

Comparison of nanoparticulate thermite mixtures formed by conventional and supercritical fluid processes

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Abstract

This work compares the properties of nano-particulate thermite mixtures of conventionally formed composites with those mixed by a supercritical fluid technique (RESO: Rapid Expansion of a Supercritical Dispersion).

Decreasing the particle size of a thermite system (e.g. aluminum and iron oxide) leads to an increase of reaction front velocity (RFV) from the order of cm/sec for conventional particle sizes in the sub-millimeter range to 50 m/sec and above for systems in the nanometer particle size range.

The conventional way of mixing Fe_2O_3 and Aluminum nanoparticles was realized by suspending both components in an organic solvent and mix them by a homogenizer. EDX images from the prepared samples show a higher degree of mixing for the RESO composite in comparison to the conventionally formed sample.

1. Introduction:

Thermite mixtures are meta-stable intermolecular composites (MIC) typically consisting of at least two species: a fuel and an oxidizer. The most commonly used oxidizer is aluminum. The best examined fuel is iron oxide (Fe_2O_3) and both were examined within this work.

The reaction kinetic and therefore burning behaviour depend highly on the physical shape of the used materials. Especially particle size and the condition used for the compounding have significant influence on the reaction [1].

Some work has been done to determine the influence of the degree of mixing of both particular fractions [2]. It is not surprising, that especially in the range of nano-scale particle sizes the mixing homogeneity is of particular interest. The more uniformly distributed the formed bulk of particles in a thermite mixture is, the better the reaction can take place [3].

In this range where Nanoparticles have to be arranged in a random structure a previous step must break up the commonly existing agglomerates of each species.

In the work presented here different ways of mixing and desagglomeration were discussed to form varying homogeneities of aluminum and iron oxide nanoparticles.

The RESO technique uses a dispersion of the components in a supercritical fluid and the impact of the expanding fluid to form the composite bulk material [4].

Supercritical fluids penetrate porous systems like gaseous substances. They also have high expansion coefficients, which is the reason for a high acceleration rate during the expansion from supercritical to atmospheric conditions. The expansion path typically leads through nozzles with diameters from 50 μm to 200 μm .

In this work supercritical CO_2 have been used, which is gaseous under atmospheric conditions and inert so that the processed material is dry and protected from oxidation.

2. Experimental details

2.1 Materials

The used iron oxide Fe_2O_3 ("NANOCAT® Superfine Iron Oxide") was supplied by MACH1. The primary particle size was declared by the manufacturer to be 3 nm; the size of the existing agglomerates was measured by laser diffraction using a Malvern Mastersizer without any additional treatment to 28 μm . The size of remaining agglomerates after ultrasonic treatment of 5 min was measured to 2.3 μm .

The powder impression is free flowing and very dusty, particles are easily attracted by electrostatic charges.

The aluminum used for this work is the so-called ALEX from TOMSK University. The primary particle size of this material varies from 10 nm to up to 250 nm. The laser diffraction analysis of the particle again gives information about the size of the existing agglomerates with a mean particle size of 2.6 μm .

The powder material is again free flowing but in comparison to the iron oxide it is less dusty.

The analysis of XRD spectra the primary grain size of the Fe_2O_3 particles confirmed the order of magnitude of the declared primary particle size. The interpretation of the peak width fits to a grain size of 1.5 nm for the original raw material.

The mean particle size of the ALEX raw material was determined to approx. 26 nm.

2.2 Mixing experiments

Two different mixing procedures were tested. A conventional procedure uses a homogenizer and an organic solvent to suspend and mix both species. After a drying step the bulk material was re-suspended for the particle size measurement. The supercritical RESD technique mixes the particles by suspending the particles in a supercritical fluid and expands the dispersion from supercritical state to atmospheric conditions. A subsequent drying step is not necessary.

2.2.1 Conventional mixing procedure

The conventional mixing procedure uses fraction forces in an accelerated liquid to break the originally existing agglomerates.

The conventional technique uses a homogenizer which mixes a suspension of both species:

13.5 g of ALEX and 40 g of Fe_2O_3 were suspended in 800 ml dichloromethane.

