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SYNTHESIS OF NANOSTRUCTURED TITANIUM CARBIDE FROM TITANIUM OXIDE AND FERRO-TITANIUM THROUGH MECHANICAL ACTIVATION

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Abstract

Carbides of Ti have been synthesized directly from its oxides and ferroalloys through high energy mechanical milling and heat treatment. Powders of TiO_2 and Fe-Ti mixed with various proportions of graphite were milled in a planetary ball mill for 30 to 90 hours. The milled mixtures were then heat treated at 1100-1300^{o}C for 1 to 2 hours. The as-milled and heat treated powders were characterized by SEM-EDAX, XRD, Pycnometer, and BET techniques. Higher graphite content in the mixture apparently impeded the impact action during milling. Even though longer milling time ensured diminishing particle size, as revealed in SEM, agglomeration was noticed. Formation of carbides of Ti was detected by XRD even in as-milled powders milled for various lengths of time with reduced graphite content along with the change in phase from anatase to rutile. Nanostructured titanium carbide was successfully synthesized under suitable processing conditions using various raw materials. Density, specific surface area and average particle size of the as-milled and heat treated mixtures were correlated with milling time and heat treatment temperature.

Introduction

Titanium carbide is a material with high hardness and excellent wear resistance to find applications as cutting tools, hard second phases in composites, polishing paste, abrasive and wear resistant materials, as mirror scanners, space mechanisms, medical applications, etc. [1]. In nanocrystalline form, it can be used in the manufacture of microdrills for microelectronic circuits industry. Nanostructured carbides may also be used in the production of composites with a far more uniform particle distribution with reduced directionality in the product leading to improved and homogeneous properties. Titanium oxides are reduced to produce metallic titanium which in turn is carburized to synthesized titanium carbide. Thermodynamic requirements to reduce the oxides, however, pose the major stumbling block towards synthesizing the carbides, requiring very high temperatures.

Titanium carbide is commercially synthesized by carbothermal reduction of titanium oxide at elevated temperature using carbon black as follows [2]:

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g) \quad (1)$$

Titanium carbide can also be synthesized by ensuring direct reaction between titanium and carbon, gas phase reaction of titanium tetrachloride ($TiCl_4$) and appropriate gaseous hydrocarbons, and magnesium reduction of titanium chloride and carbon tetrachloride ($TiCl_4$ and CCl_4). However, major drawbacks for these methods are formation of a coarse sintered structure, formation of a non-stoichiometric composition TiC_xO_y, need for high purity titanium powder as input, etc [2]. Carbothermal reduction requires high temperature (1973-2372 K) and long reaction time (10-24 hours) [2]. Mechanical milling prior to carbothermal reduction is expected to significantly reduce the reaction temperature and time to synthesize TiC. Thermal plasma has also been used for the synthesis of titanium carbide using titanium and methane as starting materials [2]

$$Ti(s) + CH_4(g) = TiC(s) + 2H_2(g) \quad (2)$$

Another method of TiC synthesis is by reacting between the solutions of liquid titanium chloride and tetrachloromethane ($TiCl_4$ and CCl_4) through magnesium thermal reduction process [3]. Spark erosion is another technique used for the synthesis of TiC [4].

In the present study, nanostructured carbides of titanium are produced from mixtures of titanium oxides and graphite through high energy ball milling followed by heat treatment at a temperature far lower than required to reduce the oxides directly by carbon.

Experimental

Pure TiO_2 (99.5%, 80-250 nm), ferro titanium (with 40 %Ti, 2 %Al, - 40 mesh), and graphite powders (99.4 %, 10-100 μm) were used in the present study for the synthesis of titanium carbides. 1 ml Toluene ($C_6H_5CH_3$) was used as a dispersion agent during milling and 1g Zinc stearate ($C_{36}H_{70}O_4Zn$) was added into the powder mixture to promote de-agglomeration. The TiO_2-C powder mixture was mixed thoroughly in a horizontal mixing machine at 20 rpm for 2 hours. Then 25 g of this mixture was milled in a high energy planetary mill with steel balls of 20mm size (average). A constant ball to powder ratio (BPR) of 10:1 and a rotational speed of 400 rpm were maintained all throughout. The powder mixture was milled for various milling durations (30-90 hours) with intermittent sampling. A portion of the milled samples were heat treated at 1300 ^{o}C in a tube furnace under argon atmosphere for 1-2 hours. Characterization of the samples were done using SEM-EDAX, and XRD techniques. Similar procedure was followed while milling ferro-titanium and graphite mixtures.

