

Effect of Mechanical Activation on the Reactivity of Composites for Flameless Heaters

A. Kaliyeva^{1*}, Ye. Tileuberdi^{1,2}, L. Galfetti³, Ye. Ongarbayev^{1,2}

¹Al-Farabi Kazakh National University, 71 Al-Farabi ave., Almaty, Republic of Kazakhstan

²Institute of Combustion Problems, 172 Bogenbai Batyr Str., Almaty, Kazakhstan

³Politecnico di Milano, Space Propulsion Lab (SPLab), Milano, Italy

Article info

Received:

4 October 2019

Received in revised form:

21 December 2019

Accepted:

6 March 2020

Keywords

Flameless heaters

Mechanochemical activation

Exothermic reaction

Powder mixtures

Heat transfer sources

Self-heating

Abstract

The work is devoted to the activation of metal powder mixtures suitable for use in flameless food heaters. Four activated powders have been manufactured starting from the reference material using a standard technique. Activated powders exhibited a significant increment of the reactivity for the reference mixture. Experimental tests were carried out to characterize the resulting composites in terms of the combustion rate. The oxidation reaction at a low heating rate was monitored using a SEIKO EXTAR II thermal analysis machine and its tests were carried out at open air in temperature range starting from room temperature up to 1150 °C at the heating rate of 10 °C/min. Powders activated by mechanical activations and the initial mixture of materials were characterized in terms of apparent density, absorbed surfactant with the mass of sizing, i.e. granulometry, oxidation properties at a low heating rate. With increase the grinding time, the color of the powder switches to dark tones. Powder granulometry was performed on a MALVERN laser granulometer MASTERSIZER 2000 using dry block SCIROCCO. Three measurements for each sample were performed and the results were averaged. The tests were recorded and processed by digital technology to make the combustion rate of the powders, also the experimental setup used for investigations was presented. The sample Al_S-Al_F-MnO₂-SiO-150 is characterized by the lowest metal content, and by the most regular combustion propagation. The powder Al_S-Al_F-MnO₂-SiO-50 features the highest metal content, but the less regular combustion propagation. The use of mechanical activation allows increasing the number of nanoscale materials, which contributes to the synthesis of highly effective flameless food heaters.

1. Introduction

Nowadays, in many countries of the world, great attention is paid to the development of new formulations for flameless food heaters. Heaters along with canned products are part of the individual rations of military personnel in the United States, Europe, Japan, Russia, and other countries. They provide an easy and safe method for heating food [1–4].

The technology of manufacturing flameless heaters has been known for over a hundred years. Flameless food heaters which consist of a variety

of their compositions found wide application. A well-known flameless ration heating is exothermic reaction provided by calcium carbonate, sodium carbonate, calcium oxide and aluminum powder mixtures. Another type of flameless ration heater is oxidized metals, such as magnesium, which is activated by adding water. Flameless heating devices suitable for using at night without producing visual effects and which are not affected by wind or inclement weather are of an urgent need [5–6].

The compositions being developed have an excellent perspective in the field of application in all facilities of the Ministry of Defense of the Republic of Kazakhstan, where military personnel and staff are fed in the field conditions. Hunters,

*Corresponding author. E-mail: asem.kaliyeva@mail.ru

professionals of a survival, fans of adventures and active recreation also have a huge interest in the flameless food heater (FFH).

The new method of obtaining compositions for flameless food heaters is aimed at using mechanochemical activation of metal powders and other components, increasing the efficiency of interaction between reagents.

Unfortunately, there are no published investigations in the development of flameless food heaters in Kazakhstan. Flameless food heater (FFH) compositions in Kazakhstan are mainly imported from different countries of the world. Therefore, conducting research and technological development for the creation of domestic compositions of flameless food heaters is relevant and practical importance within the framework of national interests.

