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STUDIES ON THE KINETICS OF SYNTHESIS OF TiC BY CALCIOTHERMIC REDUCTION OF TiO_2 IN PRESENCE OF CARBON

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Abstract

Reaction kinetics of the formation of TiC by calciothermic reduction of TiO_2 in presence of carbon have been investigated using thermal analysis (TG-DTA) of a powder mixture of TiO_2, Ca, and C in argon atmosphere at different heating rates. Both the reaction initiation and the peak temperatures are found to increase with heating rates. The appearance of exothermic peaks in the DTA plots after Ca melting indicates the reduction of TiO_2 by liquid calcium and formation of TiC by in-situ reaction of Ti with C. The apparent activation energy of the process has been found to be 170.8±0.5 kJ mol^{-1}.

Keywords: activatin energy, carbides, kinetics, metallothermic reduction, thermal analysis (TG-DTA)

Introduction

Titanium carbide (TiC) has many superior properties, such as high melting point (2940°C), high hardness (3000 kg mm^{-2}); high electrical conductivity, high chemical and thermal stability and high wear resistance. It has great potential in reinforcement and hardening of various materials including light metals and alloys. TiC is the principal component for heat and oxidation resistant cemented carbides. TiC is commercially produced by the reaction of TiO_2 with carbon black at 1900–2300°C. However; such a process being endothermic, is highly energy intensive. The metallothermic-reduction reactions are generally exothermic in nature and are widely employed for the preparation of various metals and alloys. Reduction reactions involving Ca metal as reductant have been used for the preparation of zirconium, hafnium, thorium, niobium and tantalum metal powders [1, 2] from their oxides. In the present study, an attempt has been made to prepare TiC by the reaction of TiO_2 with Ca in presence of carbon in pure argon atmosphere as per the following reaction:

$$TiO_2\ (\text{rutile})+2Ca(l)+C(s)=TiC(s)+2CaO(s) \tag{1}$$

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This reaction initially involves reduction of TiO_2 with Ca to form Ti metal powder, which reacts in-situ with carbon to form TiC. Both CaO and TiC have high thermodynamic stability and hence the reaction is driven in the forward direction. Such a reaction has two distinct advantages. It is a low temperature synthesis and the CaO formed can be easily removed from TiC product by leaching with water and acetic acid/dilute HCl. The study also includes thermal analysis of the reaction mixture to investigate the kinetics of the reaction. The apparent activation energy of the reaction has been derived from DTA plots using Kissinger expression [3, 4]. Similar studies have been carried out on the kinetics of crystallization processes in some glass systems [5, 6].

Experimental

TiO_2 (99.9% pure, rutile with average size 1 μm), calcium metal globules (99.9% pure average size 0.2–0.3 mm) and graphite (99.9% pure, average particle size 20 μm) were used as the starting materials. The reaction was carried out by heating a mixture of TiO_2, Ca metal and carbon powder in a graphite container under purified argon atmosphere. The process essentially consisted of mixing the charge of calcium metal granules, titanium oxide and carbon powder in the molar ratio of 2:1:1 with 50% excess of Ca over the stoichiometric requirement and heating the mixture at the required temperature (800–950°C) for 2 h in flowing argon atmosphere. The products were leached first with cold water and then with dilute acetic acid or 1 M HCl to remove CaO and excess Ca metal. It was then vacuum dried and weighed to determine the yield of TiC.

The dried samples were characterized by X-ray powder diffraction using Phillips X-ray diffractometer (Model PW 1830). The particle size of TiC sample was measured using BET surface area measurement technique. The composition of TiC was also determined by the chemical analysis.

The studies on the kinetics of the calciothermic reduction reaction were carried out using a Setaram simultaneously recording TG and DTA thermo-balance (Model 92-16.18). A mixture of TiO_2, Ca metal and carbon powder was taken in a 200 μL capacity graphite crucible and placed inside the reaction chamber of the instrument. Purified argon was flushed through the apparatus for 24 h before the start of the experiment in order to make the system free of oxygen. The DTA runs for the samples were recorded at the heating rates of 3, 5, 7.5, 10, 12.5, 15 and 20 K min^{-1}. The onset temperature and the peak temperature (T_m) for the reaction at each heating rate were determined from the DTA curves. The onset temperature for the peak was determined from the deviation of the base line. The kinetic parameter i.e. activation energy for the reaction was determined from the peak temperatures of the reaction using Kissinger's method [3].

