

The effect of low-temperature auto-ignition of W–Cu₂O nanopowders with core-shell structure

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ARTICLE INFO

Keywords:

Nanopowders
In situ X-ray diffraction
Core-shell structure
Electrical explosion of wire

ABSTRACT

In this work, the effect of in-vacuum low-temperature auto-ignition of a W–Cu₂O nanopowders mixture obtained by natural oxidation of W–Cu composite nanopowders is demonstrated. The powder is obtained via electrical explosion of wire technique and consists of bimetallic particles instead of Cu and W mixture. The evolution of the phase composition has been studied using in situ X-ray diffraction technology during heating. The structural investigation shows that particles have a core-shell structure, increasing a contact surface between reactants. The ongoing reactions are described, and studies of the structure of powders and combustion products are given. Combustion occurs in the solid-phase temperature range, which is confirmed by the thermal imaging data.

1. Introduction

Tungsten-copper (W–Cu) composites/pseudo alloys are desirable for applications as electrical contacts or electrode materials, electronic packaging materials, functional graded materials [1,2], and others [3–8]. According to the equilibrium phase diagram, tungsten and copper are completely immiscible in solid and liquid phases [9] and W–Cu alloys are considered as pseudo alloys. One of the methods for synthesizing pseudo alloys is powder sintering [7,10–14]. When sintering nanopowders, it is possible to form a nanostructured alloy that has better homogeneity and exhibits better mechanical properties [15–21].

Copper nanopowders are intensively oxidized due to the large surface-to-volume ratio and the absence of a passivating oxide film. Sintering of W–Cu nanopowders is carried out in an inert atmosphere (vacuum, argon, or other) or a reducing atmosphere of hydrogen if the copper powder is oxidized already. In both cases, the reaction proceeds without significant exothermic effects. However, exothermic reactions are possible when using more complex mixtures (for example, adding aluminum [22–24]).

In this work, the effect of vacuum auto-ignition of a W–Cu₂O nanopowders mixture obtained by natural oxidation of W–Cu nanopowders is demonstrated for the first time. The evolution of the phase composition has been studied using in situ x-ray diffraction (XRD) technology during heating [25–27]. The ongoing reactions are described, and studies of the

structure of powders and combustion products are given.

2. Materials and methods

Composite nanopowder W - 30 wt% Cu was prepared by the Electrical Explosion of Wire (EEW) method with intertwined copper and tungsten wires in argon atmosphere. The W:Cu ratio was defined using energy dispersive spectroscopy on scanning electron microscope. The resulting powder was left in the EEW chamber, and the air was gradually introduced over 24 hours. This process is necessary to passivate the powder and suppress its pyrophoricity typical of the EEW powders. The resulting powder was compacted in tablets (diameter 20 mm) by cold pressing at a 50 tons load.

The initiation of the combustion reaction was carried out on an electron beam setup described in Ref. [28]. The structure of the materials was studied using an LEO EVO 50 scanning electron microscope (SEM) and a JEOL JEM-2100 transmission electron microscope (TEM). The phase composition study was carried out on an in situ XRD setup described in Ref. [26]. Thermal imaging control was carried out using InfraTEC VarioCAM HD head infrared camera at 30 fps.

3. Results and discussion

The XRD method (Fig. 1, initial tablet) identified phases of α - and

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<https://doi.org/10.1016/j.vacuum.2021.110837>

Received 7 October 2021; Received in revised form 9 November 2021; Accepted 16 December 2021

Available online 22 December 2021

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β -tungsten, cuprous oxide, and minor amounts of metallic copper in the initial W–Cu nanopowder. It is worth noting that β -W and tungsten oxide W_3O completely coincide [29] in XRD patterns. Almost all of the copper in the W–Cu nanopowder was oxidized to Cu_2O . The formation of the Cu_2O phase is typical of the EEW copper nanopowders passivated in the air at room temperature [30]. The metastable β -phase of tungsten in a form of a thin film is stable for a long time and can contain 13–22% oxygen [31]. In the synthesis of tungsten by the plasma method [32], in addition to the main phase α -W, β -W and tungsten oxide WO_3 were found.

