TEM) images revealed an average particle size of 20–40 nm (see Fig. 2, *b*). The corresponding SAED pattern (see Fig. 2, *b*, inset) indicates that the sample is polycrystalline, confirming the particle size is relatively small. The high magnification TEM image recorded three Ti_5Si_3 nanocrystals about 20 nm of size shown in Fig. 2, *c*. The average distance between the neighboring fringes (shown in Fig. 2, *d*) is about 0.245 nm, corresponding to the (210) plane of hexagonal Ti_5Si_3.

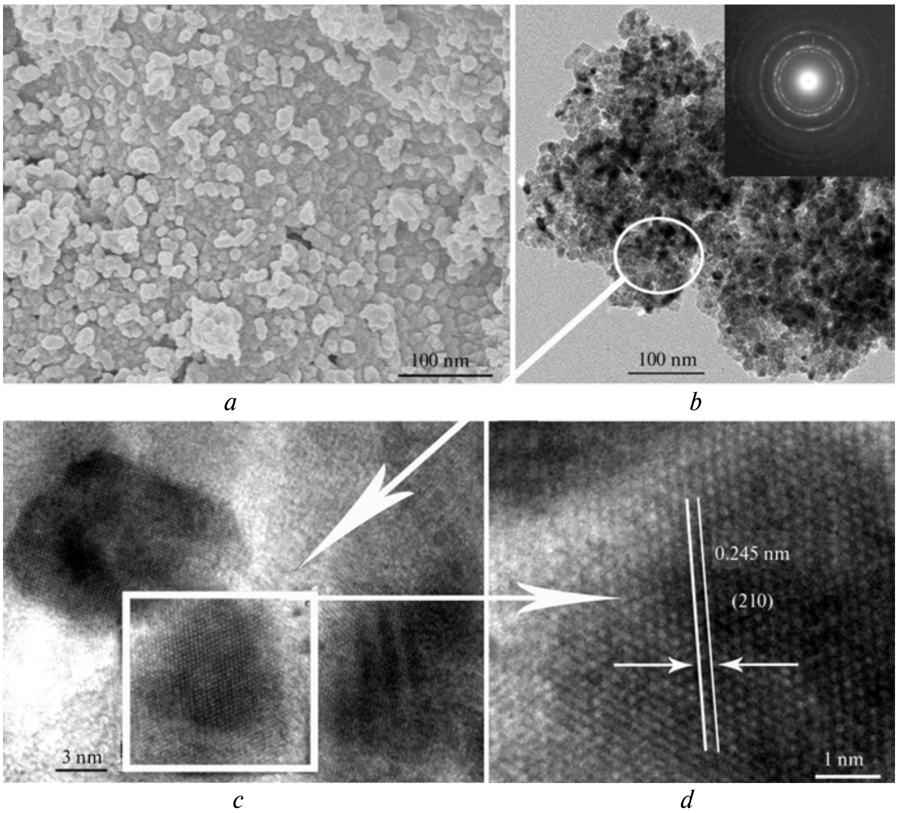

Fig. 2. SEM image (*a*), TEM image and SAED pattern (right corner) (*b*), higher magnification TEM image (*c*), HRTEM image (*d*) of the as-prepared Ti_5Si_3 nanoparticles.

The thermal stability of the as-prepared Ti_5Si_3 nanoparticles was examined by TGA-DTA under flowing air. The TGA-DTA curves of Ti_5Si_3 nanoparticles oxidation tests (air flow) are shown in Figs. 3, *a* and *b*. From the TGA curve (see Fig. 3, *a*) it is found that the weight of the product does not change significantly below 300 °C. From 300 °C to 1000 °C, the weight of the powder increases gradually by about 70 %. As shown in the DTA curve (see Fig. 3, *b*), there is only one big exothermic peak, which starts at 500 °C and ends at 570 °C. Combining the results of the two curves, we can reach the following conclusions: the sample has basically been not oxidized from the room temperature to 300 °C. From 300 to 1000 °C, the sample suffered gradual oxidation. The oxidation process becomes intensified as the temperature rises to 540 °C, concluded from the DTA curve (see Fig. 3, *a*) and DrTGA curve (Fig. 4).

