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High temperature synthesis of single-phase Ti_3Al intermetallic compound in mechanically activated powder mixture

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A B S T R A C T

The influence of the duration of preliminary mechanical activation on the microstructure of the powder mixture of 3Ti + Al and the features of the kinetics of the thermal explosion processes in milled powder mixtures were studied. It was shown that the formation of highly defective crystalline structures with high curvature of the lattice and high internal stress gradients took place with the increase of milling time. It was found that the features of heating during the thermal explosion process were determined by the features of the microstructure of the milled mixture. As a consequence, the composition of the product depended on the milling time and also on the heating rate of the mixture by the external heating source. Thus, the milling time and the heating rate can be considered as the control parameters in the research.

The reacting system turned into the stable mode of phase formation characterized by the formation of mechanocomposites with the increase of milling time. The process was accompanied by the decrease in the effective activation energy of the synthesis down to the anomalous low value. The modes of the synthesis realization were determined to obtain a strictly single phase compound Ti_3Al. It was hypothesized on the transition of the process from the diffusion regime of phase formation to the kinetic one with milling time.

1. Introduction

In the recent years, the combination of the SHS and mechanical milling has attracted a lot of interest. This is due to new possibilities of solid–solid combustion opening the perspectives to inorganic materials synthesis on the basis of mechanically milled powder mixtures [1,2]. It is possible to widen the concentration limits for combustion and utilize the compositions that cannot be ignited under the standard conditions using mechanical milling; pre-compaction of the initial mixtures becomes unnecessary and the solid-state combustion can be realized even in compositions with low melting temperature components, such as Al. Preliminary mechanical activation of dispersed powder mixtures changes their reactivity that can lead to a significant reduction of the ignition temperature in solid state reactions [3–5]. It is usually associated with reagents grinding to the sizes of several tens of nanometers accompanied by the expanding of the contact area between the reagents and elimination of impurities and oxide films [6]. In addition, the change in reactivity is determined by the formation of extremely defective crystal structure facilitating the formation of a new phase during crystallization [2].

It is well known that SHS can be realized in two modes: frontal combustion and thermal explosion. It should be noted that most of the research on high-temperature synthesis is associated with a frontal combustion. At the same time, the synthesis in a thermal explosion mode has several advantages related to the possibility of external influence on the reactivity of the mixture. The advantages are the following: the possibility of preheating, changing of ambient temperature, changing of heating rate, and changing of exposure time of the mixture at a given temperature. A combustion wave is considered to be an auto wave and it is very difficult to manage the dynamics of phase formation during its propagation. In the case of a thermal explosion, the realization of the external influence on the reacting mixture in combination with the possibility to change its reactivity by mechanical activation allows controlling phase-formation processes. Thus, we can speak about the “internal” and “external” activation of synthesis.

Intermetallic compound Ti_3Al (α-phase) in the bulk form and in the form of coatings is in high demand in various branches of engineering [7]. The reason is the combination of properties, such as: low specific weight and high heat resistance, but the traditional methods of high-temperature synthesis are not applicable to this compound. In this connection, the preparation of this compound is carried out with the use of the expensive metallurgical technology.

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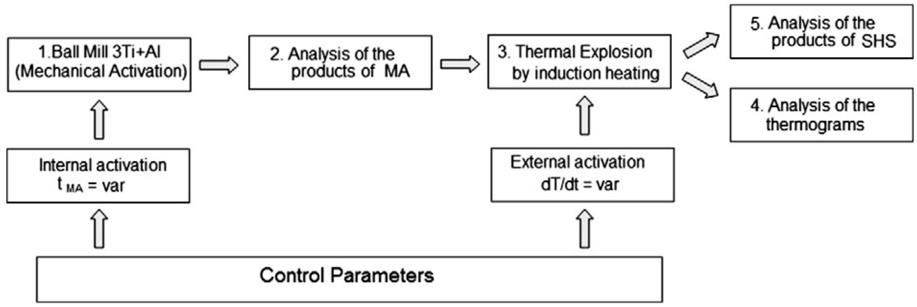

Fig. 1. The scheme of experimental method.

Therefore, the goal of the work was to find the optimal mechanic activation (MA) parameters of 3Ti–Al powder mixtures and those of the subsequent high-temperature synthesis in the thermal explosion (TE) mode in order to obtain the single-phase compound Ti_3Al.

