

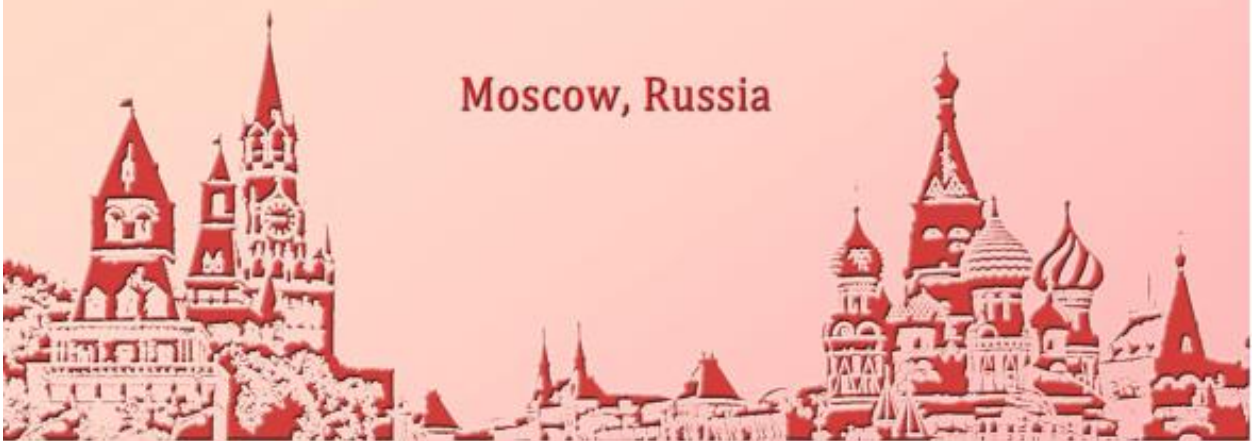
A graphic element for the SHS 2019 logo, featuring a crown-like top and a vertical bar with horizontal stripes in shades of orange and yellow.

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THERMITE SYNTHESIS OF NANOCOMPOSITE Co–In₂O₃ AND Fe–In₂O₃ FILMS

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Granular nanocomposites consisting of ferromagnetic nanoparticles embedded in semiconductor (In₂O₃, TiO₂, ZnO, and SnO₂) or dielectric (SiO₂, Al₂O₃, MgO, and ZrO₂) matrices have been intensively studied as objects interesting both for fundamental research and application. The most common methods for synthesizing magnetic nanocomposites and hybrid materials use wet chemistry; these include sol-gel methods, solvothermal methods, sonochemical synthesis, thermal decomposition, chemical reduction, and radiolysis [1, 2]. After wet chemistry, the next most important method of obtaining functional magnetic nanocomposites is the formation of magnetic granular films created from a joint deposition of metal and an insulator [3, 4]. The search for new methods to create ferromagnetic nanocomposite films is relevant. This paper discusses the synthesis of ferromagnetic nanocomposite film materials on the basis of solid-state thermite reactions between layers of oxides of 3d metals (Co₃O₄ and Fe₂O₃) and the metal In. Ferromagnetic nanocomposite Co–In₂O₃ thin films were synthesized using thermite reactions between layers of In and Co₃O₄ (1) by vacuum annealing of In/Co₃O₄ film bilayers.



Ferromagnetic nanocomposite Fe–In₂O₃ thin films were synthesized using thermite reactions between layers of In and Fe₂O₃ (2) by vacuum annealing of In/Fe₂O₃ film bilayers.

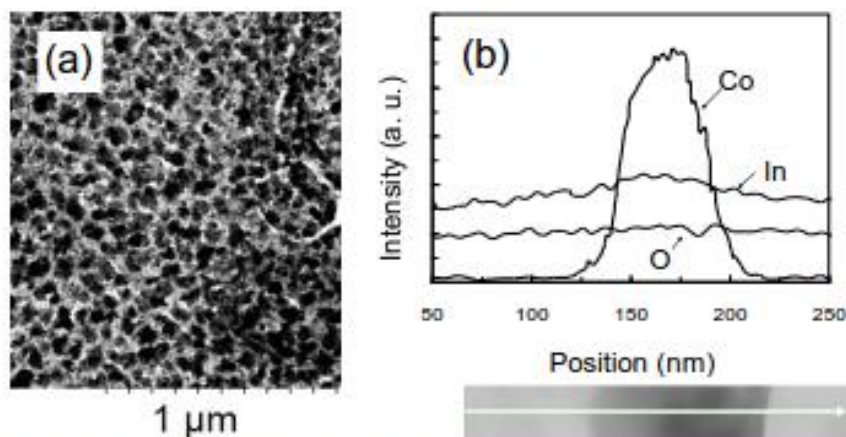


Fig. 1. (a) Electron microscopy image and (b) elemental composition of the Co–In₂O₃ nanocomposite film.

