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MACROKINETICS OF HIGH-TEMPERATURE TITANIUM INTERACTION WITH CARBON UNDER ELECTROTHERMAL EXPLOSION CONDITIONS

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Because of the intense development in research on the theory and applications of self-propagating high-temperature synthesis the study of macrokinetics of high temperature exothermal reactions in powder mixtures has become important. The goal of the present study is to investigate the interaction of titanium with carbon at high temperatures. The titanium-carbon system is the one which has been studied most thoroughly [1-3] as a model for self-propagating synthesis.

One of the most informative methods of studying macrokinetics of exothermal reactions is experimental determination of the characteristics of thermal explosion [4]. However use of classical methods for study of thermal explosions for investigation of the macrokinetics of self-propagating synthesis reactions presents grave experimental difficulties, since these reactions begin to occur at high rates only at quite high temperatures. Only one study by this method has been performed for thermal explosion of iron-aluminum thermite [5].

In the present study, to investigate the reaction occurring in mixture of titanium and graphite powders we will use a variant of the thermal explosion method — the so-called electrothermal explosion (ETE), the unique feature of which is specimen heating not by external heat exchange, but by passage of an electrical current through the specimen itself. The electrothermal explosion method was first suggested for kinetic and technological applications in [6, 7]. It permits heating the specimen to quite high temperatures. Its use has the following advantages:

- a) with sufficient Joulean heating external heat losses need not be considered over a quite wide parameter range;
- b) additional information on reaction kinetics may be obtained by varying the heating rate.

Chernogolovka. Translated from Fizika Goreniya Vzryva, Vol. 21, No. 3, pp. 69-73, 1985. Original article submitted April 27, 1984.

The macrokinetics of the reactions occurring in the electrothermal explosion were studied by a plan similar to that used for the traditional variant of thermal explosion. Thus, it was shown in [8] that by varying the Joulean heating power P in ETE experiments from experiment to experiment one can use the dependence of induction period on P to determine the activation energy, and with additional information on thermal effect in the form of a reaction law, the preexponential term can also be calculated.

In [6] ETE in a titanium-carbon system was studied with attenuated heat loss from the faces of a cylindrical specimen clamped between electrodes. Processing of thermograms then yielded the activation energy and preexponential for the effective rate constant for solid phase interaction in this system.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The major components of the experimental setup for ETE study were similar to those described in [6, 7], but differed in operating at a higher power level, which in principle made it possible to study the interaction mechanism at temperatures above the specimen ignition point. A new element added was a multiplier circuit for recording power, as well as a more convenient pyrometric technique which permitted recording of thermograms over the temperature range 1200-3500°K to an accuracy of 5%.

A schematic diagram of the experimental equipment is shown in Fig. 1. Specimen 3, a tablet pressed from a stoichiometric mixture of PTM brand titanium and flaked graphite, was heated by an electrical current to the ignition point. Heating was accomplished by a high power stepdown transformer 2, which allowed passage of currents up to 10^4 A through the specimen.

The Joulean heating level was controlled with a thyristor regulator circuit 1. The regulator output is a periodic nonsinusoidal voltage, so that it is practically impossible to determine the power level from separate current and voltage measurements. Thus a special system was used for power measurement. A ballast resistor 6 was connected in series with the specimen, so that its voltage drop was proportional to the current through the specimen. Voltages from the ballast resistor and the specimen were applied to multiplier circuit 8, which uses a 140MA1 integrated circuit and produces an output voltage proportional to the time-averaged product of the input signals, i.e., the power. The power was recorded by an N117/1 loop oscilloscope 9.

The specimen surface temperature was determined from the intensity of the radiation it produced. For this purpose lens 4 formed an image of the specimen at the input diaphragm of FD7 photodiode 5, the signal from which was fed through dc amplifier 7 and also applied to the loop oscilloscope. An SIRSh6-100 tungsten reference bulb was used to calibrate the temperature measurement system.

EXPERIMENTAL RESULTS

To study the principles of high temperature titanium interaction with carbon during the development of ETE the time dependence of specimen Joulean heating P and specimen surface temperature T were recorded. The characteristic form of such curves under supercritical conditions is shown in Fig. 2. It is evident that P increases at some moment, which when the structural features of the power transformer and thyristor regulator are considered indicates a drop in electrical resistance of the specimen. In a number of experiments electrical heating was terminated after the increase in Joulean power. Upon repeated heating the power level was high immediately (Fig. 3). This effect can be explained by sintering of the specimen. After sintering the power level remains practically constant to the completion of the electrothermal explosion.

