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Review paper

Combustion synthesis in nanostructured reactive systems

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A B S T R A C T

New classes of reactive systems that are characterized by nano-scale heterogeneity and possess extremely high reactivity, as compared to that for similar reactive systems with micro-scale heterogeneity, have attracted a vast attention of many researchers. The recent developments and trends in combustion science toward such "nano" reactive media are presented. These systems include mechanically induced composite particles, sol–gels, super thermites and multilayer nano-foils. Various combustion-based applications of such nanostructured reactive systems are also discussed.

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1. Introduction

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an attractive technique to synthesize a wide variety of advanced materials including powders and near-net shape products of ceramics, intermetallics, composites, and functionally graded materials. It is based on the ability of exothermic reactions to self-propagate in the heterogeneous media in the form of a glowing combustion wave producing solid materials with the desired microstructures, as well as physical and chemical properties. This method was discovered in the late sixties in the former Soviet Union [1,2]. The history of this discovery and development of its technological applications have been described in many books and reviews [3–7]. It is not necessary to reiterate these publications. We emphasize that the development of SHS has encountered-the hot enthusiasm and confidence for the enormous potential of this method, as well as the complete negation of the idea to use 'uncontrolled' combustion processes for the direct synthesis of materials. This is vividly described in the memoirs of A.G. Merzhanov, who is one of the founders of SHS [8].

It is worth noting that the combustion synthesis can be considered as a specific part of the powder metallurgy [3,7]. Indeed, the traditional metallurgical methods based on the aluminothermic and magnesiothermic processes, have the basic features of combustion synthesis, i.e. local ignition, self-heating and self-acceleration of the reaction, propagation of the reaction wave, and formation of a useful product e.g. metal from ore. But the development of SHS has brought many new advances in the field. The search for gasless flammable compounds was first based on the use of iron–aluminum thermite heavily diluted by alumina in order to lower combustion temperature and suppress evaporation of the components. In these works the metallothermic process was studied using the methodology, which had been developed to study the combustion of gunpowder. This approach involves the organization of the plane front of the combustion wave propagating in one direction; recording the linear velocity of reaction front propagation; the study of the thermal structure of the wave; the identification of controlling stages and burning patterns. The novelty was already in the fact that the metallothermy was not studied as a process of metallurgy, but as a combustion process. Such approach led further to the discovery of other (non-thermite) type of combustible systems, which can be used for synthesis of materials.

Another traditional powder-based method, which has similarity with SHS is the reactive-bonding or reactive sintering, i.e. the consolidation process that involves the reaction between the components. However, during reactive sintering the technologies try to avoid the self-propagation reaction at any point of the consolidated media, since it may result in non-uniformity of material's microstructure. In the above context, SHS can be considered as a limiting case of the reactive sintering. The CS technologies became feasible because the fundamental studies showed that if the physicochemical parameters of the medium, along with the instantaneous spatial distributions of temperature and concentration are known, one can calculate the combustion velocity and reaction rate throughout the reactive mixture. Thus, the SHS is a controllable, well-organized wavelike process, which leads to synthesis of materials with desired microstructures and properties.

Currently, scientists and engineers in many countries are involved in research and further development of combustion synthesis, and interesting theoretical, experimental, and technological results have been reported from various parts of the world. The number of recent publications on CS of metals, alloys, ceramics and composites, approaches ten thousand. Thus it is not possible to even briefly overview all of the latest achievements in this field. Our previous reviews on combustion synthesis were dedicated to specific aspects of this effective energy saving route to produce materials, which includes solution combustion synthesis of oxides [9], CS of nanopowders [10] and exothermic reaction waves in multilayer nano-foils [11] and other nano-systems [12]. This review places emphasis on material science aspects of nano-structured reactive systems.

Analysis of recent research papers on heterogeneous combustion has clearly revealed that the new classes of reactive systems, which are characterized by nanosized-scale and possess extremely high reactivity, as compared to similar reactive systems with micro-scale heterogeneity, has attracted the attention of researchers and has dominated R&D. The present paper gives an overview of four classes of such reactive nano-media: (i) mechanically-structured composites; (ii) sol–gels; (iii) mixtures of metal and metal-oxide nanopowders, i.e., so-called, super thermite compositions and (iv) multilayer nano-foils. Research in each of these areas is being performed almost independently and cross-references are rare. However, a comparison of specific features of these phenomena is critical for fundamental understanding of interaction mechanisms in nanostructured combustible systems. The above systems are also attractive for a variety of advanced applications, such as: (i) synthesis of materials with pre-defined nano-crystalline structures and thus properties (mechanically-structured composites); (ii) synthesis of nanopowders including a wide range of catalysts (sol–gel systems); (iii) new generation of energetic materials (nano-thermite); (iv) joining/soldering of microelectronic components, refractory or dissimilar articles (multilayer reactive nano-foils). This review also attempts to discuss some of the above applications.

2. Mechanically fabricated reactive microstructures and combustion synthesis

High energy ball milling (HEBM) is a complex process that involves multiple deformations, fragmentation, cold welding, micro-diffusion, agglomeration, recrystallization, amorphization, micro-melting, crystallization and heterogeneous chemical reactions [13]. Two basic types of the HEBM process can be outlined [14]. First, is the so-called mechanical alloying process (MAP), which is used to produce novel alloys (phases) during HEBM. The second one is the mechano-chemical processing (MCP) which describes the chemical reactions and phase transformations occurring in materials upon application of mechanical energy. MAP has resulted in the formation of large number of materials like Al-, Cu-Ni- and Fe- based alloys reinforced with nano-oxide particles [15,16], supersaturated crystalline solid solutions [17,18], amorphous phases [19,20], nanocrystalline solids [21,22], solid solutions containing immiscible components [23], and other unique