The initiation temperature of reactions (T_{in}) and the structural and magnetic properties of the nanocomposite films were identified. Electron-microscopic study of films showed the creation of Co, Fe (60–100 nm) nanoclusters surrounded by a layer of In_2O_3 over a large area (Figs. 1, 2). Thus, the termite method is promising for synthesizing ferromagnetic nanocomposite thin films consisting of ferromagnetic clusters embedded in oxide matrices and characterized by the high magnetization and chemical stability.

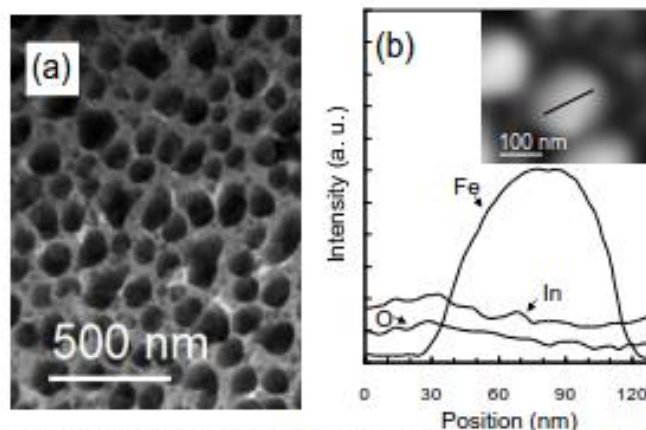


Fig. 2. (a) Electron microscopy image and (b) elemental composition of the Fe- In_2O_3 nanocomposite film.

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THE EXCLUSIVE ROLE OF THE INITIATION TEMPERATURE IN THE START OF NANOSCALE SOLID-STATE REACTIONS

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Control and predictability of the synthesis of new materials is one of the most fundamental challenges in material science. The prediction of the phases in binary systems that will be formed during the thin-film solid-state reaction has been a subject of numerous studies, and different empirical rules have been developed for predicting first phase formation. Studies of solid-state reactions in nanolayers showed three fundamental features that strongly distinguish them from bulk powders:

(i) Formation of only the first phase at the film reagent interface at a certain temperature called the initiation (formation) temperature T_{in} . As the annealing temperature is increased, other phases can occur and form the phase sequence.

(ii) The threshold of the reaction, characterized by intense intermixing at the interface and formation of compounds, arises at temperatures above initiation (formation) temperature T_{in} . The values of T_{in} in the first phase can be about room temperature or even at cryogenic temperatures.

(iii) Migration of the dominant diffusing species through the interface during first phase formation.

The formation of only the first phase among equilibrium phases, low initiation temperatures, and migration of the dominant diffusing species are unique, unexplained features of solid-state reactions in nanofilms. From the above results it follows that the first phase and its initiation temperature T_{in} are control characteristics of the thin-film solid-state reactions. The initiation temperatures T_{in} of the first phase for most bilayers (multilayers) lie below 400°C. However, many thin-film reactions are initiated near room temperature and even at cryogenic temperatures. At such low temperatures, diffusion is extremely small and cannot provide the transfer of atoms in the solid state. This suggests an alternative view, in which chemical interactions rather than diffusion ones take place, plays a crucial role in the initiation and kinetics of interphase reactions in the solid state [1–3].

Previously, it was shown that the initiation temperatures T_{in} are close or coincide with the solid-state transformation temperatures T_k of the reagent-based binary system, such as order-disorder transitions, the superionic transition, the spinodal decomposition and others [1–3]. In particular, initiation temperatures $T_{in}(\text{Cu}/\text{Au})$, $T_{in}(\text{Pd}/\text{Fe})$, $T_{in}(\text{Co}/\text{Pt})$, $T_{in}(\text{Ni}/\text{Fe})$, and $T_{in}(\text{Cu}/\text{Fe})$ of reactions in the Cu/Au, Pd/Fe, Co/Pt, Ni/Fe, and Cu/Fe bilayers coincide with the minimum temperature of the order-disorder phase transition in Cu–Au, Pd–Fe, Co–Pt and the eutectoid decomposition temperature in the Fe–Ni, Cu–Fe binary systems, respectively. Martensitic transitions are not diffusion transformations; however, they also satisfy ($T_{in} = T_k$) equality. It is well established that the ordered B2 alloys, such as NiTi, AuCd, NiAl have reversible low-temperature martensitic transformations, in which the high-temperature austenite B2-phase develops into a low-temperature martensitic phase through a complex process of the formation of intermediate phases. We have shown earlier that the initiation temperatures $T_{in}(\text{Ti}/\text{Ni}) < 150^\circ\text{C}$, $T_{in}(\text{Ni}/\text{Al}) \sim 180^\circ\text{C}$, $T_{in}(\text{Cd}/\text{Au}) = 67^\circ\text{C}$ in Ti/Ni, Ni/Al, Cd/Au bilayers, respectively [1–3]. These temperatures are close or coincide with reverse martensitic