The homogenizing procedure was carried out stepwise. The homogenizer was actuated for 3 minutes each followed by a 2 minutes break because of the low boiling point of dichloromethane of 40°C. This was repeated four times. The subsequent drying step in a Rotavapor was carried out under argon atmosphere in order to prohibit oxidation of the ALEX. Beilstein tests confirmed that there are no significant residues of chlorine in the mixed product.

The resulting bulk material is a granular powder which is not free flowing not dusty and easy to handle. The powder density is typically higher comparing to the raw materials.

2.2.2 RESD mixing procedure

The RESD technique benefits from the specific properties of the supercritical fluid. It penetrates the pores of the agglomerates because of the complete absence of surface tension. Consequently, it has a complete wetting behaviour to all surfaces. While passing the nozzle and expanding to atmospheric conditions the expanding fluid blasts the agglomerates from the inside.

The smaller high pressure vessel volume allows preparing a sample size of 5 g.

Both fractions were added to the pressure vessel which was pressurized to 300 bar and heated to 50°C. The pressurized vessel was stirred for 10 minutes for equilibration

purposes. The valve at the bottom end of the pressure vessel was pneumatically switched for 1 second. The open valve allows the suspension to expand into a collecting vessel with a filter covered outlet. The expansion path leads through a nozzle. After each switching the pressure vessel was pressurized again, automatically. After reaching 300 bars again, the suspension was allowed to equilibrate for 1 minute. The switching was repeated 15 times until the content of the pressure vessel was completely expanded to the collecting vessel.

The processed powder is free-flowing and very dusty. The macroscopic appearance is similar to the Fe_2O_3 .

2.3 Particle size analytics

As a result of the mixing process the particle size of the existing agglomerates change. After the mixing procedure the particle sizes measured by laser diffraction provide information about changes in size and stability of the remaining agglomerates.

The processed particle mixtures have been characterized again by laser diffraction. The procedure of the sample preparation by ultrasound treatment is similar to the measurements of the raw material. The laser diffraction allows characterizing particles from 0.3 μm and bigger and is therefore a suitable tool to provide information about the size of agglomerates, but not of the size of the primary particles.

From the particle size analytics by laser diffraction it can be seen, that the size and the stability of the existing or by the mixing process formed agglomerates change. The XRD analytics allows proving whether the sizes of the nano-scale grains have changed by the homogenizing step as well.

By interpretation of the peak width from XRD measurements for Fe_2O_3 in Figure 1 and 2 it can be seen that the smallest units of each species haven't changed due to the mixing procedure. The sizes of the nano-scale units of the pure material before and after the homogenizing step are nearly of the same size:

Fe_2O_3 raw material:	1.5 nm
Fe_2O_3 after homogenization:	1.7 nm
ALEX raw material:	26 nm
ALEX after homogenization:	24 nm

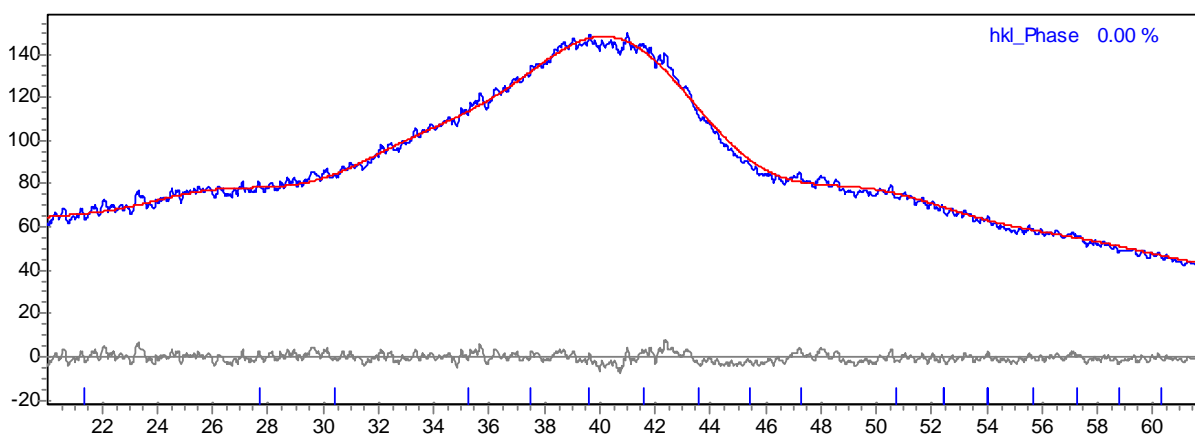


Figure 1: XRD peak width interpretation of primary particle size of the raw material Fe_2O_3 with 1.5 nm