Results and discussion

X-ray diffraction pattern of the product obtained from the reaction of TiO_2, Ca metal (50% excess) and C powder at 950°C for two hours under purified argon atmosphere showed the presence of lines due to TiC and CaO. The product was then washed

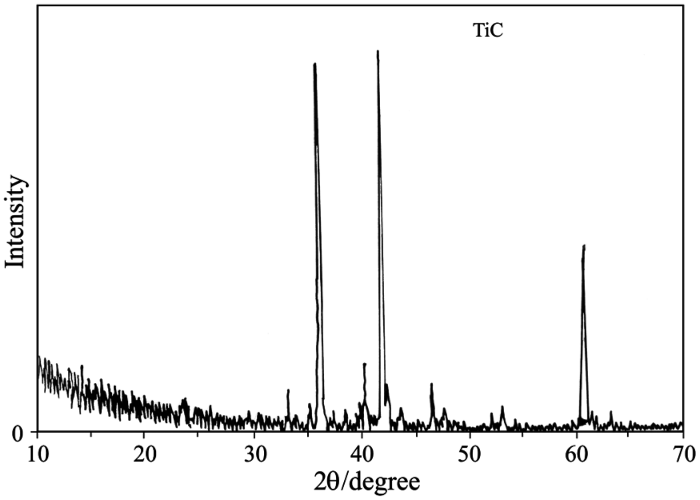

Fig. 1 XRD pattern for TiC obtained by calciothermic reduction of TiO_2 in presence of carbon

twice each with cold water and dilute HCl solution to remove excess Ca and CaO. The resulting solid was vacuum dried. A black color product was obtained. From the mass analysis of the product, the yield of TiC was found out to be >99%. The composition of the dried sample determined by the chemical analysis corresponded to TiC.

The XRD pattern of TiC powder is shown in Fig. 1. The XRD lines due to TiC could be indexed to cubic structure with cell parameter a=0.4323(1) nm *vs.* the reported [7] value of 0.4327. These results indicate that there is insignificant non-stoichiometry present in the sample. The particle size of TiC powder as determined from the BET surface area measurements was found to be 10 μm.

Thermal analysis

The DTA plot obtained for a charge containing TiO_2, Ca and C in the molar ratio 1:2:1 (with 50% excess Ca) at a heating rate of 10 K min^{-1} is shown in Fig. 2. No DTA peak could be observed until the melting point of Ca metal was reached at 842°C. At this point instead of an endothermic peak due to the melting of Ca metal, an exothermic peak was observed which was immediately followed by another exothermic peak. The first exothermic peak is attributed to the reduction of TiO_2 by fused calcium metal to form Ti metal and CaO, whereas the second peak is due to the in-situ formation of TiC by the reaction of freshly produced titanium metal with carbon. Depending on the heating rates, these two peaks some times merge to give a single peak especially at higher heating rates. No change of mass was observed in the TG plot during the reduction reaction. From the above observations, the overall reactions could be expressed by the following equations:

$$TiO_2(s)+2Ca(l)=Ti(s)+2CaO(s) \qquad (2)$$

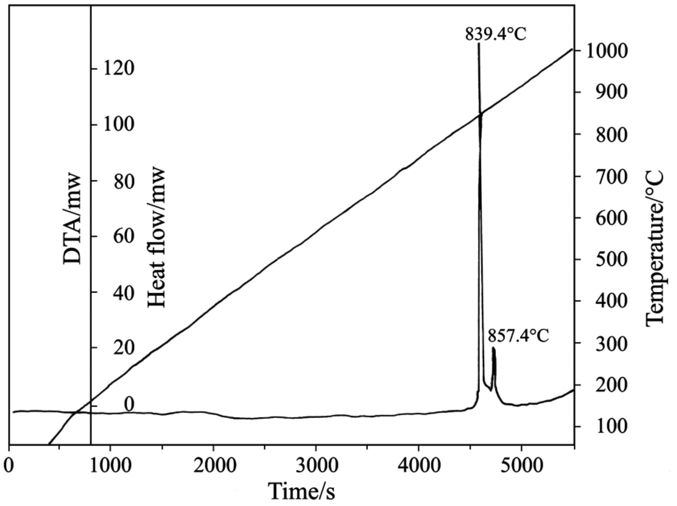

Fig. 2 DTA plot for TiO_2+2Ca+C sample at a heating rate of 10 K min^{-1}

$$\mathrm{Ti}(s)+\mathrm{C}(s)=\mathrm{TiC}(s) \qquad (3)$$

In this process, the charge consists of a mixture of fine powders of $TiO_2(s)$+C and coarse granules of Ca metal. So it is not possible to prepare a uniform mixture of the reactants. However, this does not affect the kinetics of the reaction because the reaction starts only after Ca melts. Once Ca melts, it spreads across the charge and the reaction proceeds by solid–liquid reaction. The overall reaction is highly exothermic and quite fast. This sometimes results in overlapping of the two stages of the reaction especially at higher heating rates. The problem of loss of Ca metal due to vaporization has been taken care of by having sufficient excess of Ca in the charge.