transformation starting temperatures $A_s(\text{B2-TiNi}) \sim 100^\circ\text{C}$, $A_s(\text{B2-NiAl}) \sim 180^\circ\text{C}$, $A_s(\text{B2-CdAu}) = 67^\circ\text{C}$. As mentioned above, with increasing of the temperature of the bilayer above T_{in} leads to the beginning of intermixing of the reagents and first phase synthesis on the interface and consequently physical characteristics of the film samples, such as electrical resistance, magnetization, transparency, heat release begins radically change. Obviously, the start temperature of these changes is the reaction initiation temperature T_{in} . In most cases the energetic properties of thermite nanocomposites were investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). In this case the initiation temperature T_{in} is the temperature at which heat release starts.

The one important characteristic of reactive multilayer films is the ignition temperature T_{ig} which can be defined as a minimum temperature of onset of a self-sustaining reaction for given experiment. As known, the self-sustaining regime of reaction arises then the rate of heat generation $Q_{reaction}$ overcomes the rate of heat losses Q_{loss} ($Q_{reaction} > Q_{loss}$). Unlike T_{ig} the initiation temperature T_{in} is start temperature of reaction at which the rate of heat generation $Q_{reaction}$ less than the rate of heat losses Q_{loss} ($Q_{reaction} < Q_{loss}$) and so always the initiation temperature T_{in} is less than the ignition temperature T_{ig} ($T_{in} < T_{ig}$). As discussed above the initiation temperature T_{in} is threshold temperature: no reaction below T_{in} and reaction initiate just the temperature of sample overcomes T_{in} . Thus, the initiation temperature T_{in} is fundamental temperature for given reaction couple. In contrast to T_{in} , the ignition temperature T_{ig} is a kinetic quantity that depends on the heating rate and the rate of heat loss.

In contrast to the universally accepted diffusion mechanism, the above clearly demonstrates that the same chemical interactions underlie and control both the thin-film solid-state reactions and corresponding solid-state transformations [1–3]. Under the impact of chemical interactions above the initiation temperature $T > T_{in}$ the chemical bonds in the reactants are broken. the reacting atoms are transfer through of the reaction product layer and the synthesis of new compounds are occurring. This proves that there is no reaction below T_{in} . The equality $T_{in} = T_k$ indicates that low-temperature solid-state thin-film reactions in A/B bilayers occur only in A–B binary systems, which have corresponding low-temperature solid-state transformations. Therefore, the study of reactions in A/B bilayers with different layer ratios is a study of the A–B phase diagram.

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THE INITIATION TEMPERATURES IN NANOTHERMITE REACTIONS

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Over the past decade, investigations focused on the nanoenergetic materials, such as reactive multilayer thin films and nanostructured reactive mixtures. Thermite mixtures belong to a wide class of energetic materials that comprise a metal fuel (e.g. Al, Mg, or B) and an oxidizer (e.g. Fe_2O_3 , MoO_3 , CuO , Bi_2O_3 , or WO_3). These mixtures react with a lot of heat release; therefore, the thermite reactions often occur in a self-sustaining mode. In recent years, there has been an increasing interest in nanothermites (superthermites) where the particle size is reduced to a few nanometers. Studies of nanothermite combustion are mainly aimed at measuring the combustion wave velocity, burning temperature, delay time, and their dependences on density, morphology, and composition of the reaction mixture. Despite the intense investigations of thermite reactions, their general regularities and mechanisms remain unclear. Currently, the classical nanothermite Goldschmidt reaction $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$ and other Al-based reactions are well studied.

In this work, we extend the existing concepts of the first phase and its initiation temperature T_{in} which describe the initial stage of solid-state reactions in nanofilms onto thermite reactions and demonstrate that in all Al-based nanothermite mixtures the synthesis of the Al_2O_3 phase starts at the same initiation temperature $T_{\text{in}} \sim 510^\circ\text{C}$. These results open up a way for understanding the exclusive role of the initiation temperature T_{in} in the solid-state reactions at the nanoscale.

The enthalpy of formation of the first phase is a good measure of the free energy variation during the solid-state interaction; therefore, the heats of formation were used in several initial models to predict the first phase and phase sequence formation. Pretorius et. al. [1] proposed an effective model for the enthalpy of formation, which was successfully used for predicting the first phase formation in many binary systems.

