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EXOTHERMIC CHARACTERISTICS OF ALUMINIUM BASED NANOMATERIALS

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ABSTRACT

Nano-structured energetic materials have been recently proposed as novel energy storage media where the exothermic reaction is the key to control the heat release process. The properties of nano-alloys, which can be engineered not only by the particle size, but also by varying their elemental compositions, are very appealing. This work conducts a comparative experimental study of the exothermic characteristics of two nanomaterials in the air, aluminum nanoparticles (nAl) and aluminum-copper nanoalloys (nano-AlCu) based on TGA/DSC studies. The results show that the general exothermic characteristics of nano-AlCu are very similar to that of nAl but the nano alloy is more reactive. The nano-AlCu oxides and ignites at lower temperature, and influenced by the heating rate. An early ignition is found for both nanomaterials, and melting of the nano-alloy is believed to be responsible for its early ignition.

Keywords: Nanofuel; Nanoalloy; Oxidation; Ignition; Aluminium; Copper

1. Introduction

Increasing use of energies generated from renewable resources, including biomass, wind energy, hydroelectric power, and solar energy, will become viable where the geographical and climatic prerequisites are favorable, and pumped hydro, compressed /liquefied air, flying wheels, or super-capacitors have been conventionally proposed for stationary energy storage applications. Such regions, however, seldom coincide with the areas of high energy consumption, namely industrial and city regions with a high population density. Alternative mobile energy storage medium is required. Examples include hydrogen and batteries but both have significant problems to overcome. A novel energy storage concept by using nano-structured energetic materials (nanofuel), such as aluminium, iron, silicon, and magnesium, was recently proposed [1].

The reduction of particle size to the nanoscale represents both opportunities and challenges. At the nanoscale, it becomes possible to engineer different melting, oxidation and ignition temperature of the materials by controlling the particle structure and morphologies to suit different applications. The increased specific areas at the nanoscale will lead to rapid oxidation and combustion, resulting in a fast release of the stored energy. However many challenges exist, which ranges from large-scale production of nanofuels, controlled oxidation and ignition of the materials, capture and regeneration of the burned fuels. From the physics aspect, many deviations from the established laws at the bulk scale have been reported. For instance, the ignition temperature of energetic nanomaterials is more sensitive to the passivation layer and the external heating conditions, and the burning time of nanomaterials is deviated from the conventional d^2 law [2, 3].

The oxidation and ignition characteristics of aluminium particles have been widely investigated in the past decade [4-7]. However in order to have more controllability over the material's properties, aluminum is usually alloyed by mixing with several other elements at the bulk scale. Due to the synergistic effects of the constituent alloying materials, the physiochemical properties of the alloys can be improved by chemical reordering and spatial redistribution of the atoms [8]. In addition, the alloying increases the surface area of the particles that will increase the rate of reaction and improve the reaction mechanism [9-11], which in turn shall improve the rate of heat release and the performance of propellants and thermites [12]. Many studies have been conducted in the last a few decades to investigate the thermo-mechanical and chemical activities of aluminum based alloys. However the investigation of nano-alloys (NA) is still very limited. For instance, investigated by the TGA/ DSC method, Singh et al. [13] observed a reduction in the ignition delay for bimetallic

nanoalloys of Ni mixed with Cu, Co and Zn. Some studies have shown that nano aluminum particles (nAl) in combination with copper possessed some excellent properties and can be potentially used in resistance welding electrodes, electrical connectors, lead frames and the metastable intermolecular composites (MICs) [14-17]. However there is still no detailed study of the thermal-chemical kinetics of nano alloy of copper and aluminum (nano-AlCu). Their properties in relation to the bulk behavior and the individual compositional element are still unclear.