Therefore, conducting research and development of technological methods aimed at the creation of domestic composite materials for the flameless food heaters can be performed by the use of mechanical activation, which allows the powder to get out of equilibrium and acquire special properties. As the distance from the equilibrium state increases, the number of parameters that determine the state of the system increases, thereby expanding the variety of structures implemented in the material, and, consequently, its properties. Mechanical activation allows creating active states in a solid body, opening up a certain perspective for carrying out and accelerating chemical reactions between solid bodies and obtaining materials in a highly non-equilibrium state. The use of the method of mechanical activation is also a promising direction in the synthesis of composite materials for flameless heaters for the rational supply [7–10].

2. Materials and methods

2.1. Aluminum powder

Aluminum is a high-density energetic material (enthalpy of aluminum oxidation in O_2 by mass was 31.0 kJ/g and by volume was 83.6 kJ/cm³). This, together with the relatively low O_2 -demand and the reduced cost, yields to the extensive use of Al in condensed energetic systems. Typically, Al particles are passivated by air and present a layered structure with a metal core surrounded by an amorphous Al_2O_3 shell. The latter is purposely generated by controlled powder exposure to a dry air environment during the production phase. The Al_2O_3 layer prevents the fast Al reaction with the

surrounding environment at ambient conditions. The thickness of the oxide shell is primarily controlled by the diffusion of oxidizing species (in particular, O_2) toward the metal core. For temperatures in the range ambient-temperature to 673 K, the limiting thickness of this layer (4–5 nm) seems independent of powder morphology and size [11]. For $T > 673$ K, the oxide layer thickness and its crystalline structure change in the presence of O_2 . Currently, commercial powders are based on air-passivated Al. The key features of Al powders in the micron-sized range are high Al content (typically higher than 95 wt%) with specific surface area (SSA) usually lower than 1 m²/g. While the metal content grants a high theoretical energy content to the powder, the relatively low SSA yields in limited reactivity (i.e., high ignition temperature). Nano-sized Al (nAl) powders exhibit increased reactivity over the conventional micron-sized Al (Al) [12]. In general, air-passivated nAl shows SSA ≥ 10 m²/g, and a reduced Al (< 90 wt%). Taking into account the enhanced performance in a combustion environment, nAl with a high reactivity may yield issues related to aging under storage. In particular, powders may lose Al during storage. As a consequence, the effects of their combustion are altered (i.e., reduced enthalpy release, different reaction mechanism). In general, air-passivated nAl shows SSA ≥ 10 m²/g, and a reduced Al (< 90 wt%).

In the work were used Al powder with particle sizes ranging from micron to submicron and nanoscale. Nanosized aluminum particles have several features, which make them interesting for energy applications. Compared to micron-sized aluminum, they have a higher reactivity and lower flash point. The advantages of using aluminum nanoparticles are regarded to provide agglomeration characteristics of larger particles, earlier ignition, a higher overall rate of thermal evolution and a further increase in the combustion rate for functionalized particles. In the course of the analysis, various properties of powders are investigated with an emphasis on application in energy systems. Specific surface area (SSA) measurement are conducted for comprehensive characterization of powder morphology (particle size, shape and texture), structure and composition [13, 14].

In this process, two different powders, spherical and flakes, were investigated. The microstructural features of the powder particles were determined with scanning electron microscopy (SEM). Figure 1 presents the shape and microstructure of the two types of different aluminum particles.