As mentioned above, an increase in the temperature of the bilayer above T_{in} leads to the beginning of intermixing of the reagents and first phase synthesis on the interface and consequently physical characteristics of the film samples, such as electrical resistance, magnetization, transparency, and heat release, begin to radically change. Obviously, the start temperature of these changes is the reaction initiation temperature T_{in} . In most cases the energetic properties of thermite nanocomposites were investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). In this case the initiation temperature T_{in} is the temperature at which heat release starts. An important characteristic of the DSC curves is also the exothermic peak temperature, which, unlike the initiation temperature T_{in} , depends on the heat removal conditions from the reaction zone. It is important to note that the contaminants that form on the reagent interface during various methods of sample preparation (especially for chemically produced samples) can form thin barrier layers that slightly change the initiation temperature T_{in} but do not suppress the reaction. An error in finding the exact value of the initiation temperature T_{in} can also follow from the certain inaccuracy in determining T_{in} from DTA, TGA, and DSC plots. To find the exact T_{in} value, low heating rates are required. Therefore, we referred only to the studies in which the heat release curves were obtained at minimum heating rates (5, 10 or $20^\circ\text{C}/\text{min}$).

The main results of the work based on an analysis of more than 60 papers presented in the literature and our papers are summarized in the schematic diagram in Fig. 1. showing the initiation temperature $T_{in} \sim 510^\circ\text{C}$ of the Al_2O_3 phase in $\text{Al}/\text{Fe}_2\text{O}_3$, $\text{Al}/\text{Co}_3\text{O}_4$, Al/NiO , Al/MnO_2 , $\text{Al}/\text{Bi}_2\text{O}_3$, Al/CuO , Al/MoO_3 nanothermite reactions and oxidation of Al nanomaterials.

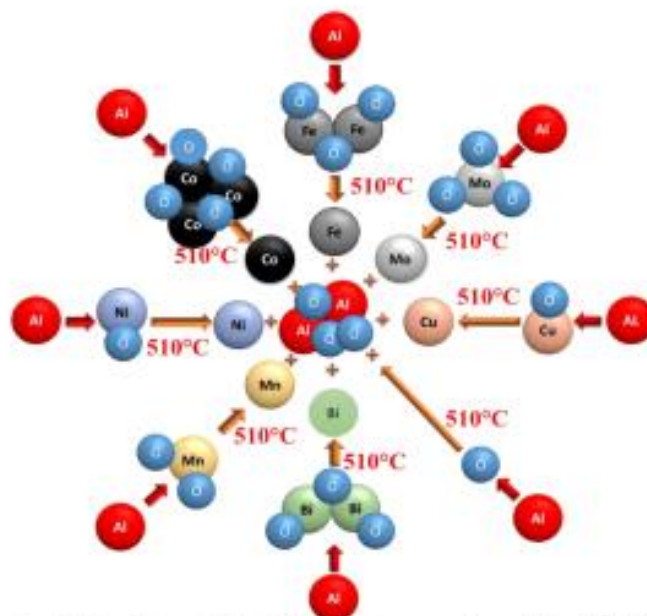


Fig. 1. The schematic illustration of the initiation temperature $T_{in} \sim 510^\circ\text{C}$ for the Al-based nanothermite reactions with Fe_2O_3 , Co_3O_4 , NiO , MnO_2 , Bi_2O_3 , CuO , MoO_3 oxidizers and the oxidation of Al nanomaterials. The initiation temperature $T_{in} \sim 510^\circ\text{C}$ is characteristic of the leading Al_2O_3 phase (first phase), which has a high negative enthalpy of formation ($\Delta H_f = -1676 \text{ kJ/mol}$) and is the driving force of all the Al-based nanothermite reactions.

These results suggest the following reaction mechanism: below the initiation temperature $T_{in} < \sim 510^\circ\text{C}$, Al and O atoms remain chemically neutral. At $T_{in} > \sim 510^\circ\text{C}$, strong chemical interactions occur between Al and O atoms that break old chemical bonds causing the directed atomic migration to the reaction zone and the synthesis of Al_2O_3 regardless of the system they exist in. Therefore, the initiation temperature $T_{in} \sim 510^\circ\text{C}$ is a universal parameter of all Al-based nanothermite reactions.

The main concepts of this study are the first phase and its initiation temperature T_{in} , which describe thin-film solid-state reactions and were extended onto nanothermite reactions. The paper results prove that all Al-based nanothermite reactions have the same initiation temperature and they only start higher $T_{in} > \sim 510^\circ\text{C}$. Analysis presented in the literature and our papers of Zr-, Mg-, and In-based nanothermite reactions show the same initiation temperatures ~ 250 , ~ 450 , and $\sim 180^\circ\text{C}$, respectively. Finally, these findings predict that nanothermite reactions based on other fuels (e.g. Ti and B) must have their own initiation temperatures. This approach can be widely applicable in the study of the multicomponent thin-film solid-state reactions.

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Self-Propagating High-Temperature Synthesis

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