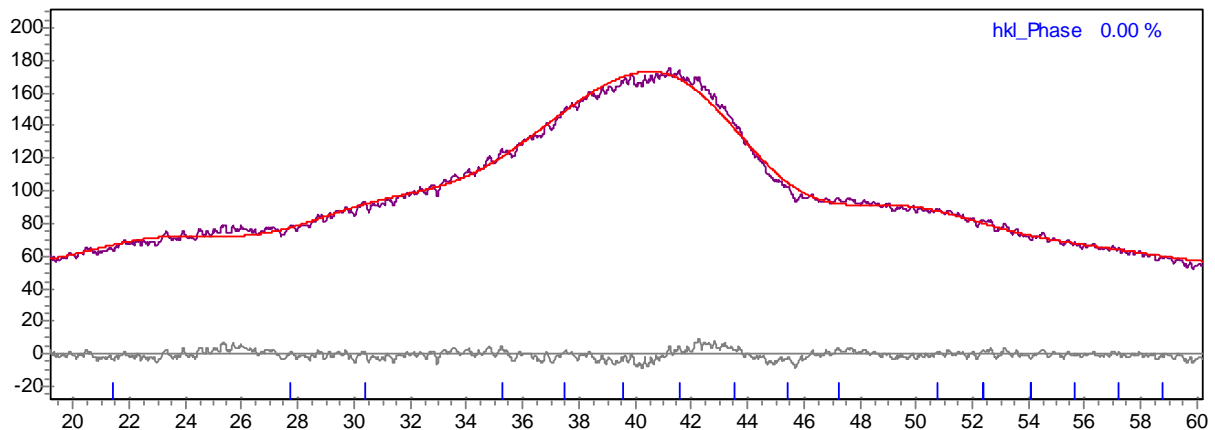


Figure 2: XRD peak width interpretation of primary particle size of homogenized Fe_2O_3 with 1.7 nm

It can be assumed, that the blasting effect of the expansion is not affecting the primary particle size when the sample was RESD processed.

2.4 Mixing quality

The quantification of the mixing quality is difficult to achieve, but a macroscopic impression of mixing quality and a pragmatic way to achieve information about the mixing quality is the interpretation of EDX images gained from the SEM.

The limitation of the EDX analytics is that the spatial resolution is restricted to the lower μm -range. The EDX distinguishes different elements; in this work the EDX focussed on aluminum and iron.

Figures 3 shows the comparison of the EDX images of RESD and conventionally mixed samples.