The DTA plots were recorded at different heating rates of 3, 5, 7.5, 10, 12.5, 15 and 20 K min^{-1}. The peak temperature for the formation of TiC as observed in the second exothermic peak was found to increase with the heating rate. Figure 3 shows the shift in the peak temperature as the heating rate is increased from 5 to 15 K min^{-1}. Data from this plot has been used to calculate the kinetics of the formation of TiC.

Kinetics of formation of TiC

The activation energy for the formation of TiC was calculated by the method of Kissinger [3, 4], that is based on the shift in peak maximum with heating rate and makes use of the equation:

$$\frac{\mathrm{d}\left(\ln\frac{\varphi}{T_\mathrm{m}^2}\right)}{\mathrm{d}\frac{1}{T_\mathrm{m}}}=-\frac{E_\mathrm{a}}{R} \qquad (4)$$

where T_m is the temperature (K) corresponding to the maximum in the DTA exotherm at a heating rate φ. E_a is the activation energy. The values of T_m at different heating rates were obtained from the DTA plots. The values of $\ln(\varphi/T_m^2)$ were plotted *vs.* $1/T_m$ and the linear plot obtained is given in Fig. 4. The activation energy for the formation of TiC was calculated from the slope of the plot and was found to be –170.8±0.5 kJ mol^{-1}.

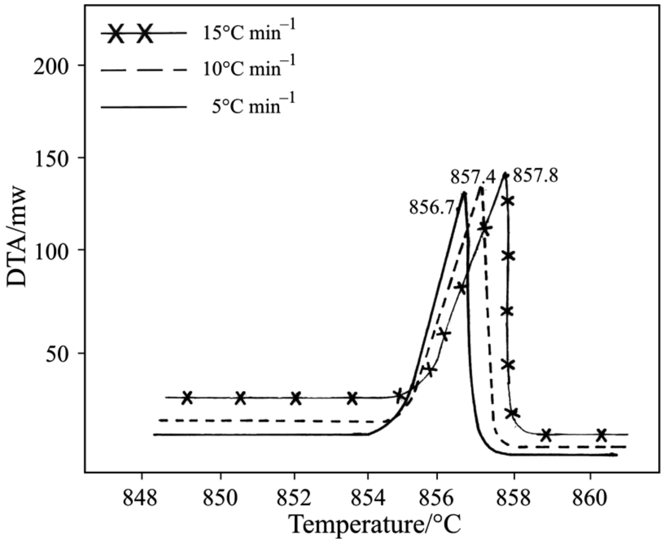

Fig. 3 DTA curves for TiO_2+2Ca+C samples at different heating rates

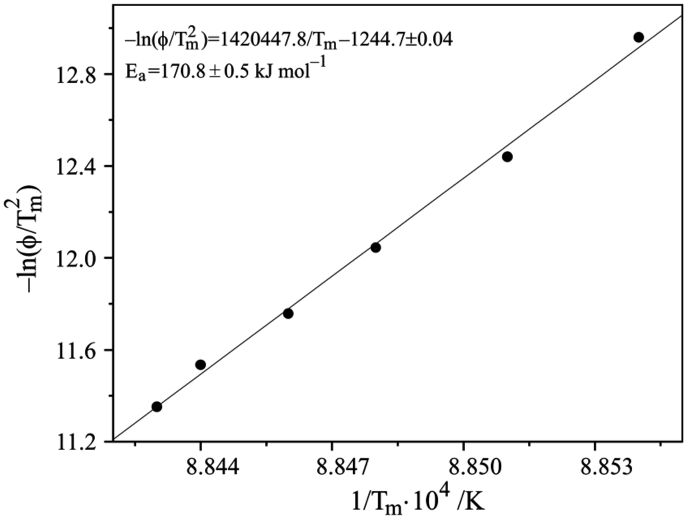

Fig. 4 Plot of $-\ln(\varphi/T_m^2)$ *vs.* $1/T_m$

Conclusions

Calciothermic reduction of TiO_2 in presence of C is a novel route for the preparation of TiC at low temperature with high yield. The CaO, which is also formed in the reaction, can be easily removed by simple leaching with water and dilute acetic acid/HCl.

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