Experimental studies of the fundamental mechanism for phase formation in reactive solutions toward creation of the functional materials

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Abstract. In this work, we examined several modifications of solution combustion synthesis (SCS) method to produce new nanoscale non-oxide phases (nitrides, intermetallics, and alloys). In particular, two approaches were outlined: (i) so-called, catalytic SCS, where existence of one metal promotes reduction during combustion; (ii) synthesis by using media, which contains both reactive solution and solid metals, i.e. combination of solution and heterogeneous combustion.

1. Introduction

Solution combustion synthesis (SCS) has attracted considerable attention of scientists from around the world for versatile synthesis of a variety of nanoscale materials [1–7]. SCS is based on the generic idea of using exothermic self-sustained (combustion) reactions, which can be initiated in solutions of oxidizer (typically metal nitrate) and organic fuel (glycine, urea, citric acid etc.). One of the unique advantages of SCS is the ability to prepare high-quality multi-element compounds with complex crystal structures, such as garnets, perovskites, spinels, silicates, phosphates, and others [4, 6, 8, 9]. The mixing of reactants at the molecular level enables efficient doping of materials, even with a trace amount of elements. Proper selection of fuel and optimization of the process allows for avoidance of secondary calcination step and prepare materials in one macroscopic stage. Finally, the process can be performed in continuous schemes providing high throughput synthesis of nanoscale materials [3].

A limitation of SCS is related to the relatively low level of control over the morphological uniformity of the fabricated materials. The rapid increase in temperature leads to spontaneous nucleation, growth, and agglomeration of the products’ particles [1, 5]. The most critical role in determining the morphology of the final products is played by maximum temperature and gas release. Another limitation of synthesis related to chemical nature of the mixture is preparation of predominantly oxide materials. It is well-known that the high temperature decomposition of metal nitrates leads to the formation of corresponding metal oxides [10, 11]. However, recently it was demonstrated that this method also allows synthesis of pure metals (Ni, Cu, Co, Pt etc.) and alloys (NiCu, NiCo etc.). It was found that under certain conditions (typically excess of fuel) the intermediate gaseous combustion products have a reduction (typically
hydrogen-based) nature and thus allow reduction of metal oxide to form metals or alloys during SCS [12].

These promising results suggest that by understanding the fundamentals of combustion in reactive solutions we will be able to synthesize other compounds including intermetallics, carbides, nitrides and others, thus significantly widen specter of SCS materials. It is worth noting that since reactants are mixed on molecular level in the solutions it typically leads to formation of high surface area, nano-structured powders with small crystallites, which is not easy to produce by other techniques. Such materials already found applications in different fields, including catalysis, microelectronics, are used for further fabrication of nanostructured ceramics and alloys [1, 13–17]. In the above context, it is difficult to overestimate the importance of the research targeting routes for spreading the application of SCS to produce wide variety of non-oxide based compounds.

In this work, we examined several modifications of SCS method to produce new non-oxide phases (nitrides, intermetallics, and alloys). In particular, two approaches should be outlined: (i) so-called, catalytic SCS, where existence of one metal promotes reduction during combustion; (ii) synthesis by using media, which contains both reactive solution and solid metals, i.e. combination of solution and heterogeneous combustion.

2. Results and Discussion

2.1. Iron-based systems: SCS of Iron nitride

Reactive solutions with different fuel (hexamethylenetetramine, $C_6H_{12}N_4$) to oxidizer (iron nitrate nonahydrate, $\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}$) ratio ($\varphi$) were investigated. In all cases after drying of the solutions reactions were carried out in inert (argon) atmosphere and were locally initiated by “hot” tungsten wire. The typical temperature-time profiles of the combustion wave for different solutions are shown in figure 1. As it is expected an increase of $\varphi$ value leads to the decrease of the maximum combustion temperature. Indeed, in inert atmosphere the highest combustion temperature corresponds to the stoichiometric ratio $\varphi = 1$. It can be also seen that maximum combustion temperature is in the range 900–1600 K and total duration of the reaction (calculated from the rapid increase of the temperature to its decrease) is in the range 2–3 s.

![Figure 1](image_url)

Figure 1. Time-temperature profiles of the combustion wave for solutions with different fuel to oxidizer ratio ($\varphi$)

The XRD data for the combustion products obtained for different reactive solutions are presented in figure 2. It can be seen that at $\varphi = 2$ the main products are $\text{Fe}_2\text{O}_3$ and $\text{FeO}$ oxides, while essentially pure $\text{FeO}$ was obtained for solutions with $\varphi = 3$. However, further increase of amount of
hexamethylenetetramine ($\varphi = 4.5; 5$) leads to the formation of iron nitride (Fe$_3$N). Thus we were able to obtain essentially oxygen free combustion product but it required large amount of carbon/nitrogen containing fuel ($C_6H_{12}N_4$). These elements reacted with iron forming nitrides and carbonitrides.

**Figure 2.** XRD patterns for combustion products after SCS with different fuel to oxidizer ratio ($\varphi$).

Microstructure for obtained powders are shown in figure 3. It can be seen that increase $\varphi$, while leads to decrease of combustion temperature (figure 1), results in increase of the size of the obtained powder agglomerates (figure 3a), as well as size of the individual grains (figure 3b). The morphology of the individual grains also changes: from less than 100 nm spherical type particles (FeO) for $\varphi = 3$, to platelet 500 nm particles (Fe$_3$N).

