

Cu/ZrO₂ COMPOSITES PREPARED BY SELF-PROPAGATING HIGH-TEMPERATURE PROCESSING OF THE MECHANICALLY PRE-ACTIVATED CuO/Cu/Zr SYSTEM

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Abstract

Metal/oxide composites are perspective materials for applications in machine industry, instrument engineering, and electrical engineering. Development of new approaches for the preparation of metal/ceramic materials is a very topical issue. In the present work, we explore possibilities of the preparation of copper/zirconium dioxide (Cu/ZrO₂) composites by mechanical activation of the [CuO + (Cu + Zr)] system followed by self-propagating high-temperature synthesis (SHS).

The CuO + Zr mixture cannot be used directly in the preparation of Cu/ZrO₂ composites because the reaction between CuO and Zr is highly exothermic ($\Delta H = -188$ kcal/mol) and proceeds in the thermal explosion mode. Therefore, we used the combined (double) mechanical activation of the [CuO + (Cu + Zr)] system to prepare precursors for the subsequent SHS process. The use of the CuO/Cu/Zr mechanocomposites instead of those of CuO/Zr changes the mechanism of interactions between the reactants during the SHS process from the thermal explosion to the steady-state combustion mode.

Keywords: *mechanochemistry, mechanocomposite, self-propagating high-temperature synthesis*

INTRODUCTION

Metal/oxide composites are quite perspective materials for application in machine industry, instrument engineering, and electrical engineering in comparison to pure metals due to their improved chemical and physical properties (heat resistance, strength, hardness, erosion resistance). Chemical mixing, salt mixture decomposition, hydrogen reduction in solutions, chemical precipitation from solutions, internal oxidation are well-known methods of preparing such materials having applications in industry [1]. The above-mentioned technologies allow attaining metal/oxide composites, but they are quite expensive and long-term. Based on this, a very topical issue is the development of new approaches to production of metal-ceramic materials.

In this work, we explored possibilities of preparation of copper/oxide composite (Cu/ZrO₂) by methods of mechanochemical synthesis (MS) in planetary mills and of mechanically activated self-propagating high-temperature synthesis (MA SHS).

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EXPERIMENTAL

Copper, copper oxide CuO and zirconium M-41 were used in this work as raw materials. Mechanical activation (MA) was carried out in planetary ball mills with water cooling [2] (the drum volume – 250 cm³, the balls diameter – 5 mm, the load – 200 g, sample weight – 10 g, the drums rotation speed about the general axis ~ 1000 rpm). After MA, the activated mixture was compacted (under a load of 4–6 t) in the mould up of 17 mm diameter and ~25 mm in height (till sufficient strength for the sample transfer to the reactor). SHS was carried out in an argon atmosphere; the combustion was initiated with an electrically heated tungsten coil. The temperature and burning velocity were evaluated by a thermocouple method (C-A thermocouples Ø ≈ 0.2 mm), using an outer 2-channel 24-charge analog-to-digital converter ADSC24-2T.

X-ray diffraction research was conducted with diffractometers X'TRA (Thermo ARL, Switzerland) with application of CoK_α radiation ($\lambda = 1.789 \text{ \AA}$) and URD-63 with application of CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Evaluation of effective sizes of coherent scattering area was carried out in compliance with the Scherer formula with the strongest peaks of phases analysed.

The high-resolution scanning electronic microscope (SEM) MIRA/TECAN equipped with an INCA 350 accessory for EDX analysis was used for the structure research. The electron probe diameter was 5.2 nm, excitation area was 100 nm. Images in direct electrons and back-scattered electrons were obtained and it allowed studying chemical elements distribution over the surface. Brightness distribution in the image depends on the average atomic element number in each microarea.

IR absorption spectra were registered by spectrometer IFS-66. The samples were prepared for the exposure by standards methods.

RESULTS AND DISCUSSION

Mechanochemical reduction of copper oxide with metallic zirconium was initially investigated in this system. This reaction is quite high-exothermic ($\Delta H (2 \text{ CuO} + \text{Zr} = 2 \text{ Cu} + \text{ZrO}_2) \approx -188 \text{ kcal/mol}$), i.e. it can be implemented under mechanical activation conditions. IR spectroscopic investigations have shown that the original copper oxide vCu-O band is considerably widened at 505 cm⁻¹ after 20 s of MA of CuO + Zr mixture of stoichiometric composition. This widening (Fig.1b) can testify some structural failures. After 30 s of activation, the following bands are present in the IR-spectrum of the product: 505 cm⁻¹ (original oxide CuO), 615 cm⁻¹ (the lowest copper oxide Cu₂O) [3] and 415, 585, 735 cm⁻¹ (zirconium oxide (Fig.1c) [4, 5]. X-ray-phase analysis shows the presence of a certain amount of Cu₂O already after 20 s of activation. The 30-second activation product diffractogram shows clear copper (coherent scattering area ≈ 80 nm) and zirconium oxide (coherent scattering area ≈ 100 nm) reflection and two copper oxide reflections, i.e. mechanochemical reduction of copper oxide takes place at such activation duration. This reaction speed shows that the reaction presumably takes place in the thermal explosion mode, when especially high heat dissipation speed is needed, what is very difficult to perform even in the most effectively cooled highly-energy planetary ball mills. As such a process dimensional scaling seems to be absolutely impossible in conditions of mechanochemistry, an attempt to produce composite Cu/ZrO₂ by the SHS method was made.