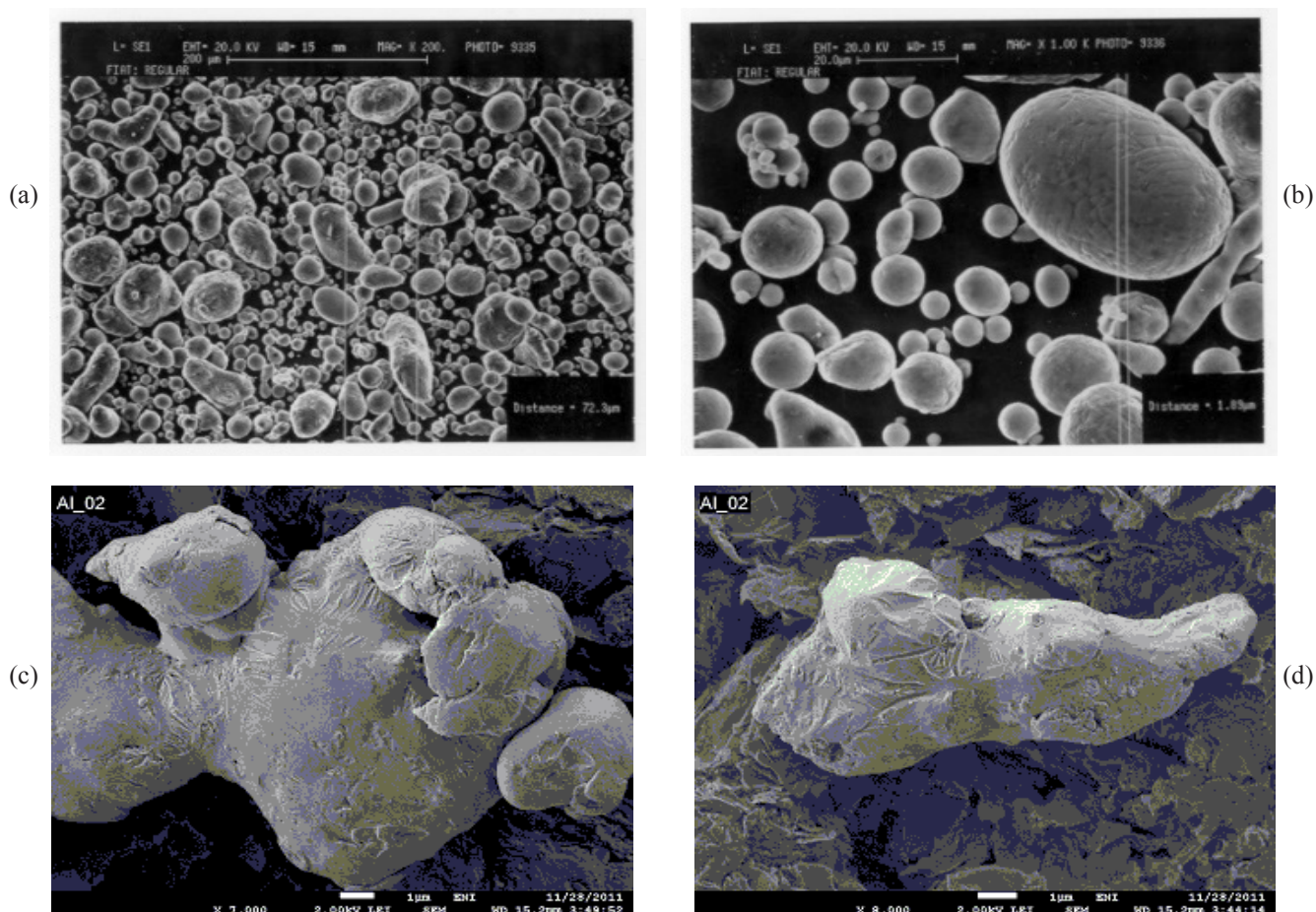


Fig. 1. SEM micrographs of spherical (a – 200 x, b – 1K x) and flakes (c – 7K x, d – 8K x) Al powder.

2.2. Mechanical Activation and Powder Formulation

Mechanical activation is a versatile technique, which can be potentially applied to produce ad-hoc materials, as well as for mixtures of metal powders to be used in flameless heaters. The parameters of the process have a strong influence on the final product characteristics and on their further behavior. Mechanically activated powders are more reactive than their corresponding mechanical mixtures and can be successfully applied in order to increase the mixture reaction rate [15, 16]. Mechanical treatment of powders was carried out in the planetary mill RETSCH PM 100, with a platform rotation rate of 100–650 rpm. The PCA (process control agent) was toluene. A process control agent (PCA) is usually used in the process of mechanical alloying to avoid bonding between the powder particles and the balls and the agglomeration of powder during the milling [17]. The additive was pre-mixed with the virgin Al through a resonant acoustic mixer (RAM technique) before the ballmilling treatment. The modified powders have

been activated accordingly to the standard procedure reported in Table 1.

