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Effect of elemental iron on the carbothermic reduction of the anatase and rutile forms of titanium dioxide

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Abstract

Effect of iron on the carbothermic reduction of anatase and rutile forms of titanium dioxide was studied. Differential thermogravimetric analysis indicated a significantly different reduction route in the presence of iron with a number of clear minima in the rate of mass loss observed. X-ray diffraction of the products at these minima indicated that rutile initially formed $FeTiO_3$ which reduced to γ-Ti_3O_5, whilst anatase reduced through the mixed Ti(III/IV) phases of general formula Ti_nO_{2n-1} to D-Ti_3O_5. The final stage was the reduction of Ti_3O_5 to the sub-stoichiometric carbide, $TiC_{0.5}$. Iron was found to stabilise the Ti_3O_5 phases which were absent from an iron-free system, this is presumed to be due to partial substitution of trivalent iron for trivalent titanium.

Keywords: Anatase; Ball milling; Carbothermic reduction; Rutile; Titanium dioxide

1. Introduction

Titanium carbide is extensively used in various branches of machine construction due to its high strength and hardness. It is useful for manufacturing of cutting tools, grinding wheels, coating cutting tips and steel-coated press tools [1].

There are a number of processes and experimental methods for synthesizing titanium carbide powder such as self-propagating high-temperature synthesis [2], direct carburisation reaction between pure titanium and carbon [3], carbothermal reduction of carbon-coated titanium dioxide [4] and between TiS_2 and C to produce TiC according to reaction (1) [5]:

$$TiS_{2(S)} + 2C_{(S)} = TiC_{(S)} + CS_{2(g)} \quad (1)$$

Each method has varying characteristics of particle size and distribution, morphology, state of agglomeration, chemical purity and stoichiometry. Despite these assorted processes, titanium carbide powder is commercially produced by the reduction of titanium dioxide by carbon, typically carbon black, over a temperature range of 1700–2100 °C. The overall reaction for producing titanium carbide is [1]:

$$TiO_{2(S)} + 3C_{(S)} = TiC_{(S)} + 2CO_{(g)} \quad (2)$$

However, this is a gross simplification of the reaction with the formation of mixed valence titanium oxides occurring during the reduction [4,6–10]. However, these all reports used isothermal processing with extended times at the stated temperatures. This technique is a poor approximation of the practical scenario where material would be heated to the required temperature and then allowed to equilibrate.

The general formula for these titanium oxides can be written as Ti_nO_{2n-1} where ($n \geq 2$), which gives a series of mixed valence Ti(III)/Ti(IV) oxides with increasing content of Ti(III) as n decreases [6]. It should also be noted that where anatase has been used, it has invariably undergone a thermal transformation to rutile prior to the onset of reduction. Thus, there had not previously been a study of the reduction of anatase to TiC, until recently [11].

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Recent work has indicated that the chemical reaction can be achieved at lower temperature and/or at greater rate in a high-energy ball mill than physically mixed powders [6,12–15]. Titanium carbide can be produced from rutile, anatase or ilmenite at temperatures around 1200 °C, which is considerably below the temperatures used in the industry [1,16].

Although the effect of parameters such as atmosphere, pressure, temperature, starting TiO_2 phase and starting particle characteristics on the carbothermic reduction of titanium dioxide have been investigated [6,17–20], there has been no research about the effect of metals on the reduction. Krishnarao et al. [21] studied the effect of potassium, nickel and heating rate on the formation of TiC whiskers and found that nickel acts as a catalyst for TiC whiskers only in the presence of potassium. Investigation of the carbothermic reduction of ilmenite ($FeTiO_3$) found that the reduction was enhanced by the presence of iron from the initial reduction step [6].

A previous paper [11] has compared the mechanism of carbothermic reduction of rutile and anatase, this paper investigates the effect of iron on the same reduction reactions.

2. Experimental procedure

The anatase and rutile samples used were obtained from pigment manufacturers and were both >99.9% TiO_2 with a particle size of >90% 2–4 μm. X-ray diffraction (XRD) of the starting powders revealed no evidence of other phases being present. Particle size analysis showed a similar starting size for the powders although the size distribution of the anatase was narrower than the rutile, this would not be expected to affect the results.