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Results and Discussion

<u>Milling of TiO_2 – Graphite Mixtures</u>

The phase evolution during high energy mechanical milling of mixtures of titanium oxide and stoichiometric amount of graphite at different milling periods are studied by using XRD peak matching as shown in Fig. 1. The changes of the XRD patterns indicate an observable peak broadening. It is agreed by Ren *et al* [5] that the line broadening is caused by reduction in crystallite size of the samples, the presence of the internal strain and local correlated disorders. This is due to large number of dislocations resulted from heavy deformation caused by high energy mechanical milling. The XRD traces also show that the peak intensities for the oxides are reduced with increasing milling duration. As milling duration increases, anatase gets transformed to rutile. TiC appears with samples milled for 90 hours. This clearly indicates the possibility of the low temperature synthesis of titanium carbide directly from TiO_2.

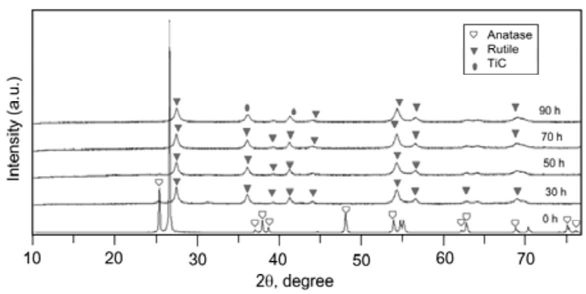


Figure 1. XRD patterns for as milled TiO_2-C mixed powders with stoichiometric carbon milled for various durations

Figure 2 below shows the XRD patterns for as milled oxide-graphite mixtures, all milled for a constant duration of 90 hours with varying carbon levels. Other than the stoichiometric level of carbon, 20% extra and 20% less carbon were used. Increasing carbon content apparently hindered the carbide formation even though anatase to rutile transformation has been noticed. This is probably due to the lubricating effect with excess amount of graphite whereby the impact action of milling on the powders is lost partially. Reduced content of graphite in the mixture, however, indicates the formation of TiC and other lower carbides ($TiC_{0.957}$, Ti_8C_5, $Ti_6C_{3.75}$). Even though an extra amount of carbon in the system increases the probability of carbide formation, it was not found effective.

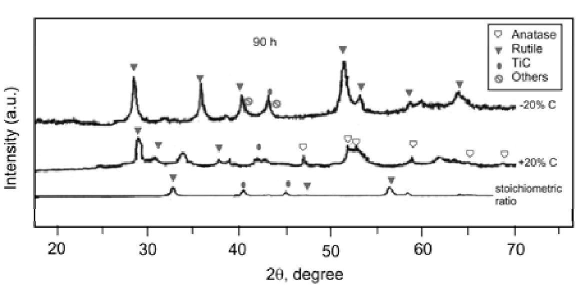
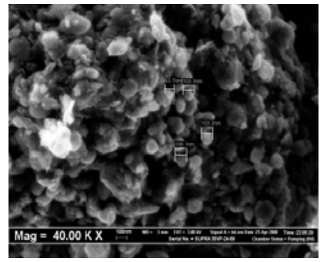
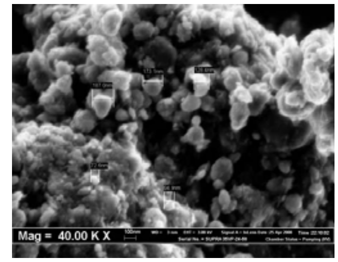


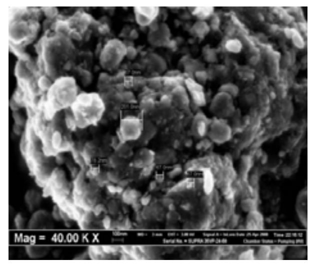
Figure 2. XRD patterns for as milled TiO_2-C mixed powders with various graphite contents and milled for a constant milling time of 90 hours

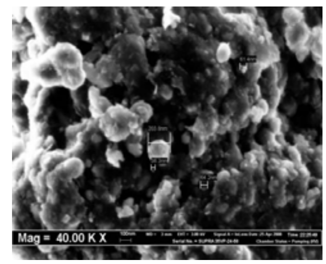
The SEM images of as milled mixtures of TiO_2 and stoichiometric amount of graphite milled for various durations are presented in Fig. 3 below. Although particle size to as low as 40nm has been noticed, agglomeration in all the samples has been observed.