2. Experimental procedure

The mixtures reactivity was changed using: 1 — internal activation by varying the milling time; and 2 — external activation by varying the furnace heating rate (Fig. 1) during the thermal explosion process. The mechanical activation of mixture 3Ti + Al was carried out using the planetary ball milling AGO-2. The milling products (and reaction products) were analyzed applying diffractometer «Shimadzu XRD-6000», Scanning Electron Microscope «JSM — 20 T», and Transmission Electron Microscope SM-30/STEM.

The raw mixtures were prepared using the aluminum powder PA-4 (98%Al) having particle sizes of 1–60 μm and titanium powder PTOM-2 (99%Ti).

The mechanical milling was performed in the AGO-2 planetary ball mill with two vials. The characteristics of the mill were the following: the volume of the vial — 160 cm^3, the ball diameter — 8 mm, the powder mass in each vial — 10 g, the mass of the balls — 200 g, and the centrifugal acceleration of balls — 400 ms^{-2} (40 g). In order to prevent oxidation, the vials were vacuum pumped and then filled with argon up to pressure of 0.3 MPa. The vials were unloaded in a glove box under argon atmosphere after mechanical milling. The milling time was varied from 1 to 7 min with an increment of 1 min. It should be noted, that milling time is not an objective characteristic of the milling process. The total energy transferred to a unit mass of powder is a more correct parameter. According to Martirosyan et al. [8], this energy D (J/kg) can be calculated with the use of expression:

$$D = \frac{NEt}{m_p} \quad (1)$$

where N is the collision frequency (the number of times the balls hit the vials in one second), $E = m_b V^2/2$ is the impact energy during the mechanochemical treatment, m_b is the mass of the milling ball, V — is the impact velocity, t is the milling time, m_p is the mass of powder butch. With the use of the date [9] for the value of milling frequency 1300 rpm (used in the experiment), we can obtain the estimation for the values of D: $D = 60 \div 420$ J/g for the interval of milling time 1–7 min.

To conduct the experiments on thermal explosion, induction furnace ILT-0,0005/1,0-22,0 (power 1 kW, frequency 22 kHz) controlling the rate of heating was used (Fig. 2). Powder mixture — 1 was immersed in an alundum crucible — 2. The temperature of the mixture was measured using a tungsten–rhenium thermocouple — 3. The signal from the thermocouple was transferred to the analog–digital converter, then to the computer. Temperature control of the furnace was carried out using a thermocouple — 4. The alumina crucible was placed in a graphite cup — 5. The system insulation was made using an insulating ceramic — 6. The mixture heating was carried out using a high

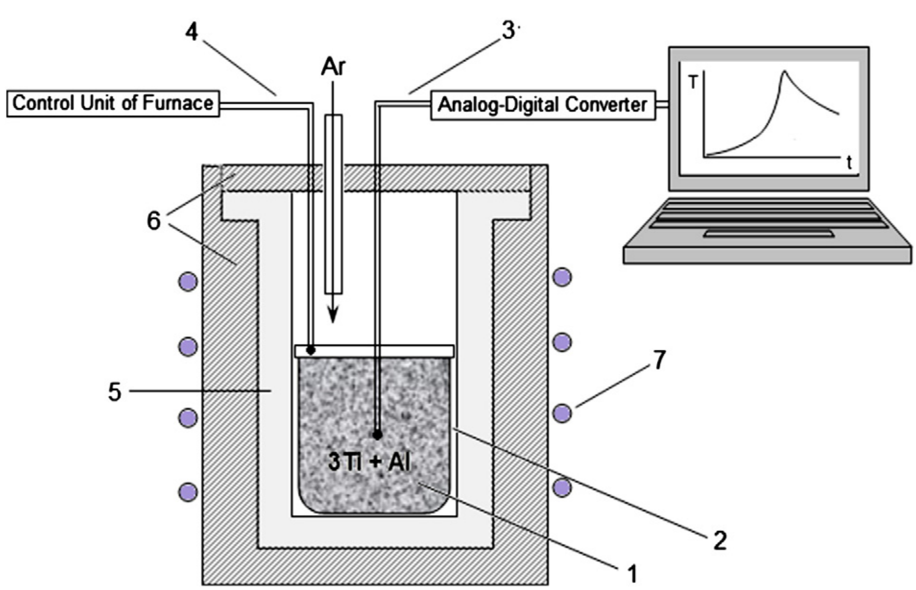

Fig. 2. The equipment for the realization of thermal explosion. 1 — Powder mixture; 2 — alundum crucible; 3 — tungsten–rhenium thermocouple; 4 — furnace's thermocouple; 5 — graphite cup; 6 — insulating ceramics; 7 — high frequency induction coil.