Table 1
Mechanical activation parameters used in the work

Parameter	Modified Reference Formulation
Mill Planetary	RETSCH PM 100
Milling Time	50' for powder Al _S -Al _F -MnO ₂ -SiO-50 65' for powder Al _S -Al _F -MnO ₂ -SiO-65 150' for powder Al _S -Al _F -MnO ₂ -SiO-150
Milling Speed	500 rpm
BPR (<i>balls-to-powder mass ratio</i>)	20:1
PCA (<i>process control agent</i>)	Toluene
Sphere Material	Stainless Steel
Vessel Material	Stainless Steel
Vessel Volume	125 ml

Table 2

Formulation selected for mechanical activation (the reference powder is reported for comparison purposes [18])

Powder	Orig. Formulation [18]	Modified Ref. Formulation
Al (spherical)	5%	5%
Al (Flake)	70%	70%
MnO ₂	25%	15%
SiO	0%	10%

The reference formulation [18] is inspired by the powder reported in Table 2. The original material is characterized by the highest combustion rate among the proposed alternatives. For this reason, the formulation has been modified as reported in Table 1 to guarantee a lower regression rate. The investigated composition also included manganese dioxide (MnO₂) and silica (SiO). Manganese dioxide was used to enhance the availability of oxygen and to control the rate of oxidation. SiO acts as a “flame retardant” used to regulate heat conductivity and heat capacity to prevent local overheating.

3. Results and discussion

The powders prepared by ball milling (mechano-activation) and the virgin material mixture were characterized in terms of apparent density, absorbed PCA in relation to the sample mass, granulometry, metal content and oxidation behavior at low heating rate. Powder features are presented in Table 3. Activated powders exhibit different colors

with respect to the reference material suggesting a significant inclusion of MnO₂ and SiO into the Al matrix. The color change is also symptomatic of the reduction of the particle size as investigated by both apparent density and the absorbed PCA. In the case of very small particles, characterized by a significant specific surface area (SSA), the extraction of the PCA by standard drying procedure is extremely complex. In this regard, the appearance of higher milling time and lower density should be noticed. Correspondingly, with an increase of the milling time, the powder color switches to dark tones. All these behaviors become dramatic with the powder activated through the innovative technique.

Powder granulometry was investigated by a MALVERN MASTERSIZER 2000 laser granulometer with the use of the dry unit SCIROCCO. Three measurements for each sample were carried out and averaged. The obtained results are summarized in Table 4.

It was found that the mechanical activation promoted a significant reduction of the average particle size of powder as shown in Table 4. Average diameter by mass D [4,3] indicates that the particle size decrease with increasing mechanical activation time (i.e. milling time). The sole exception is represented by the powder activated for 65 min, showing the highest D [4,3] among the activated materials. From this point of view, it is necessary to remember that the particle size is not directly dependent on the time in an activation process due to the peculiar phenomena occurring during the milling. Non-isothermal oxidation at a low heating rate was monitored using a

Table 3

List of the activated powders and their main properties

Powder Label	Color	Absorbed PCA, wt.%	Apparent density, g/cm ³
Al _S -Al _F _MnO ₂ _SiO-MM	Brown	-	1.18
Al _S -Al _F _MnO ₂ _SiO-50	Grey	0	0.62
Al _S -Al _F _MnO ₂ _SiO-65	Dark Grey	6.3	0.50
Al _S -Al _F _MnO ₂ _SiO-150	Dark Grey	16.7	0.38

Table 4

Main particle size parameters of the four tested powders

Powder Label	d(0.1), μm	d(0.5), μm	d(0.9), μm	D[4,3], μm
Al _S -Al _F _MnO ₂ _SiO-MM	4.96	51.53	149.81	67.12
Al _S -Al _F _MnO ₂ _SiO-50	1.05	20.23	71.88	29.28
Al _S -Al _F _MnO ₂ _SiO-65	1.34	17.46	90.19	33.57
Al _S -Al _F _MnO ₂ _SiO-150	1.39	13.35	61.04	24.85