(a) (b)





(c) (d)

Figure 3. SEM images of as milled TiO_2-graphite mixtures after milling for (a) 30 h (b) 50 h (c) 70 h and (d) 90 h

The activated powder mixtures of TiO_2 and graphite, milled for various durations, were heat treated at a temperature of 1300^{o}C for 1 hour. XRD analysis indicated the formation of TiC in samples milled for different durations (Fig. 4). A comparison among the XRD peaks also shows the transformation from anatase to rutile phase. Figure 5 below shows the XRD traces of same powder mixtures milled for various durations and subsequently heat treated at 1300^{o}C for 2 hours.

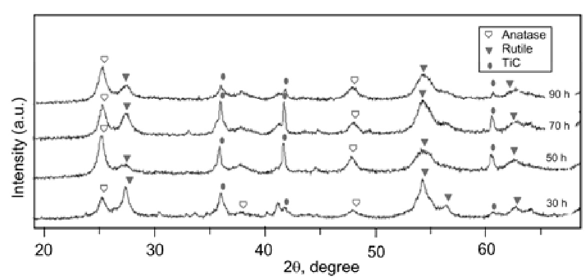


Figure 4. XRD patterns for TiO_2-graphite powders milled for various durations (30 h, 50 h, 70 h, and 90 h) and heat treated at 1300 ^{o}C for 1 hour

XRD patterns thus confirm the formation of titanium carbide in heat treated and even in as-milled oxide-graphite powder mixtures.

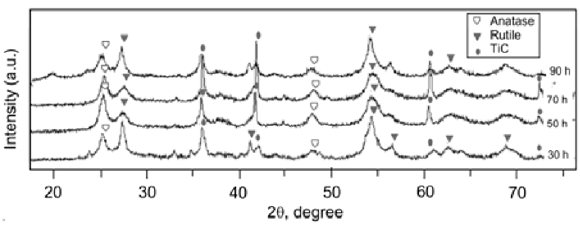


Figure 5. XRD patterns for TiO_2-graphite powders milled for various durations (30 h, 50 h, 70 h, and 90 h) and heat treated at 1300 ^oC for 2 hours

Milling of Fe-Ti and Graphite Mixtures

During milling of Fe-Ti and graphite, the reduction step to form Ti is eliminated as experienced during the milling of TiO_2-C mixtures. It was thus logically expected to expedite the formation of titanium carbide. Figure 6 below shows the XRD patterns of as milled mixtures indicating the onset of TiC formation even with 10 hours milling. This a remarkable improvement over the synthesis of titanium carbide from TiO_2. Use of Fe-Ti for the synthesis of titanium carbides has never been tried before as no published information has come to the notice of the authors.

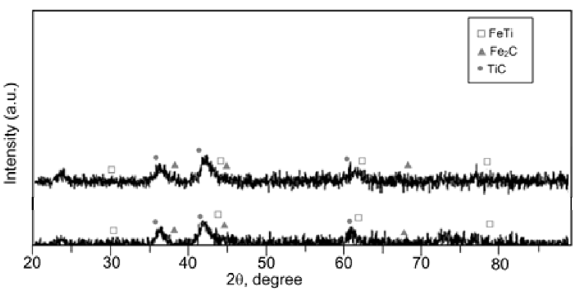


Figure 6. XRD traces for mixture of Fe-Ti and graphite milled for 10 hours and 40 hours.

Use of Fe-Ti in the synthesis of titanium carbides thus opens an alternate and convenient path. Fe-Ti is far cheaper and resistant to oxidation compared to pure metallic titanium and that promises the present route to be economically viable. Extensive research is presently underway to study the effects of process parameters and sample characterization in this syntheeis route.

Conclusions

1 Carbides of titanium have been synthesized by high energy ball milling of mixtures of titanium oxide and graphite under different operating conditions.
2 Prolonged milling induces the carbide formation which is also ensured by lower carbon content in the mixture.
3 Heat treatment of the milled mixtures at a temperature much lower than that used for normal carbothermal reduction also induces the formation of titanium carbide.
4 Milling of Fe-Ti and graphite mixtures indicates the formation of titanium carbide at an early stage of milling and promises to be an attractive alternative in the synthesis of titanium carbide.

Acknowledgements

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