**Figure 3.** Microstructure for combustion products after SCS with different fuel to oxidizer ratio ($\varphi$).
2.2. Iron–Nickel based systems: SCS of NiFe Alloy

Again reaction was organized in so-called self-propagating mode when the reactive solution was locally preheated by “hot” tungsten wire and combustion front propagates along the reactive media in self-sustained manner. Typical time-temperature profile of the combustion wave shows that maximum reaction temperature is about 1100 K, which is well above boiling point of all used precursors. The duration of the reaction, which can be estimated from the time of rapid increase of the temperature to the beginning of the cooling stage, does not exceed 3 s. The XRD patterns of the combustion product is presented in figure 4. Only one sets of peaks was detected, which corresponds to FeNi alloy (figure 4a).

\[\text{Figure 4. XRD patterns for combustion products in: (a) iron nitrate + nickel nitrate + hexamethylenetetramine system; (b, c) nickel powder + iron nitrate + hexamethylenetetramine system.}\]

SEM images of the microstructure of the obtained powders with corresponding results of EDS analysis are shown in figure 5. It can be seen that as-synthesized alloys has morphology of porous agglomerates. It is important to note that the amount of oxygen in the alloys is very small.

\[\text{Figure 5. Microstructure and EDS analysis of obtained NiFe alloy.}\]

Thus, while we could not completely reduce iron oxide to iron in iron nitrate - hexamethylenetetramine system, we were able to obtain essentially oxygen free NiFe alloy in complex metal nitrates (iron nitrate and nickel nitrate) - hexamethylenetetramine system. It is interesting to figure out the role Ni in the reduction process of iron oxide.

To light a shade on this question the following two experiments were conducted: different amount (0.7 g and 0.2 g) of Ni powders (particle size 4–5 µm) were poured into the 5 ml of aqueous solution of iron nitrate and hexamethylenetetramine (φ = 3). As it was shown above, the combustion of such solution without addition of Ni resulted in formation of FeO phase (figure 2). Initiation of reactions in Ni-powder/solution system in inert atmosphere were accomplished by local preheating of solution. The XRD pattern for thus obtained combustion product is shown in Figure 4 b,c. It can be seen that the main
newly produced phase is Fe$_3$Ni$_2$ alloy. Taking into account that the only highly exothermic reaction in such system is the reaction between Fe-nitrate and C$_6$H$_{12}$N$_4$, which without presence of Ni leads to the formation of FeO, we may suggest that Ni catalyzes the reduction reaction. Indeed, it is know that in presence of Ni iron oxide reduced faster by both carbon and hydrogen [18]. From the standpoint of the combustion synthesis method, such approach, of mixing of reactive solutions with fine reactive or catalytic solid powders, open a new venue for fabrication of the variety of materials, e.g. intermetallics.

2.3. Aluminum–Nickel based systems: SCS of NiAl intermetallics

Two chemical routes have been investigated to synthesized Ni$_x$Al$_y$ intermetallics in the solution combustion wave. First, we try to optimize reaction conditions, similarly to that for Fe–Ni system, in the solution of metal nitrates (aluminum nitrate and nickel nitrate) and the oxygen free fuel (C$_6$H$_{12}$N$_4$) in the wide range of fuel to oxidizer ratio ($\phi = 1.5–3$). Typical XRD patterns of the combustion products in such solution demonstrate that pure well crystalline Ni and amorphous Al$_2$O$_3$ phases were formed.

The second route consider idea of impregnated active layer [10]. The following experiments were conducted. The aqueous solution of nickel nitrate and fuel (glycine) was prepared and then impregnated into specific amount of solid Al powder. Reaction in such heterogeneous media was initiated in the volume combustion mode (uniform preheating) or by local preheating to accomplish the self-propagating combustion mode.

The XRD patterns for combustion products obtained after SCS in the volume combustion mode are shown in figure 6. It can be seen that one of the main parameters that control phase composition of the synthesized materials is an amount of water used. If the initial amount of water is relatively large, e.g. 100:1 wt.% for H$_2$O-Al ratio, then even applying intensive stirring we could not reach sufficient contact between the initially solid Al and formed in combustion wave Ni particles and the product consists of pure Ni and Al phases. Decrease amount of water allows us initially form essentially solid media, with solution impregnated into the porous Al skeleton. In this case, aqueous solution spread along the Al particles forming thin reactive layer. Volume combustion in such media is extremely vigorous and results in formation of intermetallic (Al$_3$Ni$_2$) phase. By changing Al to Ni ratio as well as fuel to oxidizer ratio one may control the phase composition of the obtained materials.

![Figure 6. XRD patterns of SCS products in Al–Ni(NO$_3$)$_2$–C$_2$H$_5$NO$_2$ system; Volume combustion synthesis mode.](image-url)
Based on the above findings additional experiments were conducted in self-propagating mode. In this case, the reactive solution of Ni nitrate and glycine ($\phi = 1.75$) was impregnated with Al:Ni ratio 3:2 into porous skeleton formed by Al powder. Thus prepared media was dried in the oven, under the following conditions (vacuum, $T = 450 \text{ K}; t = 2 \text{ h}$). Obtained solid samples were uploaded to the reactor and burned in self-propagating mode under Ar atmosphere. The XRD data on the obtained product demonstrates that in this case the main formed intermetallic phase is NiAl and essentially zero counts for alumina phase was detected.

3. Conclusions
To conclude, it was demonstrated that based on the knowledge of the combustion mechanism and using of the inert environment, oxygen free fuel and combination of reactive solutions and solid precursors, one may significantly widen the range of synthesized compounds by using SCS. Not only pure metals and metal alloys, but also intermetallics and metal nitrides can be thus fabricated.

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