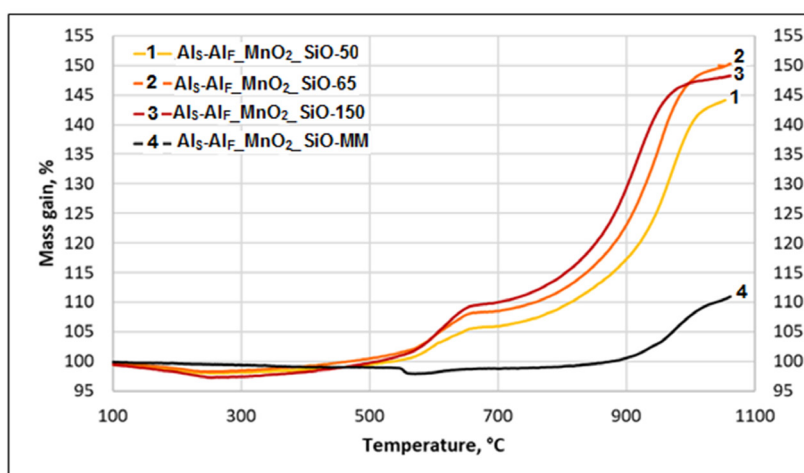


Fig. 2. Thermogravimetric traces of the tested powders.

SEIKO EXTAR II simultaneous thermal analysis machine. Measurements were carried out at open air, starting from room temperature and up to 1150 °C at with heating rate of 10 °C/min. The results of thermogravimetry are presented in Fig. 2.

Figure 2 presents the behavior of the four tested powders at a low heating rate. The mechanical mixture (reference material) is characterized by an evident mass loss (about 1.1%) starting at 548.6 °C (onset temperature). This behavior can be associated with the presence of MnO₂ and its transformation into Mn₂O₃ as observed also by other authors [19]. Independently on this peculiar feature, the reference material exhibits a different trend with respect to the activated powders. In fact, activated materials are characterized by two mass gain steps instead of the single one shown on the reference powder. Moreover, all the activated samples feature an initial mass loss due to the desorption of the PCA excess. The loss tends to be more important increasing the milling time. The sample Al_S-Al_F-MnO₂-SiO-65 was an exception probably due to the higher granulometry and then change to the lower SSA. The mass loss of the reference material is (again) related to the presence of manganese dioxide [20].

In relation to the milling time, all activated powders exhibit a significant reactivity enhancement according to the baseline. This is testified by the progressive anticipation of the second temperature onset as well as by the increment of the first step mass gain increasing the processing time (Table 5). It is worth noting, that the first temperature onset seems to be unaffected by the milling time and that the second mass gain is strongly influenced by the powder metal content. A more intense activation can lead to a reduction of the metal content thus bringing to a lower mass gain during thermal analysis (this means also less aluminum available for the oxidation). In this respect, the activation of 150 min could be too intense.

Four selected samples were preliminarily characterized in terms of the combustion rate. About 0.3 g of powder was positioned on an aluminum plate forming a stripe 4 cm long and ignited in the air by a hot wire. The tests have been recorded and post-processed by a digital technique to obtain the powder burning rate. The presence of a flame has been checked.

The results of the combustion rated of the investigated samples are presented in Table 6. The reference material does not ignite, while the

Table 5
Relevant thermogravimetric data of the four tested powders

Powder Label	Δm_{AT-250} , %	$\Delta m_{250-700}$, %	$\Delta m_{700-1050}$, %	Δm_{TOT} , °C	T_{ON-1} , °C	T_{ON-2} , °C
Al _S -Al _F -MnO ₂ -SiO-MM	-0.50	-0.72	+11.62	+10.40	N.AV	917.3
Al _S -Al _F -MnO ₂ -SiO-50	-1.87	+7.93	+37.85	+43.91	554.9	886.4
Al _S -Al _F -MnO ₂ -SiO-65	-1.72	+10.21	+41.21	+49.70	560.1	864.7
Al _S -Al _F -MnO ₂ -SiO-150	-2.77	+12.71	+38.05	+47.99	555.1	839.2

Δm_{AT} – ambient temperature, °C; Δm_{TOT} – theoretical onset temperature, °C; T_{ON} – onset temperature, °C