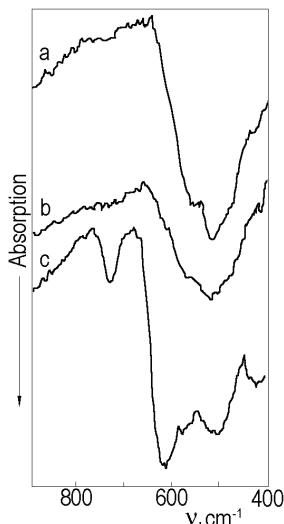


Fig.1. IR-spectra of mixture CuO + Zr before (a) and after MA for 20 (b) and 30 s (c).

At first, CuO/Zr mechanocomposite was used as the SHS-precursor. This mechanocomposite formed after 20 s of MA of stoichiometric composition mixture has a small amount of cuprous oxide Cu₂O beside the original copper oxide and zirconium. SHS process proceeds in the heat explosion mode in this system. Burning parameters fixing failed in this case because of the inertia of the equipment applied.

Not pure metal, but solid solutions, intermetallic compounds or nano-composites where metal-reducer (zirconium in our case) is distributed in the inert matrix can be used as a reducing agent to decrease the system reaction capability. At the same components ratio chemical energy of the raw mixture would be considerably lower and as a consequence heat release would reduce.

In this work, mechanocomposite, formed during mechanical activation of mixture Cu + 20 wt.% Zr for 20 min was used for copper oxide reduction.

X-ray research of the product of joint activation of mixture CuO + mechanocomposite Cu / Zr (the mixture composition corresponds to the stoichiometric ratio of copper oxide and zirconium) for 2 and 4 minutes shows that copper oxides diffraction reflections are retained in all cases, although they are substantially widened (Fig.2). The zirconium oxide reflection is not observed, i.e. mechanochemical copper oxide reduction does not take place in this time interval. CuO/Cu/Zr mechanocomposite formed as a result of joint mechanical activation of mixture CuO + mechanical composite Cu 20% Zr for 4 min, was used as a precursor for SHS.

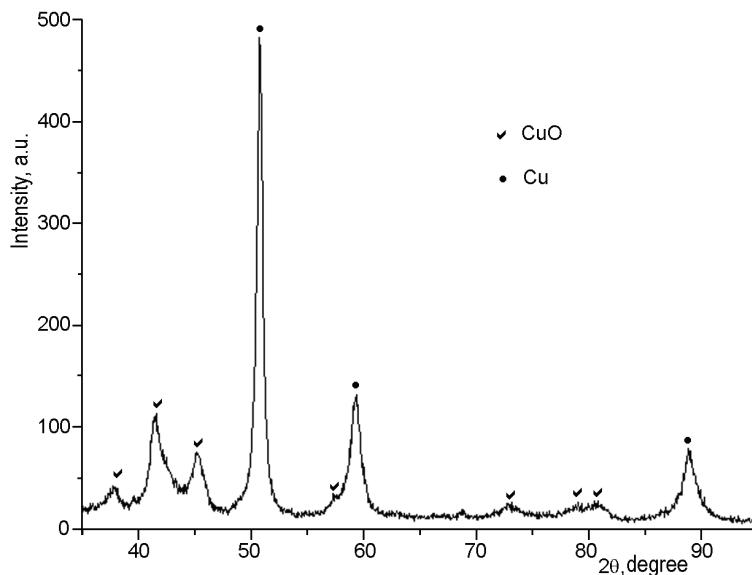


Fig.2. Diffractogram of sample CuO + Cu/Zr after MA for 4 min.

Usage of mechanocomposite CuO/Cu/Zr instead of CuO/Zr as the SHS precursor changes a mechanism of interaction between the reactants during the SHS process from the thermal explosion (for CuO/Zr mechanocomposite) to the steady-state combustion mode with the burning velocity ≈ 2 mm/s, temperature rise speed about 730°C/s and burning temperature 1044°C . The combustion temperature record (Fig.3) shows 2 isothermal plateaus. The first one is fixed at temperature maximum and most probably indicates the melting process. The second one is fixed at $580 - 590^\circ\text{C}$ and accounts for post-processes in the after-burning zone of the combustion wave.