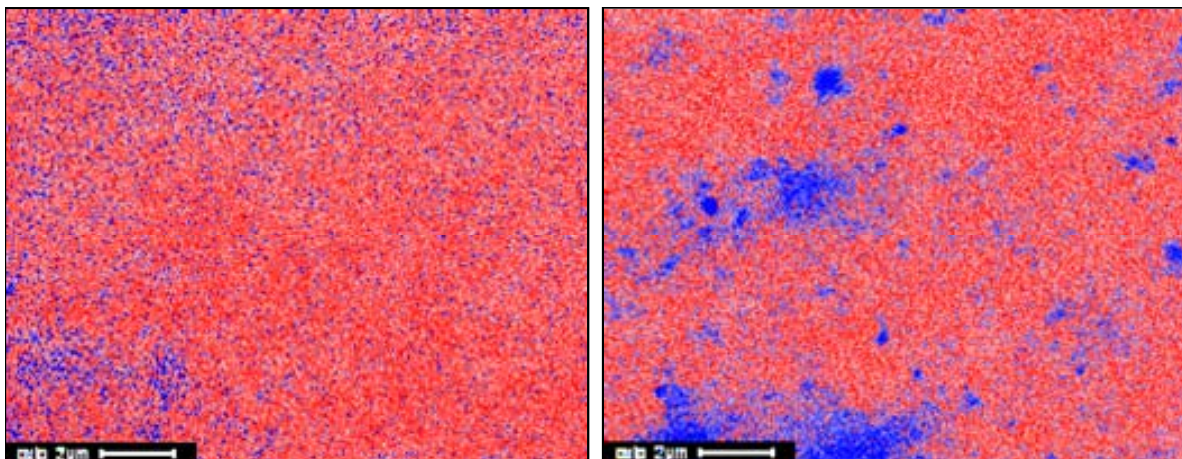


Figure 3: EDX from a RESD prepared sample (left) and a homogenized sample (right) red: Fe_2O_3 , blue: Al

Comparing both images it is obvious that the elements iron (red) and aluminum (blue) are more uniformly distributed at the left image referring to the RESD processed sample, whereas the particles from the conventionally mixed sample are still oriented in agglomerated structures, which are in size similar to the size (approx. 1-2 μm) of agglomerates measured by laser diffraction.

The measured sizes of the agglomerates of the RESD sample were about four times smaller in the range of 0.6 μm which is also confirmed by the EDX image.

2.5 Characterization by reaction front velocity (RFV)

Reaction front velocity is a suitable tool to measure the reactivity of MIC's [5]. In the setup used for this work a PMMA channel with a cross section of 5x5 mm² and a length of 40 cm was used. The RFV is measured by two techniques: The burning rate was observed by a high speed camera and the interpretation of the response signal of two optical photo diodes which are coupled with optical fibres. These fibres are connected to the channel with a distance of 30 cm. In Figure 4 an image of the high-speed camera (2000 frames per second) demonstrates the reaction front of a RFV experiment. The channel was filled with 2.2 g of homogenized sample material.

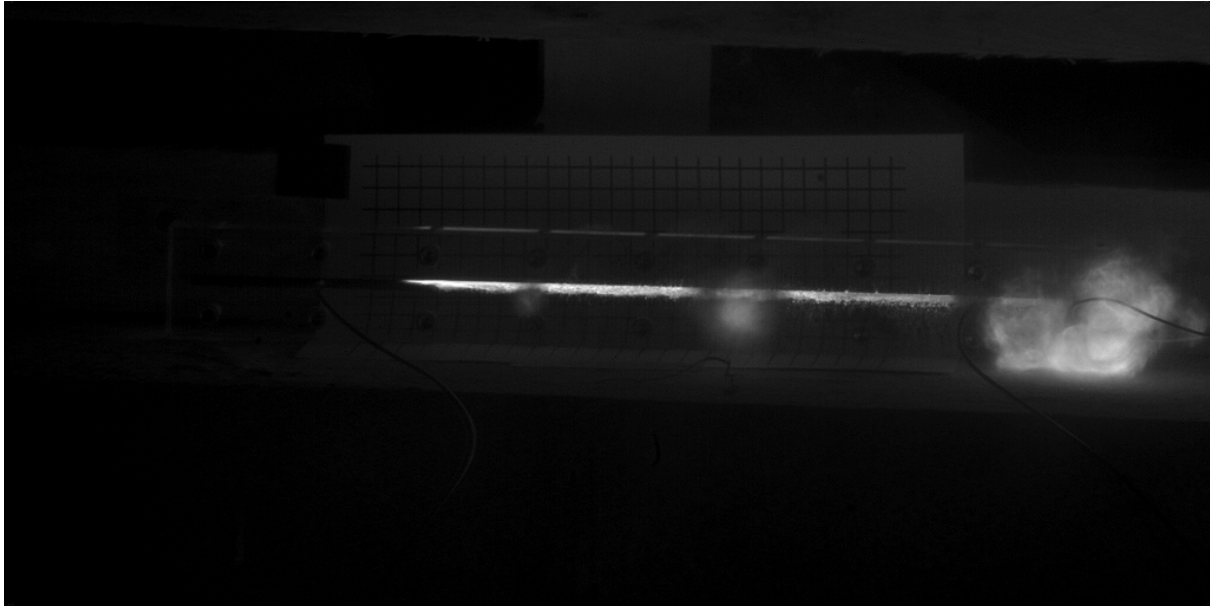


Figure 4: Still photograph from a high speed movie of reaction front velocity measurement of a homogenized sample