Very recently we reported a unique early ignition phenomenon of aluminium nanoparticles, caused by a combined effect of solid phase transformation of the alumina shell and the early melting of the aluminum core, at a heating rate over 8 K/min [18]. Such an early ignition did not change the later reaction path but was responsible for the co-existence of various polymorphs of alumina at the low temperature. It is however still unclear that such an early ignition would occur for aluminum-based nano-alloys, and a comparative study of the reactivity of aluminum and its alloy is seldom reported. This work conducts a comparative experimental study of the exothermic characteristics of two nanomaterials, aluminium nanoparticles (nAl) and aluminum-copper nanoalloys (nano-AlCu). The experiments will be performed in a simultaneous thermal analysis (TGA/DSC) under a heating rate range of 2 – 30 K/min. The oxidation, and ignition mechanism of aluminum nanoparticles and the effect of heating rate will be revealed.

2. Materials and methods

Both aluminium nanoparticles and the nano alloy AlCu particles were fabricated by the electrical explosion of wires method (EEW). For the nanoalloys, the constitutional elements were twisted in wires and the aluminum content in the explosion products was adjusted by varying the wire diameter. The particles were produced in the Tomsk State University, Russia, and stored in vacuum-sealed packs. The microstructure and the oxide encapsulation was observed with high resolution transmission electron microscope (HRTEM) using a JEOL JEM 1020 microscope operating under 200 kV. The elemental compositional analysis was performed by an Energy Dispersive X-ray Spectrometer (EDS) (Oxford Instruments) equipped with INCA Energy 300 Systems. **Fig. 1** shows that both types of particles are spherical, having a similar size range of 100 ~ 200 nm. Careful examination reveals that both types of particles were covered by amorphous layers of oxides, which act as passivation layers having thickness ~ 4-5 nm. The EDS study shows that nano-AlCu contains Al, Cu and O as its major constitutional elements whose weight percentages are given in **Table 1**. Briefly the nano-AlCu contained ~56% of Al and ~38% of Cu, and the

oxygen was in the oxide form that passivates on the particle's external surface. For the aluminum nanoparticles, the sample contained ~11% oxygen, which corresponds to ~24% of Al₂O₃ (initial oxide) and ~76% of active aluminum

The exothermic reaction and intervening physiochemical reactions occurring at different temperature ranges were characterized with STA 1500 thermal analyzer (Rheometric Scientific, Germany) in a controlled atmosphere of dry air with a flow rate maintained at 20 ml/min, similar to our previous studies [18, 19]. The changes of mass during the whole oxidation process were monitored with the thermo-gravimetric analysis (TGA) and the changes of energy were surveyed with differential scanning calorimetry (DSC). The temperature calibration of the thermobalance was conducted by the melting point standards of metals like Zn, Sn and Pb. For all experiments, platinum crucibles were selected and 6.1 ± 0.1 mg of the sample was taken. With such a small quantity of the sample, the tendencies of developing the internal temperature gradient in the pan can be reduced. To understand the effects of heating rate the samples were thermally treated at heating rates of 2, 5, 7, 10, 15, 20, 30 K/min from the room temperature to ~1200 °C.

3. Results and discussion

The experiments show that the heat flow patterns of the particles changed significantly with the heating rates. For both aluminium nanoparticles, and nano-alloys, the experiments fall into two distinct types: low heating rate ($\beta = 2-7$ K/min) and high heat rate ($\beta \geq 8$ K/min). For the low heating rate, the oxidation process completes without any sudden change of heat or mass; while for the high heating rate, there is a sudden increase of mass and heat flow, indication of an early ignition.

3.1 Example of low heating rate

An example of the low heating rate (i.e. 2 K/min) is illustrated in **Fig. 2** and **Fig. 3**. The general reaction trend of both materials is very similar. It can be seen that the whole exothermic reaction completes in three stages, one before and two after the melting of the particles, and the major heat release occurred in the first stage. Such an observation is similar to our previous observation [18]. For aluminum nanoparticle, it is believed that the sequent phase transition of the formed oxide layer from amorphous $\rightarrow \gamma \rightarrow (\delta \rightarrow \theta) \rightarrow \alpha$ -alumina as the temperature increases, and the melting of the aluminum core promote the staged oxidation [18, 20]. The exothermic path of nano-AlCu is similar

to that of the nAl. However the exothermic reaction occurs earlier for nano-AlCu and finishes at lower temperature. For instance, it reaches the first peak heat release at 534 °C while it takes 559 °C for nAl to reach its first heat peak. The lower heat release rate is believed to be related to the low enthalpy of formation of the copper element.