Table 6
Burning rate of the tested samples

Powder Label	Ignition	Burning time, s	Burning rate, mm/s	Flame
Al _S -Al _F _MnO ₂ _SiO-MM	No*	-	-	-
Al _S -Al _F _MnO ₂ _SiO-50	Yes**	15.60**	0.22**	No
Al _S -Al _F _MnO ₂ _SiO-65	Yes	14.08	0.28	No
Al _S -Al _F _MnO ₂ _SiO-150	Yes	10.00	0.40	No

* the wire has been kept incandescent for 12 s before aborting the test (3 repetitions)
** only 3.35/4.00 cm of powder burnt (quenching)

activated powders can be ignited without problems. The combustion rate of the powders is related to the activation intensity, which is increasing the milling time make it possible to enhance the combustion velocity (from 0.22 to 0.40 mm/s).

Figure 3 exhibits some representative combustion frames of the selected powders. All the activated powders are flameless and relatively slow. The sample Al_S-Al_F_MnO₂_SiO-150 features the most regular combustion, while the sample Al_S-Al_F_MnO₂_SiO-50 was the less regular. The batch Al_S-Al_F_MnO₂_SiO-65 was a midway solution between the other two powders.

Activated powders exhibited a significant increment of the reactivity with respect to the reference mixture, but also a depletion of the metal content depending on the activation intensity. Combustion tests evidenced a burning rate ranging from 0.22 to 0.40 mm/s for the samples activated with the standard technique. All the powders appeared stable

and safe to handling, suggesting the possibility to partially replace Al with Mg, with special attention on the sample Al_S-Al_F_MnO₂_SiO-50 (highest metal content). It should be noted by experimental results, that using a low amount of PCA dramatically influences the activation process (especially with the RAM technique) bringing to a strong increment of its efficacy.

4. Conclusions

The work considers the influence of activated metal powder mixtures for the application in flameless food heaters. Thus, highly intense activation processes should be avoided to hinder a strong reduction of the metal content and to prevent the generation of flames during the powder combustion due to the inclusion of PCA into the powder. The sample Al_S-Al_F_MnO₂_SiO-50 should be considered as the baseline for further experiments.

