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Production of ultra-high temperature carbide (Ta,Zr)C by self-propagating high-temperature synthesis of mechanically activated mixtures

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Abstract

The combustion temperatures and rates of mechanically activated (MA) Ta–Zr–C mixtures depending on the initial temperature T_0 are determined. The self-heating phenomenon is observed in argon atmosphere at $T_0 > 380$ K due to oxidation of the surface of zirconium particles by adsorbed oxygen. Zirconium oxide is formed in the combustion zone at the initial stage of chemical interaction; it is subsequently transformed into zirconium carbide. In addition, tantalum carbide is formed in the combustion zone, while the binary tantalum–zirconium carbide (Ta,Zr)C is formed closer to the post-combustion zone. In order to maintain the layer by layer stationary combustion mode of SHS, the initial temperature T_0 needs to be 298 K, while the duration of mechanical activation needs to be less than 5 min. After longer mechanical activation, the mixtures are prone to bulk combustion even at low initial temperatures. Single-phase (Ta,Zr)C carbide with the lattice parameter of 0.4479 nm was synthesized by forced SHS compaction in a sand mold.

Keywords: SHS; Mechanically activated (MA); Mechanism; Phase formation; Tantalum–zirconium carbide

1. Introduction

The advances in science and technology imply that novel functional materials and coatings with improved performance characteristics are designed and industrially implemented. Carbides TaC and ZrC are characterized by high melting point, hardness, resistance to corrosion and ablation (radiation-induced evaporation) [1–6]. Due to the latter property, they have been used to produce ultra-high-temperature composite materials for air and spacecraft industries. Furthermore, these carbides are used in manufacturing hard-alloy cutting tools [7–16], electrical engineering, nuclear industry, medicine, etc.

Zirconium and tantalum carbides form a continuous series of solid solutions [9,16]. According to article [4,5] the melting points of binary (Ta,Zr)C carbides are higher than those of individual carbides. Zirconium and tantalum carbides form a continuous series of solid solutions [9,16]. According to the authors [4,5] the melting points of binary (Ta,Zr)C carbides are higher than those of individual compounds. In the Ta–Zr–C system, single-phase solid solution $Ta_{1-x}Zr_xC$ based on tantalum carbide is formed when ZrC content more than 50 mol% [9]. Meanwhile, the dissolution of tantalum carbide in the ZrC structure does not cause any noticeable shifts in phase peaks of solid solution, since a tantalum atom has a smaller radius compared to that of a zirconium atom. Broadening of the residual peaks of ZrC in a TaC–75%ZrC sample at high 2θ angles results from partial dissolution of tantalum carbide in zirconium carbide and formation of a series of Zr_{1-y} Ta_yC solid solutions [9]. Although there is a region of immiscible solid solutions in the quasi-binary TaC–ZrC system, the presence of the single-phase solid solution in the TaC–25%ZrC and TaC–50%ZrC compositions proves the stability of the resulting solid solution [9].

Along with the melting point, other physicochemical properties of complex carbides (such as specific conductivity [6],

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microhardness, coefficient of thermal expansion [5,6], vapor pressure [5], etc.) are also characterized by extreme dependence on carbide composition.

The high melting temperature and corrosion stability of tantalum and zirconium carbides impose certain problems during production of materials and items made of them. The single-phase product with desired composition usually cannot be obtained by conventional powder metallurgy methods based on reduction reactions because of significant differences in chemical activity of metal oxides and diffusion coefficients of carbon in the carbide lattice. For example, zirconium carbide can be synthesized using one of the following methods [17,19]: either by direct saturation of zirconium with carbon or by reduction of zirconium oxide by carbon, when the initial components are taken in the powder form. The process runs through the formation of lower zirconium oxides followed by formation of zirconium carbide via reaction $ZrO+2C=ZrC+CO$. This method is used for industrial-scale synthesizing of technically pure zirconium carbide. The process is usually performed at $\sim 2000\ ^{\circ}C$. The reduction of Ta_2O_5 and subsequent formation of tantalum carbide is carried out at $1400-1600\ ^{\circ}C$ in hydrogen atmosphere or under vacuum. Hence, coreduction of the initial components to obtain complex carbides usually fails. However, the authors of studies [17,19] proposed a hybrid method for synthesis and controlled hydrolysis of metal alkoxides and alkoxyacetylacetonates in the presence of a polymeric source of carbon (phenol–formaldehyde resin) and carbothermal reduction at low pressure and moderate temperatures (1300–1500 °C). They have successfully synthesized refractory nanocrystalline carbides with compositions Ta_4HfC_5 and Ta_4ZrC_5 [17]. However, since this process involves many stages and takes a rather long time, searching for the alternative methods to synthesize ultra-refractory carbides remains topical.