3.2 Example of high heating rate

An example of the high heating rate (i.e. 20 K/min) is illustrated in **Fig. 4** and **Fig. 5**. Again similar reaction patterns are observed for both nAl and nano-AlCu. Different to the low heating rate case, the particles go through exothermic reactions that are characterized with a rapid rate of heat released and a sharp weight increased. This occurs during the first exothermic reaction when the amount of heat produced by the particles becomes more than the amount absorbed by the purge gases. The temperature of the particles becomes higher than that of the furnace. The temperature gradient (dT/dt) during the experiment remained constant but for a very short interval of time, it becomes higher than its set value. This run away of temperature is regarded as the ignition reaction [20, 21]. Such an ignition would not cause a global combustion event of the sample, however it accelerates the following oxidation process. For aluminum nanoparticles at 20 K/min, the registered ignition temperature is found to be ~ 600 °C, much smaller than the melting temperature of aluminum (~660 °C). According to Rosenband [22], the ignition is initiated by the melting of nAl. It is clearly shown that in our experiments, the ignition happens before the melting temperature as recorded by the TGA device. However it shall be cautious to interpret this temperature. The TGA measures the pan's temperature, which will have some difference to the real temperature of the heated particle. It is possible that at the registered ignition temperature (i.e., 592 °C for 10 K/min), the temperature of the particle is higher than that of the melting temperature. The active aluminum part might be in a molten stage contained by the solid oxide layer. As suggested earlier, the likely reason for the early ignition would be a combination of both particle melting and phase transition of the oxide layer [18].

For nano-AlCu, the ignition temperature occurs at lower temperature, ~565 °C under 20 K/min heating rate, which is much lower than the melting temperatures of its constitutional elements. However for alloys, the mixtures of elements are liquefied (or solidified) at a single invariant temperature called the eutectic temperature [23]. The eutectic temperature for the Al-Cu alloy in its bulk state is 548.2 °C. Nearly the same value for the nano Al-Cu alloy is found from the current experiment, 545.6 ±1.4 °C. From the DSC curve, it can be seen that immediately after the eutectic

melting, the alloy particles go through a rapid exothermic reaction – leading to the ignition, **Fig. 5**. It becomes clear that the ignition temperature is higher than the eutectic melting temperature. Supported by some preliminary analysis, the melting of the aluminum particles is believed to play a major role for the early ignition of the material [22]. Due to the melting, the volume of the core would increase by 6%, which creates some pressure on the shell of the alumina, increasing the porosity (or producing some cracks in certain local locations) of the shell that leads to the ignition. From the DSC/TGA data, it appears plausible that the melting of the nano-alloy plays a leading role in the early ignition.

3.3. Influence of the heating rate

The reactivity of the nano aluminum particles (NAPs) and nano-AlCu are summarized in **Table 2**, which clearly shows that the alloy particles are more reactive than the pure aluminum particles. In addition, **Fig. 6** shows the general trend of the influence of the heating rate on the final weight increase and the maximum heat flux during with ignition reaction. Again similar patterns were observed for both materials. Under low heating rates (i.e. no ignition) the peak values of the heat flux change with the heating rate in a monotonous way. For nano-AlCu, it increases slightly from 11 mW at 2 K/min to ~70 mW at 7 K/min. However as the ignition reaction is observed, a large jump in its values is observed. The heat release rate remains a similar value and is in the region of 750 mW for all heating rates above 8 K/min. This suggests that the ignition event is similar under all these heating rates, and releases similar amount of heat. The heat release rate of nano-AlCu is smaller than the pure aluminum case. A nearly opposite trend is observed for the final weight increase. The heating rate influences little on the final weight change when there is no ignition. However as the ignition occurs, the final weight change generally decreases with the increase of the heating rate, which implies a kinetic process that higher heating rate leads to less time for the reaction to fully complete.