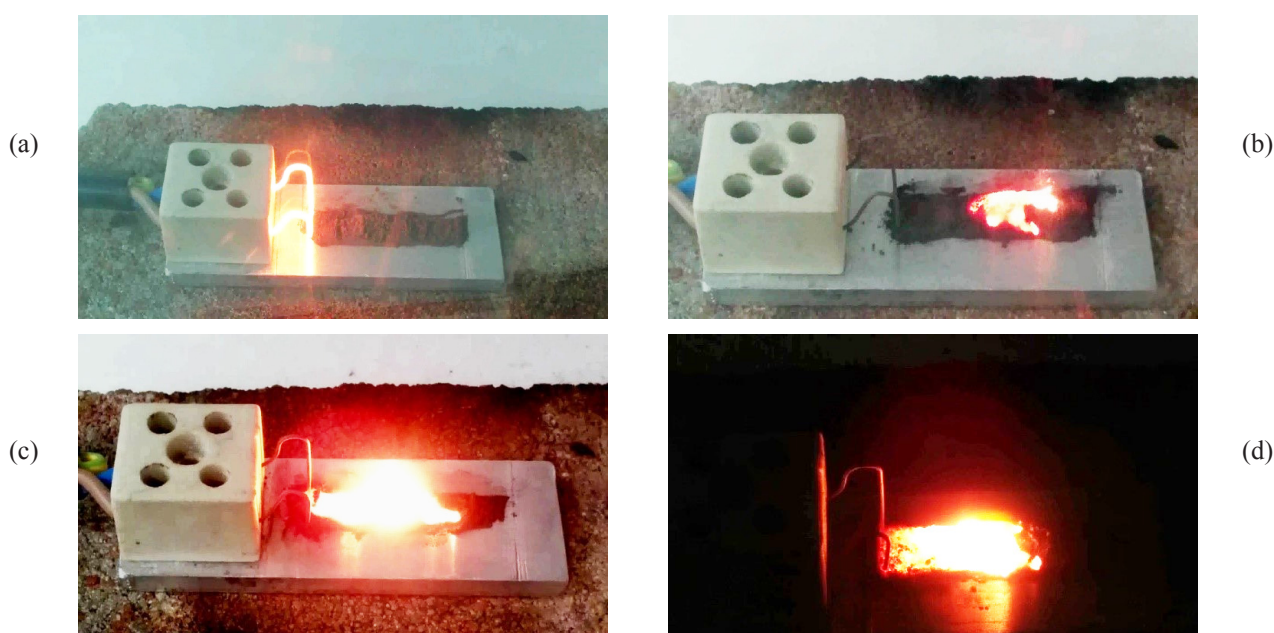


Fig. 3. Preliminary combustion tests of the selected activated samples: (a) – Al_S-Al_F_MnO₂_SiO-MM; (b) – Al_S-Al_F_MnO₂_SiO-50; (c) – Al_S-Al_F_MnO₂_SiO-65; (d) – Al_S-Al_F_MnO₂_SiO-150.

A possibility consists in changing its formulation by adding a small amount of Mg (up to 50%) to facilitate the ignition, avoid the premature quenching of the powder and slightly increase both its combustion rate and enthalpy release.

In particular, applying the RAM-technique activation, using a low amount of PCA allows in the production of nanometric pyrophoric materials with extremely high reactivity. Whereas, appeared relatively low metal content. In this respect, two opportunities should be evaluated:

- possibility to strongly reduce the activation time to obtain a material with the same characteristics using a standard ball milling procedure;
- possibility to encapsulate the powder in an inert environment by use of protective film to inspire the ignition of the powders “on demand” breaking the capsule.

The use of the technological techniques as preliminary preparation of system components involving mechanochemical processing is aimed at increasing the efficiency of creating nanomaterials of a certain functional purpose and improving the quality of the products obtained. Mechanochemical activation allows the activation of powder materials, significantly changing their properties. The synthesized powder nanocomposite materials are intended as a heat source for thermal packaging.

The heat-generating mixtures studied in this project have several advantages, such as they are stable for long periods, safe to use and can be easily disposed of after use.