TEM images show dark spherical nanoparticles surrounded by a brighter shell (Fig. 2). TEM data in the mapping mode show that the dark particles consist of tungsten, and the light shell around them is of copper oxide. Faceted particles consist of copper and oxygen and represent copper oxide in the nanopowder.

The formation of the core-shell structure is observed with the simultaneous EEW of two wires with different melting points and different electrical characteristics. The powder was obtained from intertwined tungsten (wire diameter $d = 0.2$ mm) and copper ($d = 0.2$ mm) wires. The explosion was carried out on segments 90 mm long. A capacitor $C = 3.2$ μ F was used in the electrical explosion circuit. The explosion was carried out at a voltage of $U = 27$ kV. These EEW parameters led to the “W-core - Cu-shell” particles formation.

The powder compacts were heated in a vacuum chamber. During heating, the exothermic reaction occurred and compact was auto-ignite. The ignition begins in a 220–250 °C temperature range for all samples. Repeated powder preparation using the same EEW conditions led to the auto-ignition of the samples.

The sample was placed on a copper substrate preheated to 300 °C; the sample was rapidly heated from the substrate due to thermal conductivity. At a temperature of the bottom of the sample of 240 °C, a complete explosion of the sample occurred (Fig. 3). The maximum temperature detected by the infra-red (IR) camera was 860 °C at the center of the explosion. Thus, a solid-state reaction in a W–Cu system

occurred. Sample fragments cool down quickly right after the explosion, and no signs of reheating of the fragments are observed.

The structure in cross-section of the resulting products and starting powders were examined (Fig. 4). For research, the powders were embedded in epoxy resin and then ground and polished. In the reaction products, tungsten particles retain their shape and size. No traces of crystallization of the liquid phase are observed, proving a solid-phase reaction.

The phase composition of the explosion products was analyzed using XRD (Fig. 1, after reaction). It was found that the Cu_2O phase is almost completely absent in the powder, while the content of pure Cu increased significantly. Reflections of γ -tungsten oxide $W_{18}O_{49}$, which was not present in the initial powders, are also observed. The content of α - and β -tungsten is reduced compared to the original powder. XRD results show that copper oxide is reduced to pure copper.

An in situ XRD investigation was carried out to study the dynamics of the spontaneous combustion of the nanopowder (Fig. 5). X-ray diffraction patterns were recorded in a narrow range of Bragg's angles ($2\theta = 33$ – 50°) with a 20 °C step during powder heating. After 220 °C, a sharp drop in the intensity of all phases occurred, and the Pt phase appeared. With further heating, no quick changes in intensity are observed. The decrease in intensity is associated with the blowing off of the powder due to internal reactions. As a result, the platinum substrate showed up - its reflection became visible on the X-ray diffraction pattern.

During heating, the gradual decay of the Cu_2O reflection and the growth of the Cu reflection are observed. The content of α - and β -tungsten is also growing. Presumably, the dynamics of changes in some phases were not tracked due to the narrow range of Bragg's angles at which in situ XRD imaging is possible. In particular, the phases of tungsten oxides present in the X-ray diffraction pattern of the reaction products. A significant result is detecting a temperature of 220 °C at which an intense gas evolution occurs, leading to the powder blowing off. The exothermic reaction also begins in the 200–300 °C temperature range under the electron beam treatment. However, TG-DSC of 10 mg of