Mixtures of titanium dioxide and graphite (>99% carbon) were prepared in accordance with the stoichiometry given by reaction (2). To seven grammes of this mixture, two grammes of pure iron powder (>99% Fe) was added. Each mixture was ball milled under vacuum for 50 h in a tumbling ball mill to mix them intimately. The mill was loaded with five 25.4 mm diameter stainless steel balls giving a powder to ball mass ratio of 1:33. After milling, samples were heated to 1400 °C in an alumina crucible at 20 °C/min under flowing argon (100 mL/min) atmosphere in a thermogravimetric analyser (TGA). The masses were normalised to the mass at 200 °C to eliminate any effect due to sorbed water.

The products were analysed by XRD using Co Kα radiation over a range of 25–75° 2θ, a step size of 0.05° was used with a count time per step of 3 s. Positions of the peaks were taken from the ICDD database, however, peaks for the mixed valence Ti_nO_{2n-1} phases where $n > 3$ were only present up to ~50°; 2θ and the data for these were taken from the paper by Bowden et al. [22]. Unit cell size measurements for TiC were made on the five peaks present below $2\theta = 95°$ using Unitcell [23], the peak positions were corrected for instrumental error using the main iron peak at $2\theta = 52.377°$.

3. Results

Fig. 1 shows the mass loss for anatase and rutile systems both with and without iron. The mass losses up to ~800 °C in all the systems is related to adsorbed gas, as shown elsewhere [24,25] with XRD showing no evidence for reduction in any system after heating to 800 °C.

A thorough analysis of the TGA and XRD data for the reduction in the absence of iron has been presented previously [11] and will only be summarised here as required.

The continuous mass loss up to 800 °C can be attributed to the desorption of gas from carbon. This phenomenon has been observed during heating of milled carbons up to 1200 °C in an inert atmosphere [24,25]. The absence of reduction products is clearly shown by the presence of only anatase and rutile in the XRD traces of the samples heated to 800 °C, just below the initial increase in the rate of mass loss. This supports the previous assertion that the mass loss at lower temperatures was due to desorption of gas.

The mass loss up to ~800 °C is somewhat less in the presence of iron than in its absence. Even adjusting for the mass of iron in the system, the loss is 4.5 and 4.8% for rutile and anatase, respectively, significantly lower than the 7.2 and 10.6% in the absence of iron. Clearly, iron is reducing the sorption capacity of carbon in the system, this may be due to some dissolution of carbon in iron or formation of iron–carbon compounds [26,27]. For milling times of less than 70 h, an amorphous Fe_3C phase was formed, however, its presence was only revealed by Mossbauer spectroscopy [26]. Thus, the lower sorption of gas would seem to be due to the formation of nanostructured iron–carbon phase(s) decreasing the quantity of free carbon in the system.

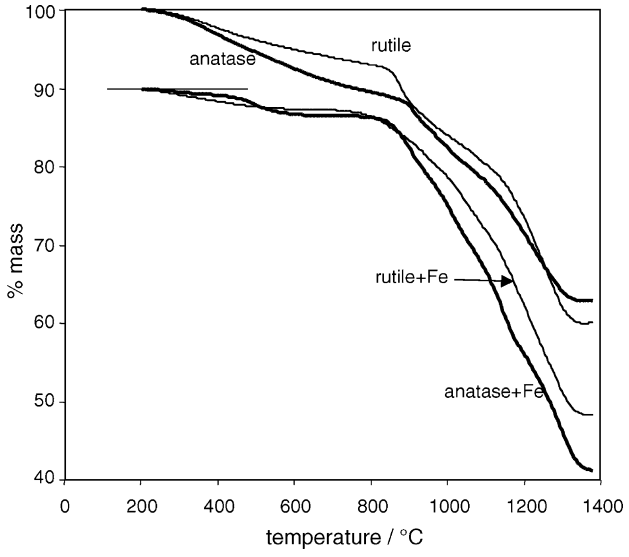

Fig. 1. Mass loss as a function of temperature for mixtures of rutile or anatase (thicker lines) with carbon, without and with (offset by 10%) iron (heating rate 20 °C/min). The data in the presence of iron has not been adjusted for the mass of iron present (~22.2%).