References

- [1]. Dale H. Huang, Thanh N. Tran, Bao Yang, *J. Therm. Anal. Calorim.* 116 (2014) 1047–1053. DOI: [10.1007/s10973-013-3619-9](https://doi.org/10.1007/s10973-013-3619-9)
- [2]. I. Majid, G.A. Nayik, S. Mohammad Dar, V. Nanda, *J. Saudi Soc. Agric. Sci.* 17 (2018) 454–462. DOI: [10.1016/j.jssas.2016.11.003](https://doi.org/10.1016/j.jssas.2016.11.003)
- [3]. B. Bohra, R. Chavan, N. Gawit, R. Ahire, R. Kale, N. Kapse, *International Journal of Engineering Research & Technology* 4 (2015) 365–368.
- [4]. I. Klarzak, E. Ura-Bińczyk, M. Płocińska, M. Jurczyk-Kowalska, *Thermal Science and Engineering Progress* 6 (2018) 87–94. DOI: [10.1016/j.tsep.2018.03.006](https://doi.org/10.1016/j.tsep.2018.03.006)
- [5]. A.M. Kaliyeva, Ye. Tileuberdi, Ye.K. Ongarbayev, Z.A. Mansurov, *Gorenje i Plazmohimija* [Combustion and Plasmachemistry] 16 (2018) 53–59 (in Russ.).
- [6]. A.D. Serikbayeva, E.E. Dilmukhambetov, K.A. Myrzabek, N.R. Amangeldi, A.B. Kuserbayeva, The exothermic flameless heaters of canned meat products. 19th International Multidisciplinary Scientific GeoConference SGEM, 30 June – 6 July, 2019, 19 (2019) 123–130. DOI: [10.5593/sgem2019/6.2/S26.016](https://doi.org/10.5593/sgem2019/6.2/S26.016)
- [7]. M. Farhanchi, M. Neysari, R. Vatankhah Barenji, A. Heidarzadeh, R. Taherzadeh Mousavian, *J. Therm. Anal. Calorim.* 122 (2015) 123–133. DOI: [10.1007/s10973-015-4704-z](https://doi.org/10.1007/s10973-015-4704-z)
- [8]. Q. Mao, Sh. Lu, Zh. Chen, A. Buekens, J. Yan, *Int. J. Environ. Pollut.* 61 (2017) 293–313. DOI: [10.1504/IJEP.2017.087772](https://doi.org/10.1504/IJEP.2017.087772)
- [9]. H. Wang, J. Huang, K. Zhang, Y. Yu, K. Liu, G. Yu, S. Deng, B. Wang, *J. Hazard. Mater.* 264 (2014) 230–235. DOI: [10.1016/j.jhazmat.2013.10.075](https://doi.org/10.1016/j.jhazmat.2013.10.075)
- [10]. Z.A. Mansurov, N.N. Mofa, T.A. Shabanova, *J. Eng. Phys. Thermophy.* 86 (2013) 848–855. DOI: [10.1007/s10891-013-0903-2](https://doi.org/10.1007/s10891-013-0903-2)
- [11]. B.S. Reddy, K. Rajasekhar, M. Venu, J.J. S. Dilip, S. Das, K. Das, *J. Alloy. Compd.* 465 (2008) 97–105. DOI: [10.1016/j.jallcom.2007.10.098](https://doi.org/10.1016/j.jallcom.2007.10.098)
- [12]. T.L. DeLuca, F. Maggi, M. Fassina, C. Paravan, A. Sossi, *Chemical Rocket Propulsion* (2017) 191–233. DOI: [10.1007/978-3-319-27748-6_8](https://doi.org/10.1007/978-3-319-27748-6_8)
- [13]. C. Paravan, F. Maggi, S. Dossi, G. Marra, G. Colombo, L. Galfetti, *Energetic Nanomaterials* (2016) 341–368. DOI: [10.1016/B978-0-12-802710-3.00013-1](https://doi.org/10.1016/B978-0-12-802710-3.00013-1)
- [14]. L.P.H. Jeurgens, W.G. Sloof, F.D. Tichelaar, E.J. Mittemeijer, *Thin Solid Films* 418 (2002) 89–101. DOI: [10.1016/S0040-6090\(02\)00787-3](https://doi.org/10.1016/S0040-6090(02)00787-3)
- [15]. M.A. Trunov, M. Schoenitz, E.L. Dreizin, *Propell. Explos. Pyrot.* 30 (2005) 36–44. DOI: [10.1002/prop.200400083](https://doi.org/10.1002/prop.200400083)
- [16]. G. Zhang, Y. Li, S. Tang, R.D. Thompson, L. Zhu, *ACS Appl. Mater. Interfaces* 9 (2017) 10106–10119. DOI: [10.1021/acsami.7b00095](https://doi.org/10.1021/acsami.7b00095)
- [17]. S. Dossi, C. Paravan, F. Maggi, L. Galfetti. Propulsion and Energy Forum, Enhancing Micrometric Aluminum Reactivity by Mechanical Activation, 51st AIAA/SAE/ASEE Joint Propulsion Conference, July 27–29, 2015 Orlando, FL. DOI: [10.2514/6.2015-4221](https://doi.org/10.2514/6.2015-4221)
- [18]. Patent Application Publication: US 2010/014.6849 A1 (June 17, 2010). Portable Heatingapparatus And Metal Fuel Composite For Use With Same. B. Coffey, R.C. Kainthila, C.E. Sesock, B. Coffey, R.C. Kainthila, C.E. Sesock.
- [19]. J. Wu, H. Huang, L. Yu, J. Hu, *Advances in Materials Physics and Chemistry* 3 (2013) 201–205. DOI: [10.4236/ampc.2013.33029](https://doi.org/10.4236/ampc.2013.33029)
- [20]. N. Obradović, S. Filipović, N. Đorđević, D. Kosanović, S. Marković, V. Pavlović, D. Olčan, A. Djordjević, M. Kachlik, K. Maca, *Ceram. Int.* 42 (2016) 13909–13918. DOI: [10.1016/j.ceramint.2016.05.201](https://doi.org/10.1016/j.ceramint.2016.05.201)