Combustion study of mechanically alloyed Fe-B (50% wt)

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Abstract

The development of improved pyrotechnic systems like ignitors, flares, tracers or inflaming agents searches always for new energetic metallic compounds which allow to adapt this systems to specific application. Purpose of this research was to study the feasibility of using a new developed boron-rich material as combustible. Raw material was mechanical alloyed iron powder with 50% boron (by weight). The elementary powders were mixed in a high-energy mill for 36 hours in inert atmosphere. This material was characterised by differential thermal analysis, sieve analysis, X-ray diffraction and scanning electron microscopy. The material thus obtained was compared with elemental Fe, elemental B, and plain elemental mix of Fe and B powders (50% wt., not mechanically alloyed). A spatula tip of every mixture was ignited under atmospheric conditions. The data analysis of each spectrum by comparing with a calculated one results in combustion temperatures and emission properties. Mechanically alloyed Fe-B show a completely different combustion behaviour as the mixture with pure boron and iron of the same stoechiometry. The Fe-B alloy reduces combustion temperature and degreases burning time.

Keywords: Mechanical alloying, powder metallurgy, boron, combustion.

1. INTRODUCTION

Mechanical alloying is widely used to prepare amorphous materials or other non-equilibrium materials [1, 2]. The Fe-B system lends itself to a detailed study of mechanical alloying. The alloys have been prepared by various techniques such as rapid solidification, sputtering, or vacuum evaporation [3, 4] and their amorphization studied by the method of mechanical alloying. A number of reports have given the amount of boron required for the maximum degree of amorphization as percentages that range from 60% to 20%. Thermodynamic calculations estimate amorphization in the range 32 – 47% of boron [5-11]. The use of boron in combustion processes presents serious problems related to ignition and combustion phenomena. In the majority of cases, the heat capacity diminishes due to poor combustion processes that reduce the efficiency of the engine [12]. To solve this problem, solid propellants can improve their combustion performance including solid additives (mainly metals) [13].

2. EXPERIMENTAL

As already stated, the Fe/B material was manufactured by powder metallurgy (P/M). The raw powders used were: iron ASC300, a water-atomized powder of 99.9% purity, supplied by Höganäs (Sweden), particle size under 45 μm; amorphous boron, supplied by Strem Chemicals, 92-95% purity (a trace of magnesium), with particle size of 1 μm; and natural graphite of particle size under 50 μm.

The base powders, iron and boron (50% by weight, from now on, Fe/B) were mixed in an attritor at 700 rpm, in argon atmosphere, with a charge/ball ratio of 15:1 and with the addition of 1.5% of the lubricant. Moreover, 1% (wt.) of graphite was added. The processes taken place in this system are reported elsewhere [14]. This material was characterised through X-ray diffraction, sieve analysis, DTA (carried out in argon) and SEM.

Metallic powder was mixed with ultrafine Ammoniumperchlorate AP (∅ 2 μm). A spatula tip of every mixture was ignited under atmospheric conditions. DV-video prints and highspeed NIR-spectroscopic measurements have been made over the complete combustion time. The data analysis of each spectrum by comparing with a calculated one results in the combustion temperatures. Combustion results were compared with plain ASC300 iron powder, plain boron, and a mix (50% wt.) of iron-boron, so 4 different samples were analysed.

2.2. HGS - NIR-Spectrometer

A grating spectrometer HGS 1700 based on a Zeiss System MCS 511 modified for flame measurements measured the NIR spectra of the sample flames. It scans the spectral range of 1.0 to 1.7 μm by a InGaAs diode array (256 elements) with a resolution of 15 nm up to a scan rate of 300 s^{-1} whereas a scan rate of 140 s^{-1} was used here. The imaging optics consist of a special optic with a narrow slit achieves a space resolution about 1 mm. The quantitative calibration occurred by a commercial black body radiator.

2.3. Data analysis of NIR/IR spectra (BAM-Fit)

The evaluation of NIR and IR spectra uses the BAM code [15,16] of ICT to model band spectra of reaction products. The code calculates NIR/IR-spectra (1 - 10 µm) of inhomogeneous gas mixtures of H_2O (with bands around 1.3, 1.8, 2.7 and 6.2 µm), CO_2 (with bands near 2.7 and 4.3 µm), CO, NO and HCl taking into consideration also emission of soot particles. It is based on the single line group model [17] and makes also use of tabulated data of H_2O and CO_2. Taking into account that there are many unknown parameters influencing the emission spectrum of an inhomogeneous gas mixture, only a simplified model can be applied. Therefore, it was assumed that the flame is just one hot emitting layer of undefined thickness, constant temperature, constant concentration of the various gases and solid particles in thermal equilibrium. These assumptions lead to a reasonable number of parameters, which can be determined by a least squares fit procedure fitting calculated spectra to experimental data. With this restriction, temperature and ”concentration length” (concentration × length) of major combustion products like water, CO_2, CO, NO and HCl have been determined. Continuum radiation of condensed materials have been calculated as a grey emitter. This was sufficient in most cases of this presented study.