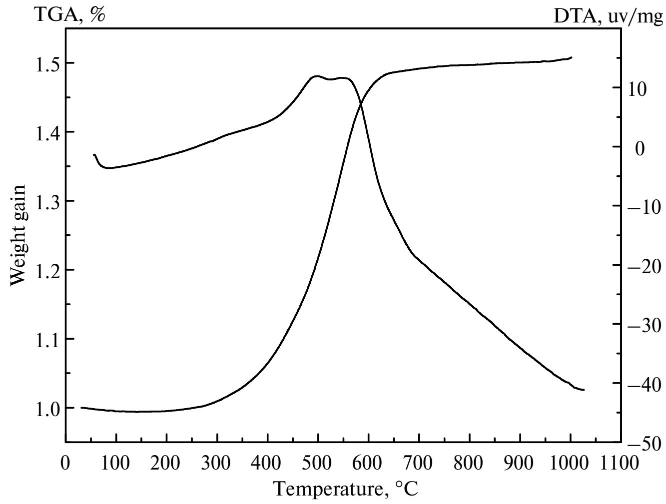

Fig. 3. TGA-DTA curves of the Ti_5Si_3 nanoparticles under flowing air.

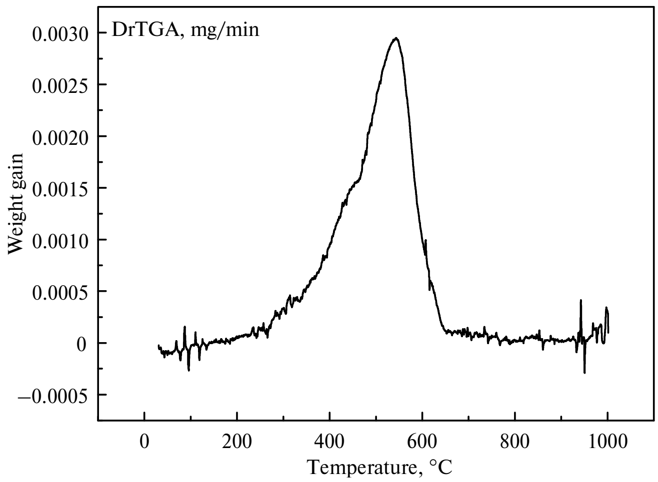

Fig. 4. DrTGA spectrum of the Ti_5Si_3 nanoparticles under flowing air.

CONCLUSIONS

It is challenging to synthesize nanostructured refractory silicides, such as Ti_5Si_3 and other metal-rich silicides (M_5Si_3). In this work, titanium dioxide, silicon powders and lithium powders placed in an autoclave at 700 °C results in the formation of Ti_5Si_3 nanoparticles with an average particle size of 30 nm. The XRD pattern indicated that the product is hexagonal Ti_5Si_3. The structure and morphology of the obtained product were derived from SEM, TEM, EDS, and DTA-TGA. The approach to synthesize Ti_5Si_3 nanoparticles in an autoclave could be exploited for industrial Ti_5Si_3 nanomaterials production and may provide new insights into the synthesis of other alloys.

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Повідомлено про новий метод синтезу наночастинок силіциду титану твердотільним шляхом в автоклаві при температурі 700 °C. Реакція силіциду титану може бути коротко записана як $5TiO_2 + 3Si + 20Li = Ti_5Si_3 + 10Li_2O$. XRD-зображення показало, що продукт є гексагональним Ti_5Si_3. Розмір частинок Ti_5Si_3 (~20–40 нм) підтверджено ПЕМ-зображенням. Також досліджено термостабільність і опір окисленню частинок силіциду титану.

***Ключові слова**: титановий сплав, нанокристалічний матеріал, дифракція рентгенівських променів.*

Сообщается о новом методе синтеза наночастиц силицида титана твердотельным путем в автоклаве при температуре 700 °C. Реакция силицида титана может быть кратко записана как $5TiO_2 + 3Si + 20Li = Ti_5Si_3 + 10Li_2O$. XRD-изображение показало, что продукт является гексагональным Ti_5Si_3. Размер частиц Ti_5Si_3 (~20–40 нм) подтвержден ПЭМ-изображением. Также исследованы термостабильность и сопротивление окислению частиц силицида титана.