In this case the RFV was determined by high-speed camera to 112 m/s (figure 5). The reaction was started by an ignition tablet

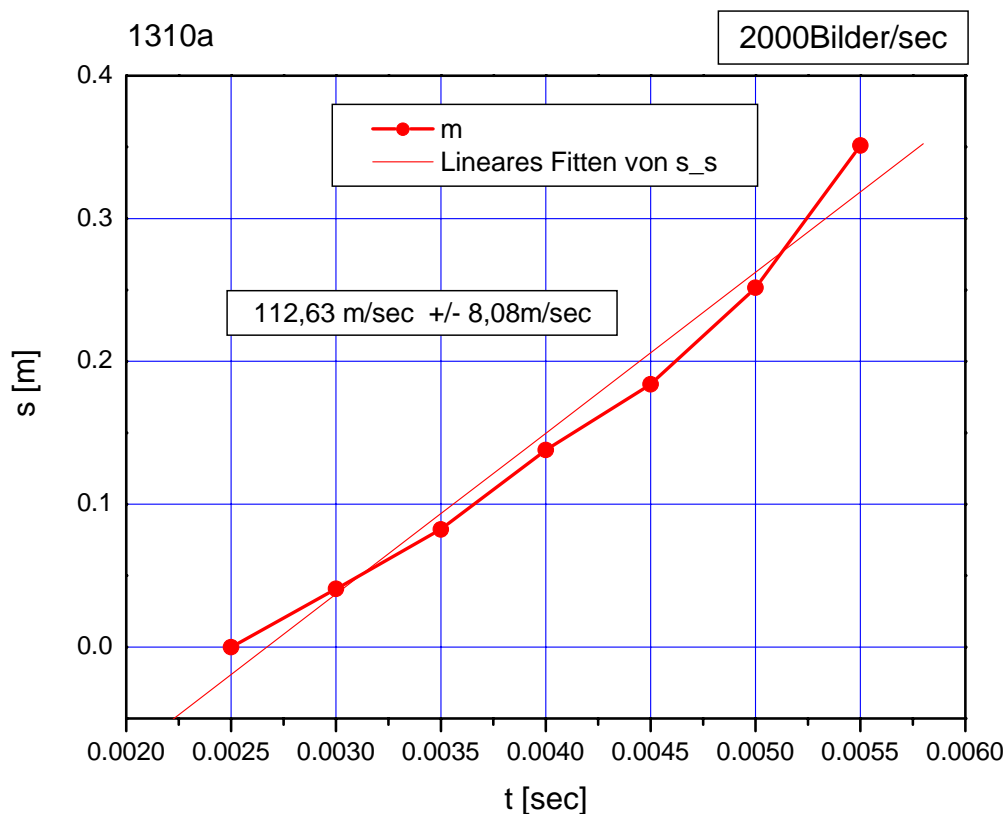


Figure 5: Interpretation of RFV from the high speed camera movie for a homogenized sample

The interpretation of the response signal of the photo diodes leads to a velocity of 85 m/s. The differences between both measurement methods may be caused by insufficient response times of the photo diodes and a weak data recording frequency of the used hardware.

The measurements of the reaction front velocity are not finished yet and will be subject of the poster presented at the annual ICT conference.

3. Discussion

Different methods for characterizing mixtures of nanoparticles have been presented. From XRD measurements it was shown, that the homogenizing step didn't influence the primary particle size at the nanometer scale. The homogenizing step influences the size and the stability of agglomerates.

Although the final comparison of both different prepared samples by reaction front velocity is not available yet, the intermediate results show that the RESD process is a suitable technique to form homogeneous mixtures of nanoparticles. The mixing didn't change the primary particle size as the XRD measurements showed. But change in size and stability of the remaining agglomerate differ between the conventional mixed samples and the RESD processed ones.

It could be demonstrated that the RFV can be measured by channel experiments.

How the size and stability of the agglomerates and the homogeneity of the species distribution of the sample influence the reaction front velocity will be presented at the poster session of the ICT Annual Conference 2006.

Lit.:

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