3. RESULTS AND DISCUSSION.

Mechanically alloyed powder was firstly characterised through XRD (Figure 1). After this time, iron is almost in amorphous state (peaks are very weak), and iron borides have been formed. To properly see this effect, Figure 1 shows the evolution of XRD patterns with time, in different samples taken each 6 h from the mill up to 36 h. Non-normalised patterns (Figure 1 left) shows the weakening of iron powders, while normalised patterns (Figure 1 right) shows the appearance of iron boride peaks. This amorphous state is confirmed by SEM (Figure 2). Sieve analysis (Figure 3) shows that obtained particle size is very small, being 50% of particles less than 5 micron. Some agglomerates exist, and thus maximum particle size found was around 35 micron. DTA (Figure 4) shows the high thermal stability of powder, not showing any reaction up to 1400ºC; only typical phenomena of rearrangement of particles are appreciated. Powder is not easily oxidized, as simultaneous TG shows, the differences in weight are due to the oxygen that powder has after mechanical milling (about 5% wt.).

3.2. Combustion.

Figure 5 shows thermodynamic combustion temperatures of AP/B/Fe-mixture calculated with ICT-Code [18]. Due to the heat of formation of the newly synthesised mechanical alloyed Fe-B was unknown, only elementary Fe and B were used as input for the calculations. The calculations show that maximum temperatures of 3000 K could be expected at 75% AP closely to the stoechiometric point.

The pyrotechnic mixtures show different combustion behaviour and flames. In figure 6 characteristic pictures of different burning mixtures are grouped. AP combined with pure boron burns fast with a highly illuminating green flame that is typical for boron [19]. Only a view particles could be observed. The mixture of AP with pure iron burns much slower with yellow emission. Many particles burning particles were thrown out the combustion pan. The mixture AP with pure boron and pure iron show a similar green flame shape as the mixture with pure boron, but some more particle emissions. The reaction is as fast as with pure boron. It appear that the combustion behaviour is a combination of this with the pure compounds. In contrast to this the burning behaviour of the mixture with the Fe-B alloy burn similar like the mixture with pure iron, showing a high amount of glowing particles only a slight green shine could be observed. The reaction was slower than with the pure particle combination.

Figure 7 shows NIR-Spectra and including BAM-Fit for temperature determination. In the detected NIR-range from 1 to 1.7 µm the emission is dominated of a grey continuum emission that is characteristic to surface and particle radiation. In the wavelength range between 1.35 and 1.60 µm boron oxide emit an additional band which is obviously strong at the mixtures with pure boron but only rudimentary in the mixture with Fe-B alloy [20].

The determined combustion temperatures a summarised in figure 8 for all investigated samples with different mixtures ratios. The mixtures with the pure components show combustion temperatures from 1900 to 2200 K. The mixture with the mechanical Fe-B alloy burns cooler with a temperature between 1700 and 1850 K. All temperatures are much lower than the calculated ones of figure 5. This can as usually explained to heat loss by surface radiation corresponding to high emission degrees of continuum radiation and temperatures. It should be remarked that the focal point of temperature measurements was set to the surface of the samples in the pan, so that mainly the reaction of the samples determines the temperature. Only the erupted particles may show a secondary reaction with air, that should have had a minor influence on these measurements.

4. CONCLUSIONS.

The preparation of mechanically alloyed Fe/B powders allows that iron reaches the amorphous state and forms the intermetallic compound.

Fe/B (50%wt) mix is good as catalyser when it is not mechanically alloyed.

The combustion measurement show clearly a completely different combustion behaviour of the mechanical Fe-B alloy compared to stoechiometrically same mixtures with pure B and Fe. The alloy has a cooling influence to the reactions and moderates combustion speed.