For low temperatures the time dependence of temperature is of a linear character, corresponding to heating of the specimen by an electrical current with heat liberation due to chemical reaction and external heat losses still being negligibly small in comparison to the Joulean power. The end of this interval corresponds to specimen ignition. As is evident from Fig. 4, the ignition temperature remains constant within $\pm 30^\circ\text{K}$ at $\sim 1850^\circ\text{K}$ independent of the electrical power level. Because the ignition temperature is close to the titanium melting point ($T_m = 1940^\circ\text{K}$) it is natural to assume that under these conditions specimen ignition is related to a phase transition in the mixture. This can be explained by an increase in specific interaction surface due to capillary spreading of the titanium over the carbon surface [2, 3].

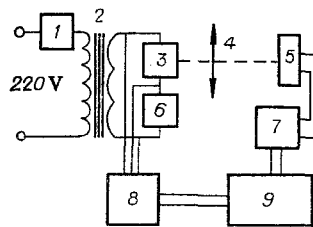


Fig. 1

Fig. 1. Diagram of experimental equipment.

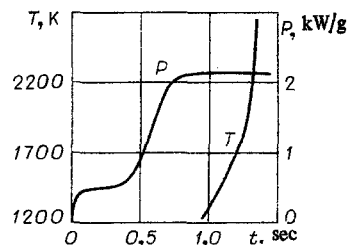


Fig. 2

Fig. 2. Characteristic forms of electrical power and surface temperature vs time under supercritical conditions.

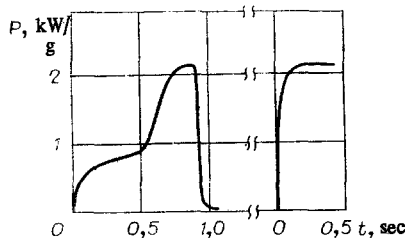


Fig. 3

Fig. 3. Joulean power vs time in experiment with interrupted heating.

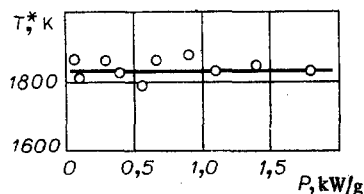


Fig. 4

Fig. 4. Ignition temperature vs power of external heat source expended in heating specimen.

The fact that the specimen surface temperature is somewhat below T_m for titanium is apparently related to the fact that the surface temperature is somewhat lower than the temperature in the center of the specimen due to radiant heat loss. The specimen will ignite internally at a time when the surface temperature has not yet reached T_m of titanium. An estimate of the maximum temperature difference between the surface and center of the specimen under these conditions gives a value corresponding within the limits of experimental uncertainty to the measured ignition temperature.

The presence of a relationship between ignition of a titanium-carbon system and fusion of the titanium under certain conditions (intense heat loss, high power level in outside heat source) was established previously in experiments on high temperature interaction of titanium filaments with a carbon black coating [2].

We will now consider the behavior of temperature in the period after ignition. A characteristic feature of this interval of the thermogram is the close to linear increase in temperature from 2000 to 3000°K. Considering that with such rapid heating of the specimen external heat losses are low and do not affect the form of the thermogram, it can be concluded that the reaction rate is independent of temperature in this range. This can occur in two cases: Either the reaction is of zeroth order and is not thermally activated, or else the activation energy may be high, but the reaction rate falls off intensely with depth, so that the one factor compensates the other. If the second case were realized, when the external source power is varied in the range where it is comparable to the chemical heat source power, the time dependence of specimen temperature would deviate from linearity. No such deviation was recorded in experiment at heater powers up to the chemical source power. This means that in the 2000-3000°K temperature range the dominant stage of the reaction is of zeroth order and thermally unactivated. This permits certain conclusions as to the mechanism of the process.

It was established above that intense heat liberation begins after fusion of the titanium. This means that the reaction occurs with participation of a liquid phase. Since the activation energy is low it is most probable that the limiting stage of the process is solution of the carbon. This agrees with the fact that the process is of zeroth order. In fact, the

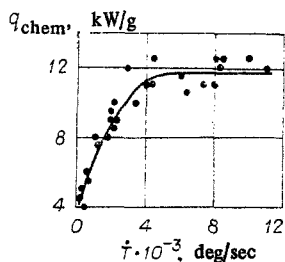


Fig. 5. Heat liberation intensity in liquid phase reaction stage vs rate at which specimen is heated by electrical current.