Self-propagating high-temperature synthesis (SHS) [14,18, 20–22] can be used as an alternative method to produce tantalum–zirconium carbide with the highest melting point [4,5,9,16].

The ternary Ta–Zr–C and Ta–Ti–C systems are similar in terms of their combustion mechanism and kinetics. There are two dominant chemical reactions for both systems: one involves the diffusion mechanism through the melt, while the other one is mediated by gas-phase transfer of reagents. Thus, the temperature profiles of the combustion wave with two characteristic heat release maxima were detected in the Ta–Ti–C system within a broad range of tantalum concentrations (10–50%) [20,21], which was indicative of the splitting mode due to consecutive chemical reactions. However, the two maxima merge as Ta concentration and the initial temperature T_0 increase; the combustion now proceeds in the merging mode, when the consecutive reactions become parallel.

The Ti–C and Zr–C systems are similar because the combustion runs through the diffusion mechanism after the formation of a metal–reagent melt, subsequent formation of the reaction surface by capillary impregnation of graphite or soot and carbon dissolution in the melt [23,24].

Solid-phase diffusion through the product layer is the rate-limiting stage during combustion of the Ta–C mixture; however, carbon transfer to the surface of tantalum particles takes place via CO and CO_2 recirculation through the Boudouard–Bell reaction [25]: interaction of a CO_2 molecule with carbon yielding two CO moles; gas-phase transfer of 2CO to the surface of Ta particles; chemisorption of 2CO on the surface; two-stage interaction between tantalum and carbon yielding Ta_2C semicarbide and subsequently tantalum carbide according to the scheme $Ta+2CO\rightarrow TaC+CO_2$; desorption of a CO_2 molecule from the surface of the newly formed tantalum carbide layer; transfer of CO_2 to the surface of a carbon particle; interaction between CO_2 and carbon yielding 2CO, etc.

The adiabatic combustion temperature $\left(T_c^{ad}\right)$ for elemental synthesis of composition $82.71\%\ Ta+10.43\%\ Zr+6.86\%\ C$, which was calculated using THERMO software [26], is 2914 K. This value is higher than the melting point of zirconium (2125 K) but significantly lower than those of zirconium and tantalum carbides and much lower than the melting point of tantalum–zirconium carbide. Hence, the zirconium carbide phase in the combustion wave can be formed by crystallization from the oversaturated zirconium melt.

Similar phenomena, observed early in Ta–Ti–C system [20,21], can be expected for combustion of ternary Ta–Zr–C mixtures: merging and/or splitting regime of combustion waves depending on mixture composition, degree of powder dispersion, mixture heterogeneity, and the initial temperature T_0. Meanwhile, the difference compared to the Ti–Ta–C system is that a strong oxide film preventing zirconium from spontaneous ignition in air is formed on the surface of pyrophoric zirconium powder during delivery and storage. This fact may make it difficult to initiate the SHS reaction. One of the possible ways to eliminate the kinetic hindrance is to mix the Ta–Zr–C ternary system under conditions when oxide films on the surface of zirconium particles are mechanically destroyed, either completely or partially.

This study focuses on the kinetics and mechanism of combustion, as well as on the stages of chemical and structural transformations in the Ta–Zr–C system during elemental synthesis with preliminary mechanical activation (MA SHS).

2. Experimental

Zirconium (PTsrK-1 grade), tantalum (TaPM grade), and soot (P804T) powders were used as initial reagents. The composition of the reaction mixture was calculated based on the criterion of formation of a refractory binary Ta–Zr carbide [9,16,27]

Before mixing, the initial powders were dried in a vacuum drying oven at 90 °C. The mixtures were mechanically activated in an AIR-0.015 ball mill with the operating parameters as follows: working drum volume, 250 cm^3; centripetal acceleration along the drum axis, 250 m/s^2; the ratio between the ball weight and weight of the raw mixture 20:1. MA was performed in an air atmosphere.

The effect of the initial temperature (T_0) of the reaction mixture on combustion temperature T_c and rate U_c was studied on a laboratory SHS reactor according to the procedure described in Ref. [22] using cylindrical briquettes (10 mm in diameter, 15 mm high, relative density of 60%). The