



Nanocomposite and mechanically alloyed reactive materials as energetic additives in chemical oxygen generators



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ABSTRACT

Chemical oxygen generators are widely used for aircraft, spacecraft, submarines, and mine rescue. Oxygen-generating compositions typically include alkali metal chlorate or perchlorate that decomposes at increased temperatures, a transition-metal oxide as a decomposition catalyst, and a metal fuel that reacts with part of the produced oxygen to provide heat for a self-sustained propagation of the decomposition/combustion wave. To increase the oxygen yield per unit mass, it is of interest to minimize the amount of metal fuel, but decreasing its content leads to pulsating combustion and undesired fluctuations of the oxygen flow rate. The present paper explores the feasibility of replacing iron and tin, currently used in oxygen generators, with reactive materials, produced by arrested reactive milling and by mechanical alloying. Because of their high energy density, easy ignition, and good storability, these materials have the potential to improve the performance characteristics of oxygen generators. Thermodynamic calculations for combustion of sodium chlorate mixed with various reactive materials identified the most attractive additives providing high temperatures and high oxygen yield. Experiments on combustion of sodium chlorate-based mixtures with nanoscale cobalt oxide catalyst and the most promising energetic additives were conducted in an argon environment, using laser ignition. Infrared video recording was used to investigate the thermal wave propagation over the mixture pellet. The experiments have shown that mechanically alloyed Al/Mg (1:1 mass ratio) material is a promising alternative to iron and tin, because significantly smaller amounts of this additive are needed for a steady propagation of the combustion wave.

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1. Introduction

Chemical oxygen generators, also called self-contained oxygen generators (SCOG) and oxygen candles, are widely used for aircraft, spacecraft, submarines, and mine rescue [1]. Oxygen-generating compositions typically include alkali metal chlorate or perchlorate (e.g., sodium chlorate, NaClO_3) that decomposes at increased temperatures with release of oxygen. Increased temperatures are achieved by an exothermic reaction between an added metal fuel (e.g., iron or tin) and part of the product oxygen. The compositions also include a transition-metal oxide catalyst (e.g., cobalt oxide, Co_3O_4) that significantly decreases the decomposition temperature of the oxygen source [2–4]. As a result, oxygen is generated

through a self-sustained propagation of the decomposition/combustion wave over the generator's chemical core [5–7].

In oxygen generators based on sodium chlorate, the metal fuel provides combustion temperatures of 400–800 °C (decomposition of NaClO_3 is exothermic and contributes to the total heat release). The minimum limit is determined by the necessity to fully decompose sodium chlorate and ensure a self-sustained combustion, while the maximum temperature is limited by the melting point of sodium chloride (NaCl) byproduct (800.7 °C [8]), melting of which hinders a uniform transport of the released oxygen outward and makes the process highly unsteady. Combustion of the metal fuel, however, consumes part of the product oxygen, thus lowering the oxygen yield per unit mass. It is of interest to minimize the amount of metal fuel, but decreasing its content leads to undesired pulsations of the combustion wave and oxygen flow rate [5–7].

The present paper investigates an approach to the design of efficient and safe chemical gas generators that exploits recently developed reactive materials. Specifically, the paper explores the

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feasibility of replacing iron and tin, currently used in oxygen generators based on sodium chlorate, with reactive materials produced by arrested reactive milling (ARM) [9–14] and by mechanical alloying [15–18].

Nanocomposite reactive materials obtained by ARM contain fully-dense, micron scale particles in which components are mixed on the scale of about 100 nm, but are not chemically bound. These materials include compositions combining metals and oxidizers as well as compositions that take advantage of uniform nano-scale mixing between components reacting exothermically and not requiring oxygen (e.g., intermetallic or metal–metaloid composites).

Mechanically alloyed powders were shown to be more reactive fuels compared to regular alloys or pure metals [15–18]. Their developed surface area accelerates ignition, which is also assisted by weakly exothermic, subsolidus intermetallic reactions. In addition, combustion may be optimized by finely tuned elemental compositions.

The nanocomposite and mechanically alloyed reactive materials have the potential to improve the performance characteristics of chemical oxygen generators. Because of a higher gas yield, more controlled heat release, and a smaller amount of energetic additives, both efficiency and process stability of chemical oxygen generators could be improved.

The objective of the present paper is to identify the reactive materials that are the most efficient additives to sodium chlorate in providing stable combustion and high oxygen yield. First, a broad range of reactive materials, including various thermites, intermetallics, and metal/nonmetal mixtures that had been synthesized by ARM, were screened through thermodynamic calculations for combustion of oxygen-generating compositions based on sodium chlorate. Then, several thermodynamically promising materials were tested experimentally as components of combustible oxygen-generating mixtures.