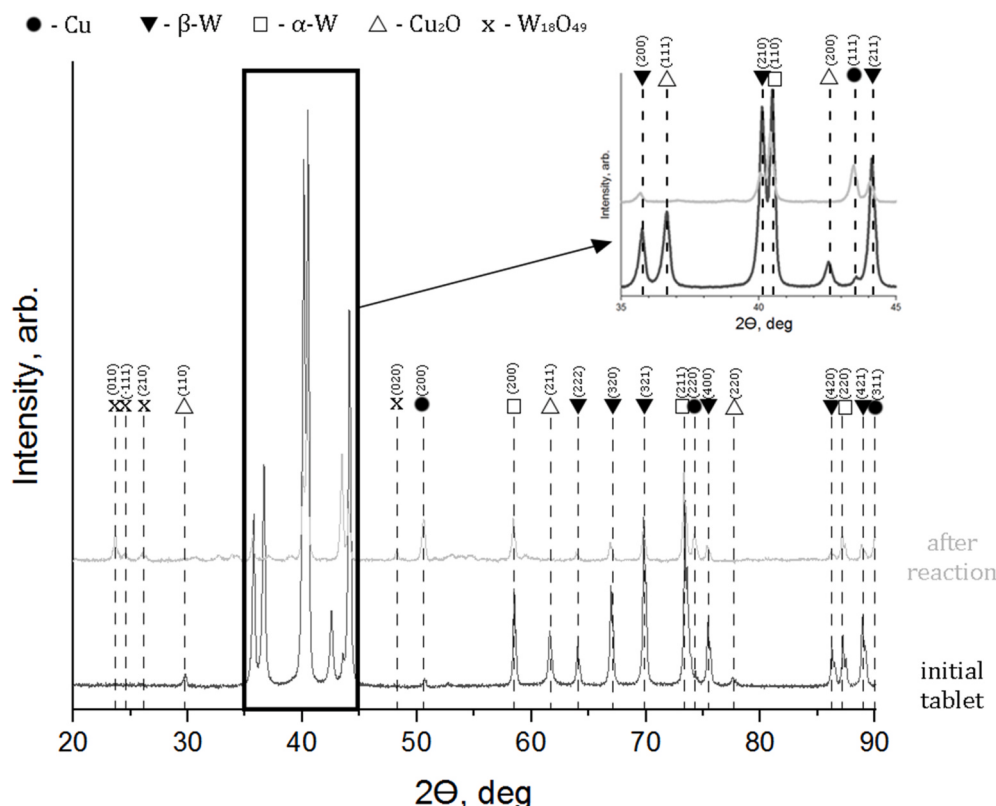


Fig. 1. XRD patterns of the initial powder in tablets and the powder after combustion.