In the literature there are still strong debates for the ignition temperature of small energetic particles (below a few micrometers). While some studies suggested that it was a fixed value around the melting temperature of the aluminum particles [21, 24], many others suggest that the ignition temperature is not a material property but depends upon the environmental variables, such as the heating rates [25-27], particle size [28], specific experimental conditions or methods employed [29, 30] and instruments used [29, 31, 32]. It is still debatable if the ignition of aluminum nanoparticles occurred before or after the melting temperature of aluminum. To better understand the ignition

phenomenon, a comparison of the ignition of nAl and nano-AlCu is shown in **Fig. 7**. The ignition temperatures of both powders under various conditions of the heating rate are calculated by the 2nd derivative of TGA and DSC curves. The ignition temperature of nano-AlCu at heating rate > 7 K/min is 564.7 ± 10.8 °C. This temperature is similar to that observed by Stamatis et al. [9] in their study of ignition of Al-CuO nanocomposites. It clearly shows that the ignition temperature is dependent on the heating rate, i.e., the higher the heating rate, the higher the ignition temperature. Comparing to the nAl, the ignition temperature of the nano-AlCu is always smaller than the pure aluminum particle, implying its higher reactivity.

4. Conclusions

This work conducts a comparative study of the exothermic characteristics of two nanomaterials, aluminium nanoparticles (nAl) and aluminum-copper nanoalloys (nano-AlCu) based on TGA/DSC studies. It is found that

- i) The general exothermic characteristics of nano-AlCu are similar to that of nAl.
- ii) The complete reaction for both materials can be described by a three-stage reaction and an early ignition phenomenon is observed for both nAl and nano-AlCu under heating rate ≥ 8 K/min.
- iii) The ignition temperature of nano-AlCu is higher than its eutectic melting temperature, and the melting is believed to be responsible for the early ignition.
- iv) The comparison of the reactivity of both materials shows that nano-AlCu is more reactive than nAl.

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Table 1

EDS analysis of nAlCu and nAl before oxidation.

Sample	O	Al	Cu	Total
	Weight %	Weight %	Weight %	Weight %
nAlCu	5.95	56.14	37.91	100.00
nAl	11.10	88.90	-	100.00

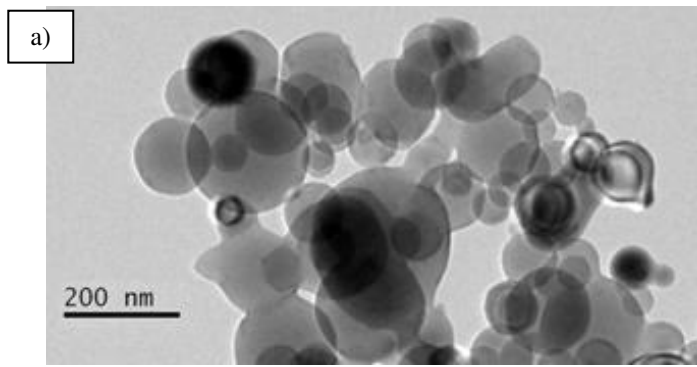
Table 2

Comparison of Onset temperature, maximum heat flux and corresponding temperature of nAl and nAlCu