2. Thermodynamic calculations

Thermodynamic calculations of the adiabatic flame temperatures and combustion product compositions were conducted using THERMO (version 4.3) software, which is based on the Gibbs free energy minimization and contains a database of approximately 3000 compounds [19]. Of specific importance is the capability of this code to handle both intermetallic and thermite reactions in addition to conventional gas-phase combustion reactions. Since the available THERMO database did not contain thermochemical properties of sodium chlorate, the formation enthalpy of this compound, -365.8 kJ/mol [8], was added to the database. Pressure was equal to 1 atm in all calculations.

Table 1 shows the amounts of 25 binary mixtures that need to be added to sodium chlorate to provide the adiabatic flame temperatures of 600, 700, and 800 °C. Table 1 also shows the mass fraction of molecular oxygen (O_2) in the combustion products.

For comparison, Table 1 presents the values obtained for iron and tin, which are currently used in chemical oxygen generators. This allows one to readily downselect the mixtures that provide higher theoretical temperatures and O_2 yield compared to the current formulations.

Further, the values obtained for pure aluminum and magnesium are presented. Aluminum is not used in chemical oxygen generators because it does not ignite at the relatively low temperatures occurring in these generators and, in addition, does not show any catalytic effect on the decomposition of sodium chlorate [20]. Because of handling and stability problems (quick aging in oxidizing and moist environments and high fire hazard), magnesium is not used either. However, Al/Mg materials obtained by

mechanical alloying are promising additives because they ignite easier than Al and, at the same time, are expected to be substantially more stable and less hazardous than pure Mg.

In Table 1, the mixtures containing smaller overall wt% of additive compared to the formulation with Fe (and shown above it) are most promising. Among the metal–metal and metal–metaloid reactive materials, B/Ti and Al/Ti mixtures provide the best results, while Al/ $NaNO_3$ is the best among nanocomposite thermites. Although calculations were not performed for various Al/Mg alloys, considering the results obtained for pure Al and Mg, such alloys are expected to perform similarly to B/Ti and Al/Ti composites. Thermodynamically, all these additives are more efficient than iron or tin. More specifically, a lower concentration of the additive provides the same adiabatic combustion temperature and, simultaneously, a higher oxygen yield.

Note that the combustion products predicted to form by the thermodynamic calculations are fully oxidized. There are no metals or unoxidized compounds such as TiB_2 and AlTi in the predicted products. At the same time, the idea of using reactive materials is based on the initial exothermic reactions between the additive's components that kick-start combustion. The generated intermetallic or other phases are expected to oxidize in the subsequent reaction with the produced oxygen.

Thermodynamic calculations were also conducted for several mixtures that included an additional 3 wt% of Co_3O_4 , which was used as a catalyst in the present experiments. Those calculations did not lead to a noticeable deviation from the data presented in Table 1.

3. Experimental

3.1. Materials and preparation of mixtures

Combustion experiments were conducted with the following reactive material additives:

- Pure metals: Fe and Mg.
- Mechanically alloyed powders: Fe/Mg (3:1), Al/Mg (4.7:5.3), Al/Mg (7:3), Al/Mg (4:1), and Al/Mg (9:1).
- Reactive metal–metal composites: Al/Ti (4:1).
- Reactive metal–metaloid composites: B/Ti (2:1).
- Nanocomposite thermites: Al/ $NaNO_3$ (5:3), Al/ $NaNO_3$ (2.1:1), and Al/ MoO_3 (8:1).

Here, the mole ratios are indicated. Note that for Al/Mg, 4.7:5.3 mole ratio corresponds to 1:1 mass ratio.

For using as single metal additives, iron (99.9% metal basis pure, <10 μ m) and magnesium (99.5% metal basis pure, -325 mesh) were purchased from Sigma Aldrich and used as received.

For preparation of Fe/Mg powders, starting materials included elemental powders of Fe (Alfa-Aesar, 98% metals basis, -325 mesh, reduced) and Mg (Alfa-Aesar, 99.8% pure, -325 mesh). Powders were mechanically milled using a SPEX SamplePrep 8000 shaker mill with 50-ml flat-ended steel vials and steel milling media (9.5 mm diameter balls). Each vial was loaded in argon with a 5-g powder load and a ball-to-powder mass ratio (BPR) of 10. To inhibit cold-welding and prevent partial reactions during the milling process, 5 ml of hexane (C_6H_{14}) was added to each milling vial as a process control agent (PCA). The powders were milled for 6 h.

The same shaker mill was used to prepare nanocomposite Al/ MoO_3 powders, following the procedure described in [10,11]. Milling time was 60 min and 8 ml of hexane per milling vial was added as a PCA.

All other materials prepared using ball milling employed a Retsch PM-400 MA planetary mill equipped with an air conditioner,

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