***Ключевые слова**: титановый сплав, нанокристаллический материал, дифракция рентгеновских лучей.*

1. *Andreiev I. V.* Effect of the thermal treatment of the initial tungsten-containing raw material on the structure and properties of WC–Co type hard alloys with particularly fine-grained structures // J. Superhard Mater. – 2015. – **37**. – P. 417–421.
2. *Chen L., Guo H., Fujita T. et al.* Nanoporou PdNi bimetallic catalyst with enhanced electrocatalytic performances for electro-oxidation and oxygen reduction reactions // Adv. Funct. Mater. – 2011. – **21**. – P. 4364–4369.
3. *Goncharov A. A., Dub S. N., Agulov A. V., Petukhov V. V.* Structure, composition, and mechanical properties of thin films of transition metals diborides // J. Superhard Mater. – 2015. – **37**. – P. 422–428.
4. *Kasraee K., Tayebifard A., Salahi E.* Effect of substitution of Si by Al on microstructure and synthesis behavior of Ti_5Si_3 based alloys fabricated by mechanically activated self-propagating high-temperature synthesis // Adv. Powder Technol. – 2015. – **25**. – P. 885–890.
5. *Liu Y. F., Zhou Y. L., Zhang Q.* Microstructure and dry sliding wear behavior of plasma transferred arc clad Ti_5Si_3 reinforced intermetallic composite coatings // J. Alloys Comp. – 2014. – **591**. – P. 251–258.
6. *Yeh C. L., Wang H. J., Chen W. H.* A comparative study on combustion synthesis of Ti–Si compounds // J. Alloys Comp. – 2008. – **200**. – P. 450–456.
7. *Xu J., Liu L., Li Z. et al.* Niobium addition enhancing the corrosion resistance of nanocrystalline Ti_5Si_3 coating in H_2SO_4 solution // Acta Materialia. – 2014. – **63**. – P. 245–260.
8. *Li C. L., Zhan Y. Z., Mo Y. F., She J.* In situ synthesized Ti_5Si_3/Ti–Mo lightweight structural composites // Int. J. Refract. Met. Hard Mater. – 2013. – **41**. – P. 432–436.
9. *Scabarozi T. H., Hettinger J. D., Lofland S. E. et al.* Epitaxial growth and electrical-transport properties of $Ti_7Si_2C_5$ thin films synthesized by reactive sputter-deposition // Scripta Mater. – 2011. – **65**. – P. 811–814.
10. *Ran H., Niu J., Song B. et al.* Microstructure and properties of Ti_5Si_3-based porous intermetallic compounds fabricated via combustion synthesis // J. Alloys Comp. – 2014. – **612**. – P. 337–342.
11. *Wang H. Y., Lü S. J., Xiao W. et al.* Reaction pathway of combustion synthesis of Ti_5Si_3 in Cu–Ti–Si system // J. Am. Ceram. Soc. – 2013. – **96**, N 3. – P. 950–956.
12. *Yeh C. L., Chen W. H., Hsu C. C.* Formation of titanium silicides Ti_5Si_3 and $TiSi_2$ by self-propagating combustion synthesis // J. Alloys Comp. – 2007. – **432**. – P. 90–95.
13. *Liu J., Bai Y., Chen P. et al.* Reaction synthesis of $TiSi_2$ and Ti_5Si_3 by ball-milling and shock loading and their photocatalytic activities // Ibid. – 2013. – **555**. – P. 375–380.
14. *Zou X., Lu X., Zhou Z., Xiao W. et al.* Electrochemical extraction of Ti_5Si_3 silicide from multicomponent Ti/Si-containing metal oxide compounds in molten salt // J. Mater. Chem. A. – 2014. – **2**. – P. 7421–7430.
15. *Huang L. J., Wang S., Geng L. et al.* Low volume fraction in situ (Ti_5Si_3 + Ti_2C)/Ti hybrid composites with network microstructure fabricated by reaction hot pressing of Ti–SiC system // Compos. Sci. Technol. – 2013. – **82**. – P. 23–28.
16. *Yu L., Lv Y., Zhang X., Wang H.* Application of in situ chloride-generated route to Ti_5Si_3 nanowires from and on Si substrate // Mater. Lett. – 2012. – **74**. – P. 46–49.

17. *Park J. B., Ham J. S., Shin M. S., Park H. K.* Synthesis and electrochemical characterization of anode material with titanium-silicon alloy solid core/nanoporous silicon shell structures for lithium rechargeable batteries // J. Power Sources. – 2015. – **299**. – P. 537–543.
18. *Lin H. K., Tzeng Y. F., Wang C. H. et al.* Ti_5Si_3 nanowire and its field emission property // Chem. Mater. – 2008. – **20**. – P. 2429–2431.
19. *Zhang Y., Geng D. S., Liu H., Banis M. N.* Designed growth and characterization of radially aligned Ti_5Si_3 nanowire architectures // J. Phys. Chem. C. – 2011. – **115**. – P. 15885–15889.
20. *Park K. L., Hwang S. K.* Synthesis of Ti_5Si_3–Nb–C by electro-pressure sintering // Scripta Mater. – 2001. – **44**. – P. 9–16.
21. *Estruga M., Girard S. N., Ding Q. et al.* Facile and scalable synthesis of Ti_5Si_3 nanoparticles in molten salts for metal-matrix nanocomposites // Chem. Commun. – 2014. – **50**. – P. 1454–1457.

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