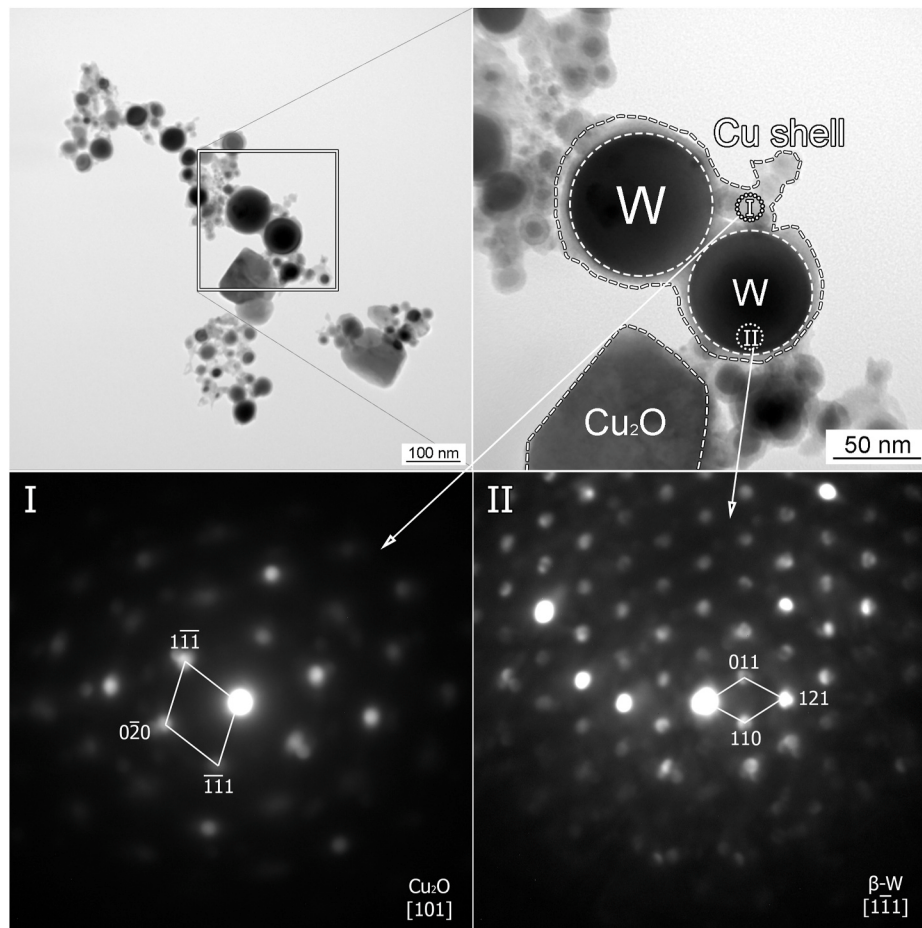


Fig. 2. TEM pictures and elemental analysis of the initial powder with a core/shell structure.

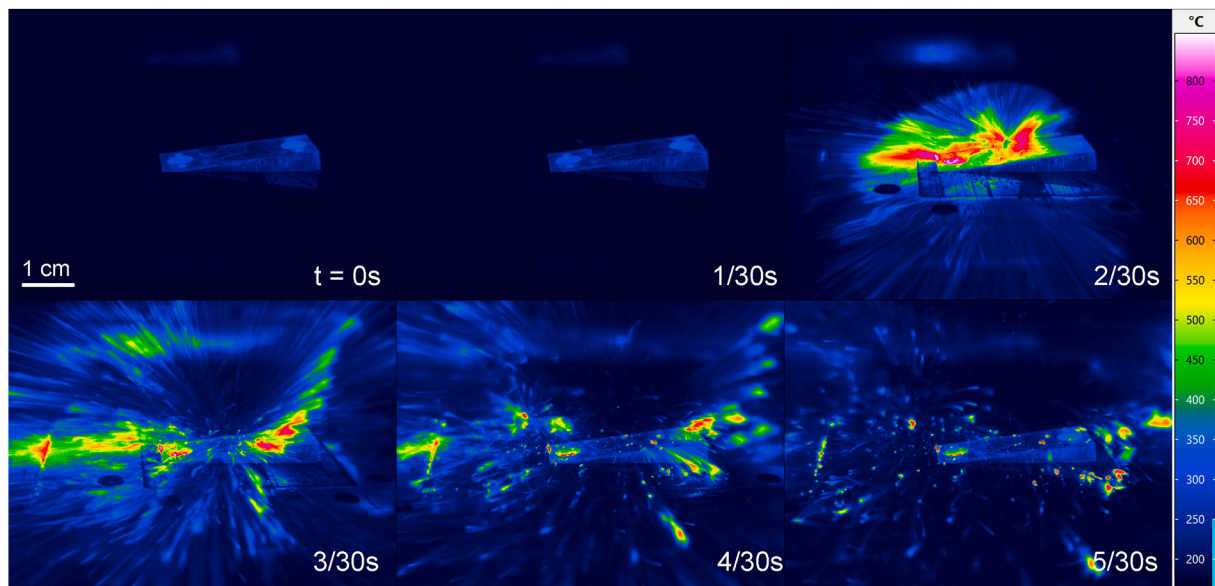


Fig. 3. IR-camera data of W-Cu₂O tablet explosion.

powder does not show any intense exo-peaks in the range from room temperature to 1000 °C. At the same time, the total mass loss in the temperature range 200–500 °C is 1.3%.