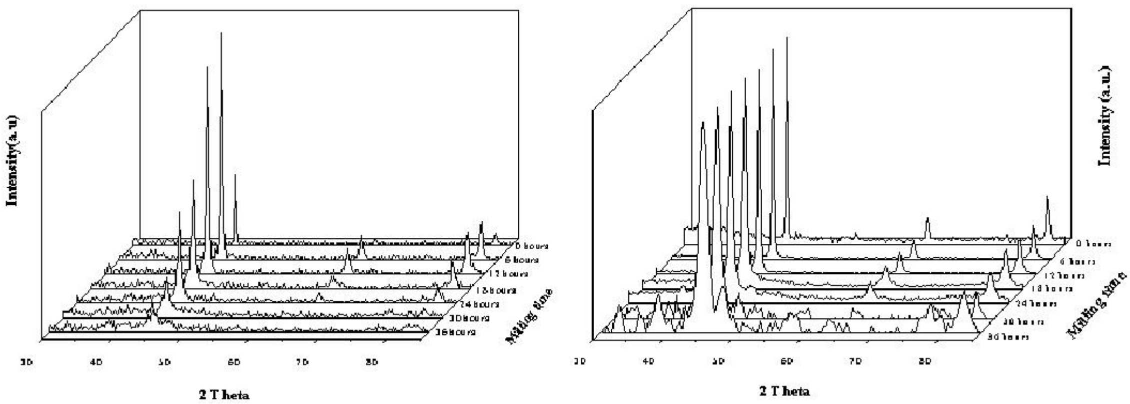

Figure 1. X-ray diffraction pattern of Fe/B mechanically alloyed for 36 hours. Evolution with time. Left, non-normalized patterns; right, normalised patterns.

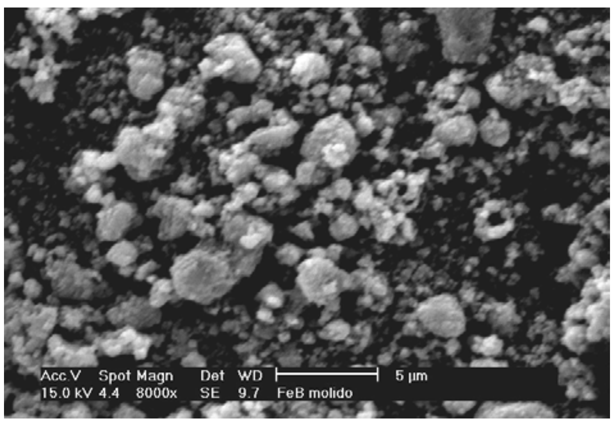

Figure 2. Microstructure (SEM) of Fe/B mechanically alloyed for 36 hours.

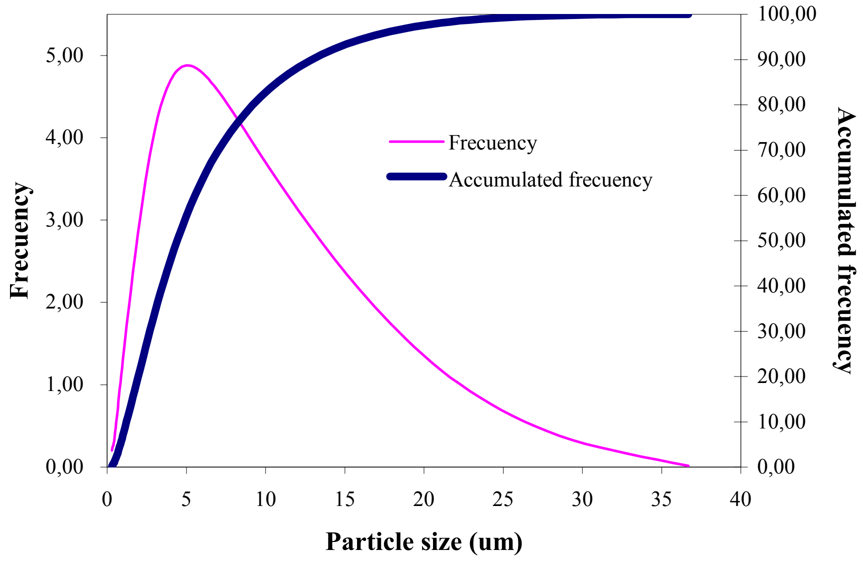

Figure 3. Sieve analysis of Fe/B mechanically alloyed for 36 hours.