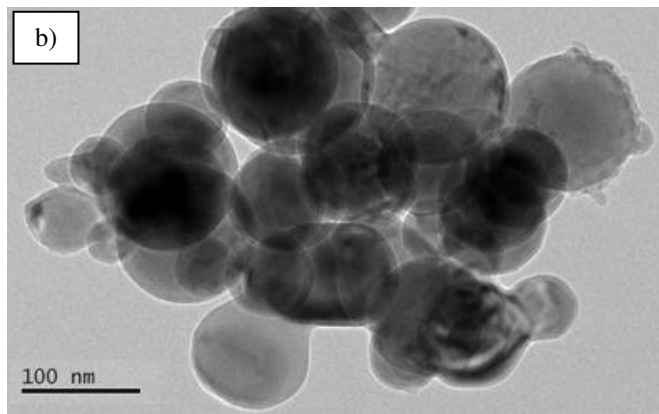
β	T_{onset}		T_{pexo1}		h_{pexo1}		T_{pexo2}		h_{pexo2}	
	K/min	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	mW	mW	$^{\circ}\text{C}$	$^{\circ}\text{C}$	mW	mW
	Al	AlCu	Al	AlCu	Al	AlCu	Al	AlCu	Al	AlCu
2	481	458	559.4	534.0	31.0	11.2	759.9	720.2	12.7	1.06
5	487	471	577.7	545.5	79.3	44.5	785.2	751.8	28.5	7.1
7	509	474	585.0	547.8	148.5	67.5	790.1	755.4	48.9	8.4
10	498	491	633.0	588.3	823.0	746.5	801.1	761.2	49.0	11.8
15	511	492	633.1	590.8	823.0	749.3	808.1	773.9	66.5	30.3
20	498	497	639.0	587.7	829.7	745.9	814.2	786.1	98.0	40.3
30	514	512	643.5	595	833.3	754.1	826.5	810.5	133.9	35.9

Note:

β is the heating rate, T_{onset} is the extrapolated onset temperature, T_{pexo1} and T_{pexo2} are the peak exothermic temperatures for the first and second exothermic reactions, respectively and h_{pexo1} and h_{pexo2} are the corresponding peak heat values.



(a) Aluminium nanoparticles



(b) Aluminium-Copper nanoalloys

Fig. 1. HRTEM image of the aluminum-based nanoparticles

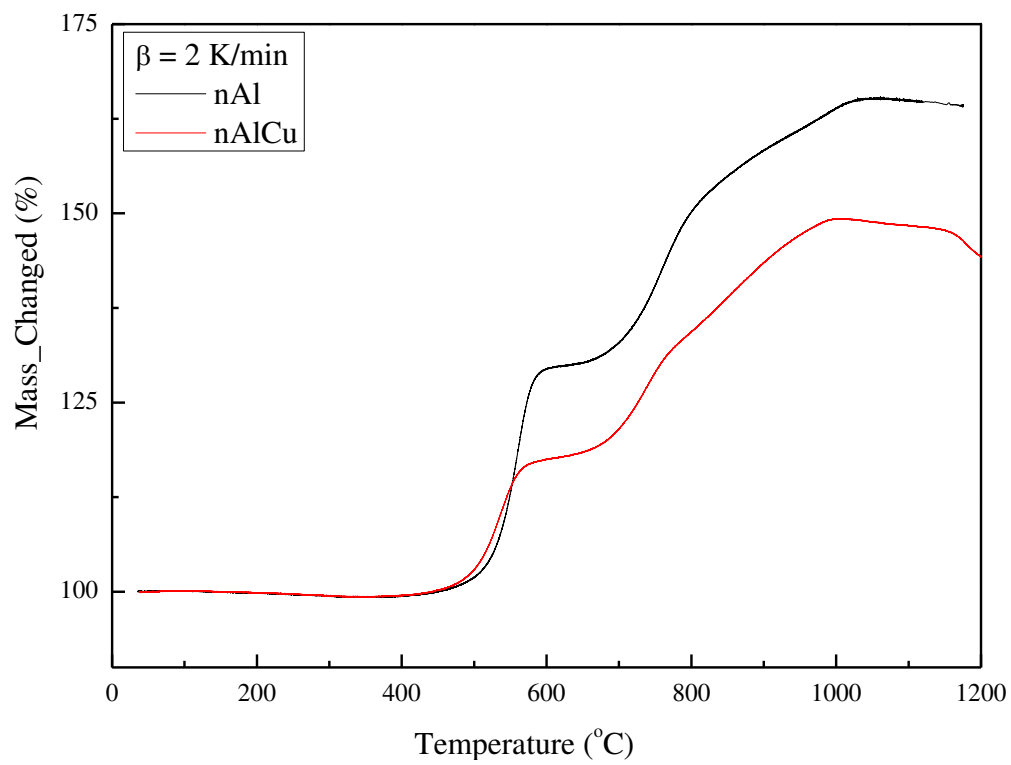


Fig. 2. Comparative thermogravimetric data for aluminium nanoparticles and aluminium-copper nanoalloy at low heating rate (2 K/min).