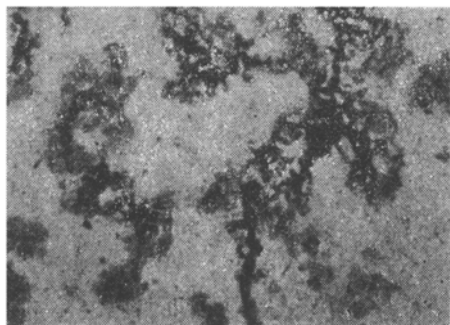


Fig. 6

Fig. 6. Electron microscope photograph of aged specimen section $\times 1250$.

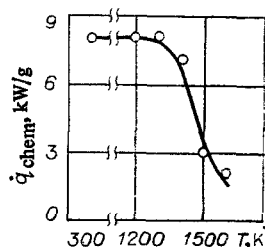


Fig. 7

Fig. 7. Heat liberation in liquid phase reaction stage vs aging temperature.

carbon solution rate in the liquid phase does not decrease while the concentration of dissolved carbon remains much lower than that of a saturated solution. Since bonding of carbon occurs more rapidly than its solution, the solution will always be far from saturation.

In the curve of specimen temperature vs time the slope in the low temperature range is proportional to the electrical power, while at high temperatures it is proportional to the sum of the electrical and chemical power. Thus the difference of these slopes will define the chemical reaction power in the liquid phase stage. It proves to be the case that at heating rates greater than $4 \cdot 10^3$ deg/sec this value is constant and equal to 10^4 W/g. When the heating rate is decreased below $4 \cdot 10^3$ deg/sec the chemical power in the liquid phase reaction stage falls (Fig. 5). This can be explained by assuming that the titanium carbide synthesis reaction also occurs before titanium fusion, but much more slowly. After titanium fusion the reaction occurs in the liquid phase, but the solid carbide formed previously by the diffusion reaction mechanism hinders solution of graphite into the surrounding melt. Thus, the liquid phase reaction rate depends on the depth to which the solid phase interaction has occurred.

Additional experiments on specimen ageing were performed to verify this conclusion. The specimens were heated to some temperature below T_m of titanium, maintained for 20 sec, cooled, then heated to the ignition point at a high rate. The structure of the material obtained by ageing at a temperature of 1500°K was studied with a scanning electron microscope. It is evident from Fig. 6 that at the boundary of the titanium grains (light spots) and graphite (black spots) interlayers of carbide are formed (gray spots) which can hinder interaction of the original components after titanium fusion. Figure 7 shows the dependence of chemical power in the liquid phase reaction stage on ageing temperature. The presence of a falling segment in this curve confirms the conclusion made.

CONCLUSIONS

It has been shown that over a quite wide parameter range ignition of mixtures of titanium and graphite is related to fusion of the titanium. It has been established that in the

temperature range from 2000 to 3000°K the dominant stage of the conversion is of zeroth order and is thermally unactivated. These effects can be explained by solution of graphite into the melt. A numerical value has been obtained for the first time for the heat liberation power in the liquid phase stage of the reaction in mixtures of titanium and graphite.

In experiments performed on pre-aged specimens it was found that the liquid phase reaction rate decreases with increase in the depth in which the preceding solid phase reaction occurs, the product of the latter hindering the solution of graphite.

The authors thank V. M. Mal'tsev and V. A. Andreev for their assistance with optical pyrometry techniques, and Yu. A. Gal'chenko and A. S. Rogachev for performing the electron microscope analysis.

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STUDY OF THE COMBUSTION PROCESS FOR ZIRCONIUM IN A MIXTURE OF NITROGEN AND HYDROGEN GASES

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In recent years studies carried out in the field of complex hydrides have caused considerable interest. Their study is due to the requirement of preparing hydrogen-containing compounds with greater thermal stability than binary hydrides [1].

One of the promising methods for preparing these compounds is the SVS method [2]. This makes it possible to synthesize multicomponent compounds directly from the elements in one production stage [3-5], whereas in other cases it is necessary to prepare previously binary components, which is quite labor-consuming and does not provide preparation of single-phase compounds.

The aim of the present work is a study of the combustion process for zirconium in a mixture of two reacting gases, i.e., nitrogen and hydrogen, and synthesis of zirconium hydride-nitrides with a hexagonal close-packed lattice (hcp) in a combustion schedule. The Zr-N-H system has not been studied very much. It is necessary to point out that only in [6] is the preparation indicated for single-phase zirconium hydride-nitride with the hcp lattice by heating a mixture of Zr + ZrN in a hydrogen atmosphere at $T = 1000^{\circ}\text{C}$.

Erevan. Chernogolovka. Translated from *Fizika Goreniya i Vzryva*, Vol. 21, No. 3, pp. 73-77, May-June, 1985. Original article submitted March 18, 1983; revision submitted November 1, 1984.