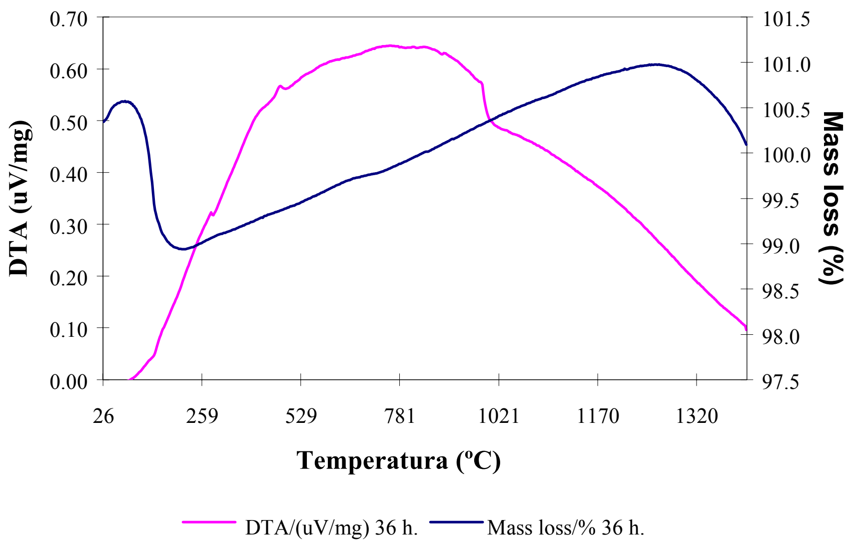

Figure 4. DTA of Fe/B mechanically alloyed for 36 hours.

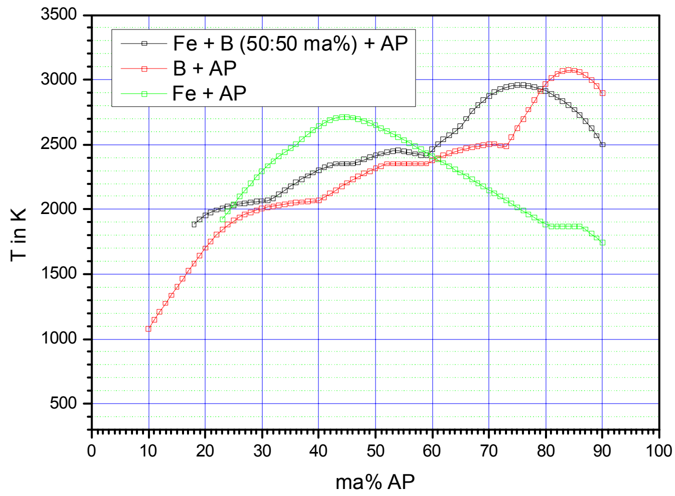

Figure 5. Thermodynamic combustion temperatures of AP/B/Fe-mixture (calculated with ICT-Code)

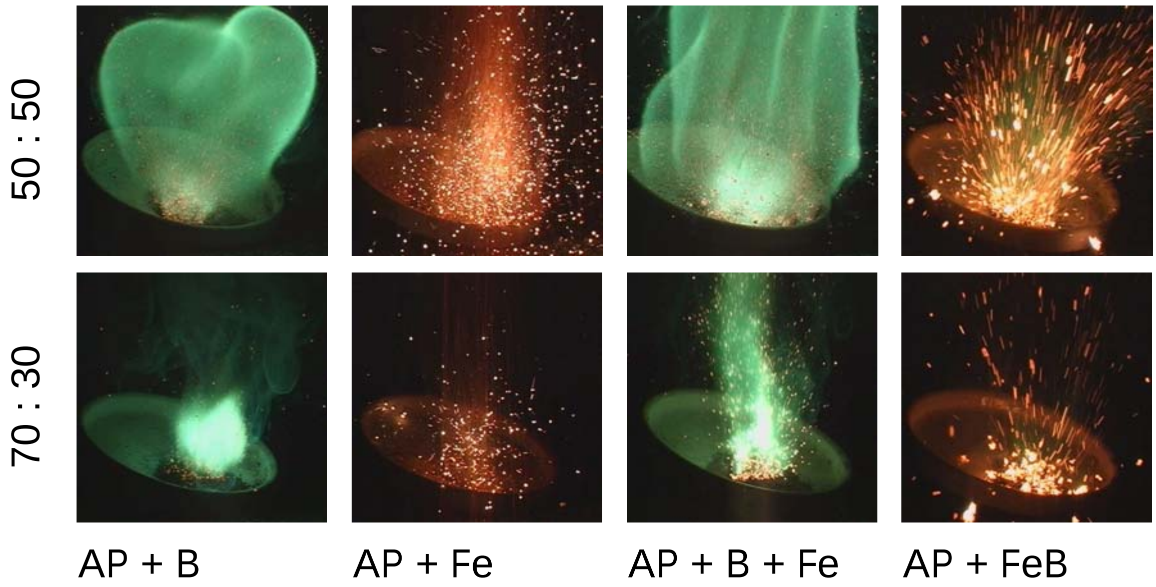

Figure 6. Flame pictures of different samples and compositions.