The literature describes the reduction of Cu₂O to Cu in the presence of carbon, C_xO_y gases, hydrogen, and during annealing [33]. In this

work, the experiments were carried out in a vacuum; before that, the powder was vacuum-dried at 110°C. The elemental analysis does not reveal carbon in the powder, and the drying temperature is much lower than the annealing temperature.

The data on the oxidation of tungsten indicate the onset of intense

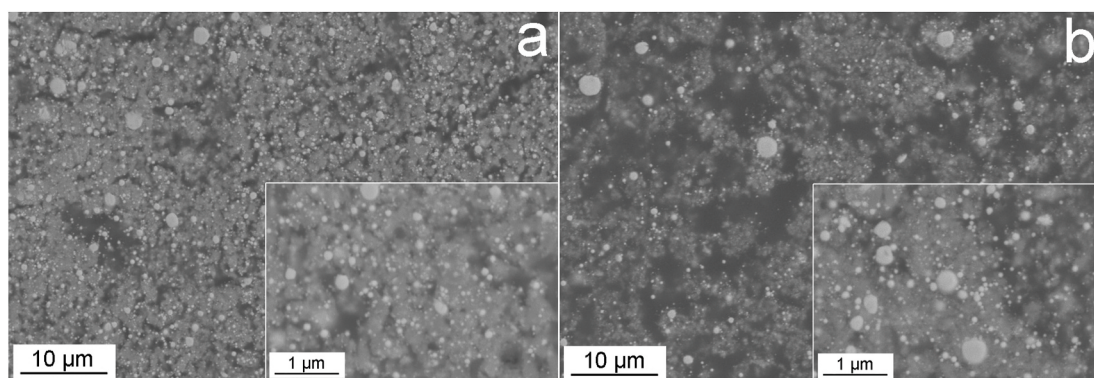


Fig. 4. SEM pictures of W-Cu powders after (a) and before (b) combustion.

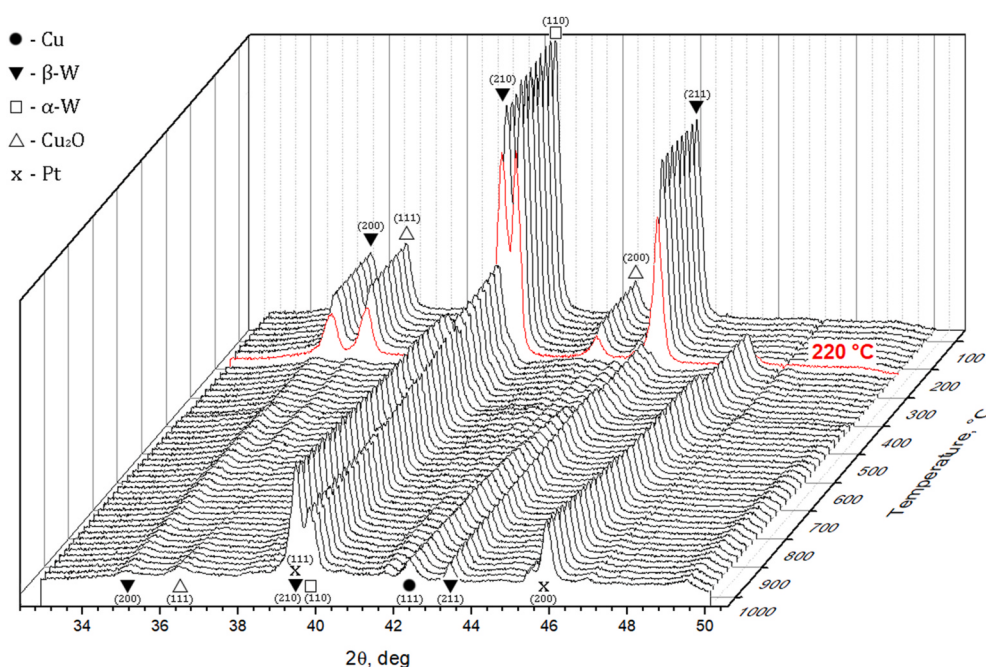


Fig. 5. XRD patterns of the W–Cu powder during the heating.