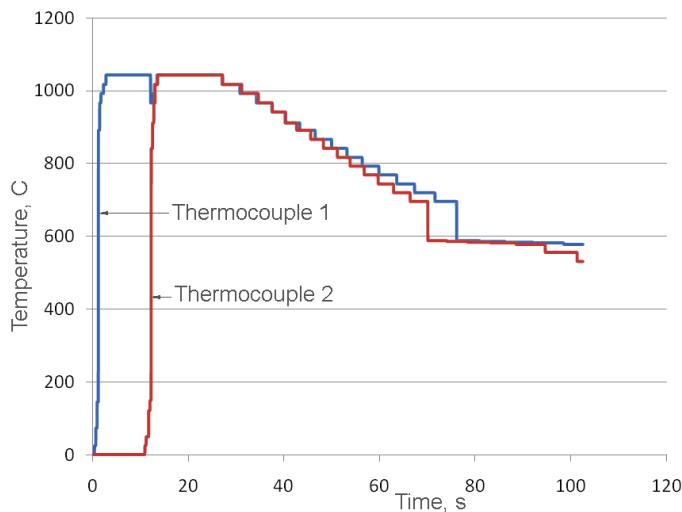


Fig.3. Temperature record of the SHS process from the mechanical composite CuO/Cu/Zr.

X-ray-phase analysis has shown that the SHS product consists of copper and zirconium oxide with Cu₂O traces (Fig.4). Electron microscopy with the EDX analysis confirms composite structure formation (Fig.5, Table 1).

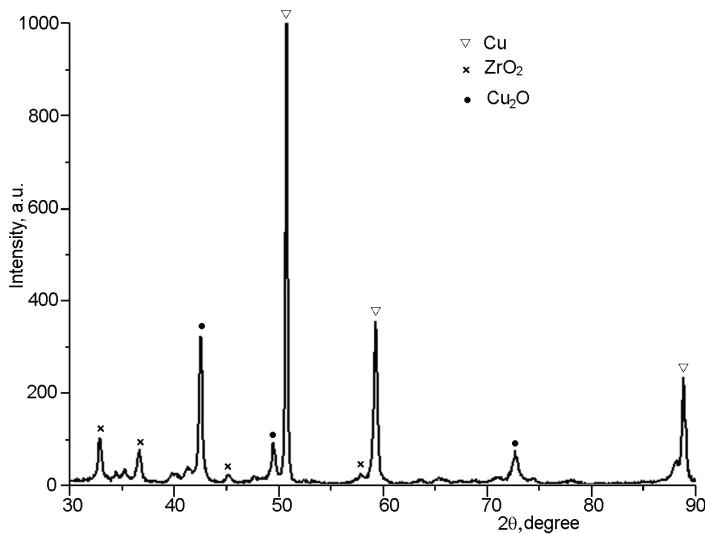


Fig.4. Diffractogram of the SHS product from mechanical composite CuO/Cu/Zr.

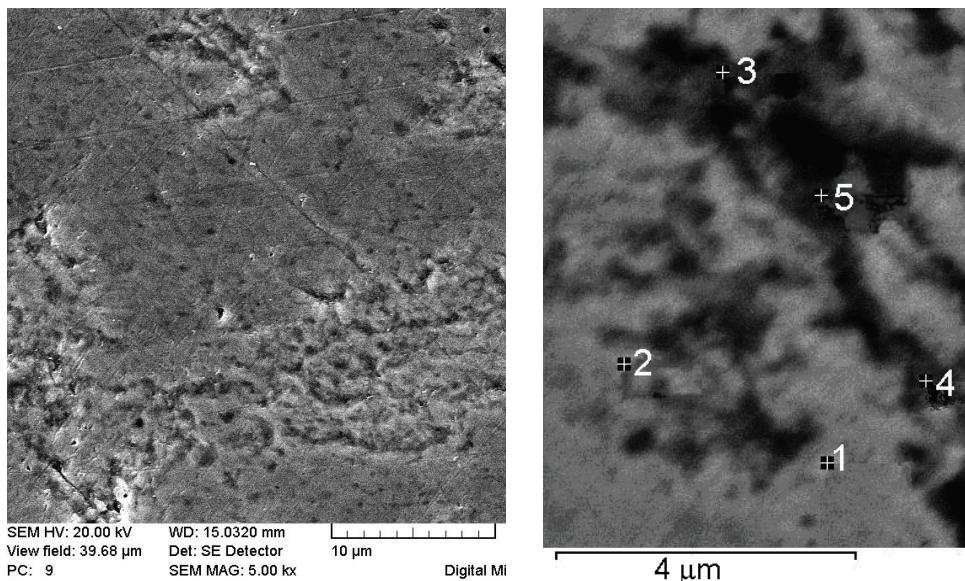


Fig.5. SEM-image of the SHS product from mechanocomposite CuO/Cu/Zr.

Tab.1. Results of the EDX analysis (from Fig.5).

Number of spectrum	O	Cu	Zr
1	3.82	87.44	8.74
2	7.14	81.52	11.34
3	28.03	27.47	44.50
4	16.53	46.40	37.06
5	23.14	29.14	47.72

CONCLUSION

Thus, our investigations have shown that copper oxide can be mechanochemically reduced with zirconium, resulting in formation of zirconium oxide and copper, but the reaction takes place in the thermal explosion mode.

To produce composite Cu/ZrO₂ by the method of MASHS usage of mechanocomposite Cu/Zr instead of pure zirconium seems to be more promising. The MASHS product is a copper-based composite with inclusions of ZrO₂ and some amount of Cu₂O.

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