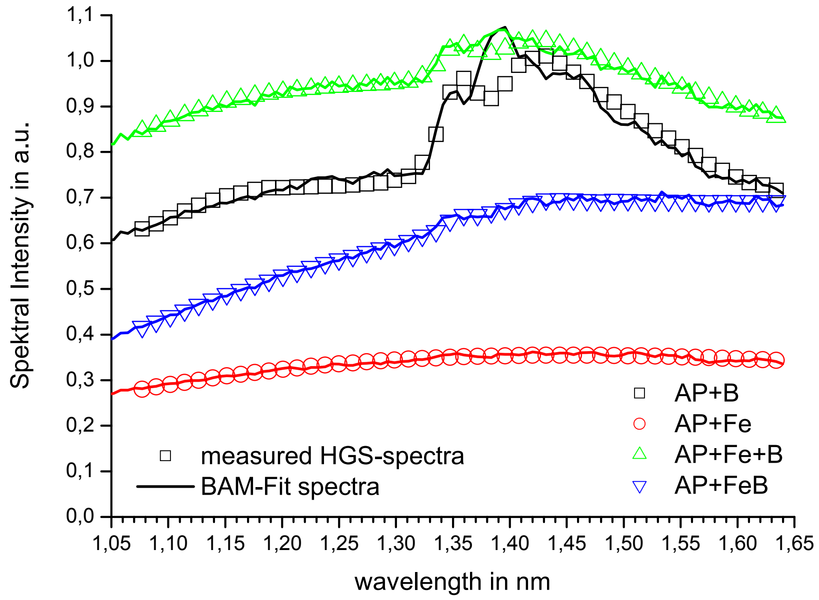

Figure 7. NIR-Spectra and BAM-Fit for Temperture Determination.

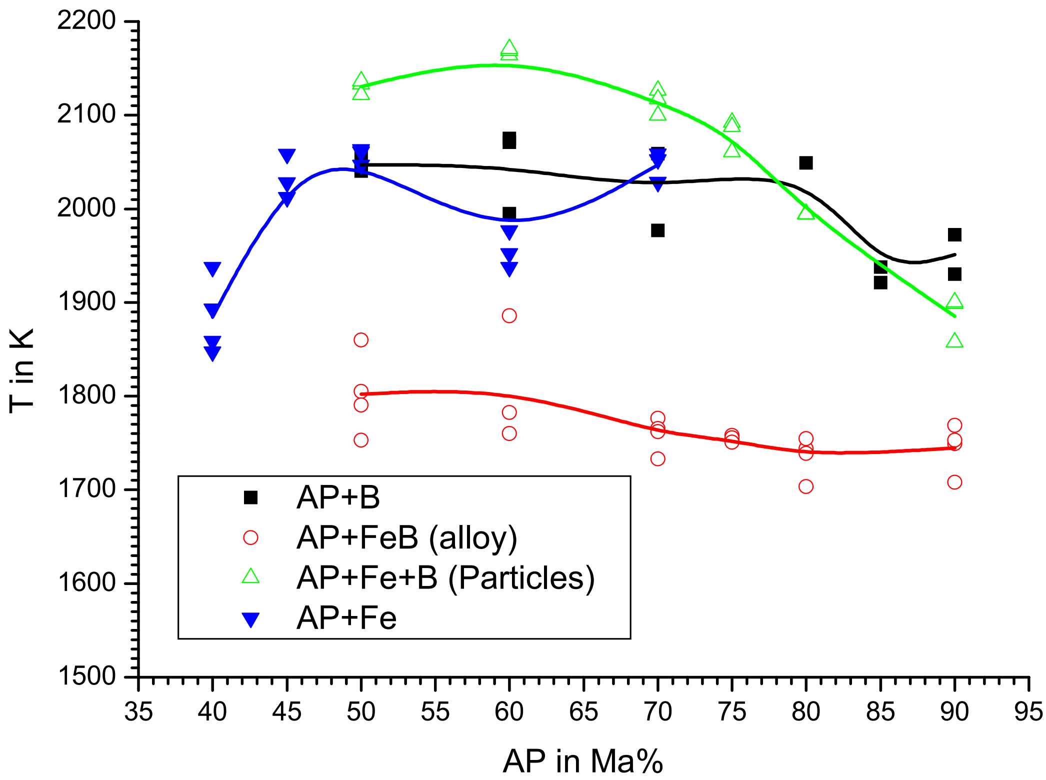

Figure 8. Temperature measured with HGS-spectrometer

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