oxidation at temperatures of 300–400 °C [34,35]. Samples can oxidize in a vacuum due to interaction with absorbed oxygen. Under such conditions, oxygen-deficient tungsten oxides (ODTO) [36] are formed. Many ODTOs can be metastable and have an amorphous or nanocrystalline structure, so XRD methods cannot detect such oxides. In addition, nano-sized ODTOs have a lower sublimation temperature than stoichiometric tungsten oxides, for which it is 700–900 °C.

The EEW powders may demonstrate high energy emissions when heated [37–39]. Explosive heating is observed in EEW oxide-contain powders with a core-shell structure. One of the reasons is a decrease in the shell density upon heating, which leads to an increase in the oxygen diffusion rate.

In [40], based on the analysis of FTIR spectra, it is shown that the W–O–W bond is weakened due to the bond of Cu–O–W, leading to the increase of the reduction properties of the W–Cu composite oxide powders. The study of the reducing behavior of the CuO–W powder mixture was carried out by Kim et al. [20,41]. Thus, oxygen transfer from copper to tungsten is possible during heating in the core-shell structure.

Copper in the reaction products could be formed during the solid-phase reaction of copper oxide reduction with tungsten (1):



Thermodynamically, reaction (1) is possible because tungsten oxide is more stable than copper oxide [42]. The reaction enthalpy is $\Delta H_{298}^0 = -241.7 \text{ kJ}\cdot\text{mol}^{-1}$. Earlier, the formation of metallic copper nuggets during the oxidation of copper-tungsten scraps was observed by the authors of [43], who also attributed this to the reduction of copper oxide by tungsten. Self-heating and passive ignition of the sample in a vacuum have not previously been observed. A tight contact surface between W and Cu_2O in nanoparticles with a core-shell structure provides a high rate of the process. As a result, reaction (1) occurs according to the thermite type without an external ignition source, with auto-heating to a high temperature and the formation of gaseous products.

The explosive destruction of the sample by gaseous products, the absence of WO_2 in the solid reaction products, and the detection of $\text{W}_{18}\text{O}_{49}$ can be explained by the fact that the WO_2 formed by reaction (1) due to self-heating of the sample with decomposition into W and $\text{WO}_{2.72}$ ($\text{W}_{18}\text{O}_{49}$) (2) and disproportionates with the formation W and WO_3 vapors in the solid phase (3):



According to the W–O system phase diagram [9,44], reactions (2) and (3) proceed at temperatures of 1530 °C and 900–1000 °C accordingly. However, under non-equilibrium conditions due to the nano-structural state of the substance, these reactions can occur simultaneously and at lower temperatures.

4. Conclusions

The article is the first to describe the auto-ignition and solid-phase combustion of W–Cu powders with a core-shell structure in the vacuum. At 220 °C the intense gas release accompanied by intense heating of the pressed samples to 700–800 °C is observed. This effect is not observed in EEW W–Cu powders without a core-shell structure. The most likely reason for this reaction is the oxidation of tungsten with desorbed oxygen to form oxygen-deficient tungsten oxides (ODTO). The reduction of Cu₂O, which begins in nanoparticles in the temperature range 200–300 °C, makes its exothermic contribution. The reaction has requirements for the minimum critical mass, for the contact surface (the reaction is more intense for tablets than for powder), and for heat removal from the reaction zone.

CRediT authorship contribution statement

M.G. Krinitcyn: Writing – review & editing, Writing – original draft, Methodology, Investigation. **N.V. Svarovskaya:** Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft. **M.I. Lerner:** Writing – original draft, Supervision, Resources, Project administration, Methodology, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by the Russian Science Foundation (grant No. 21-79-30006).

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