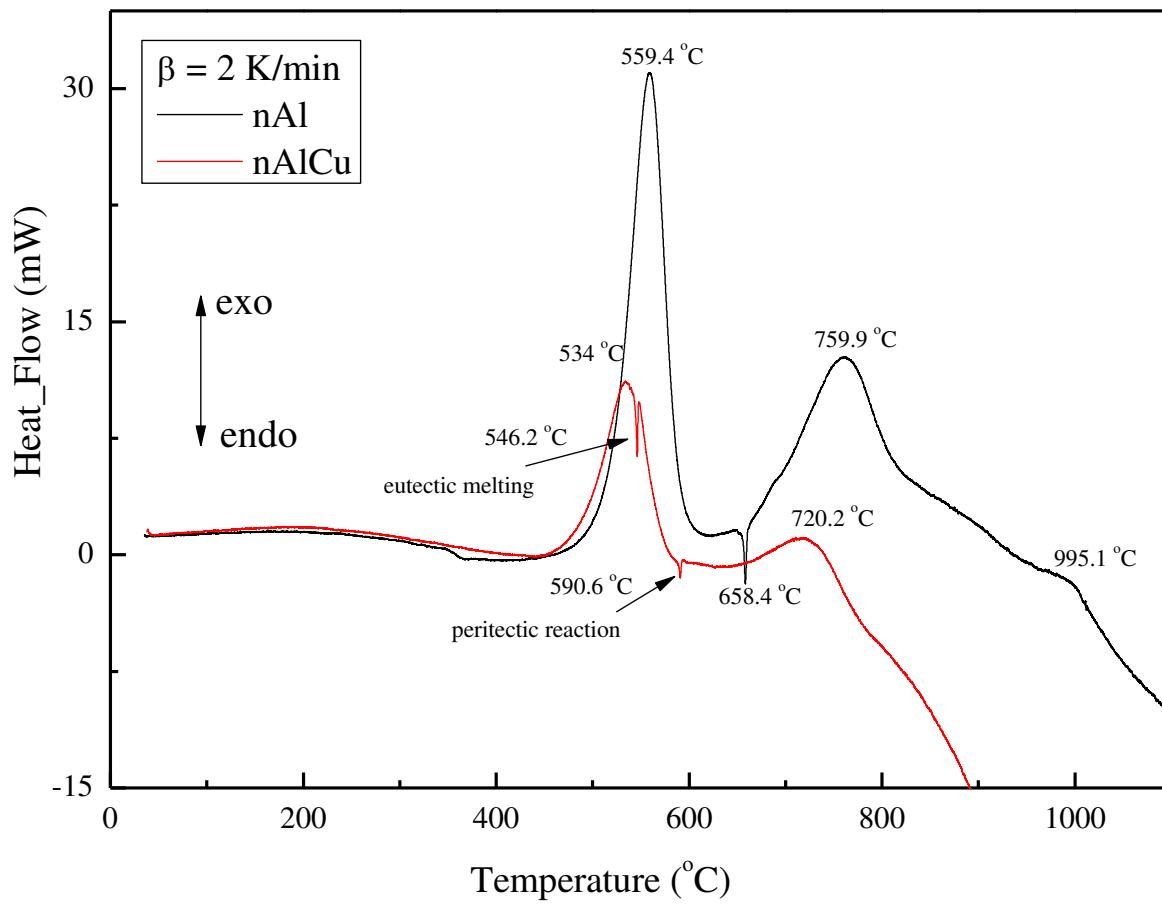


Fig. 3. Comparative DSC trace for aluminium nanoparticles and aluminium-copper nanoalloy at low heating rate (2 K/min)

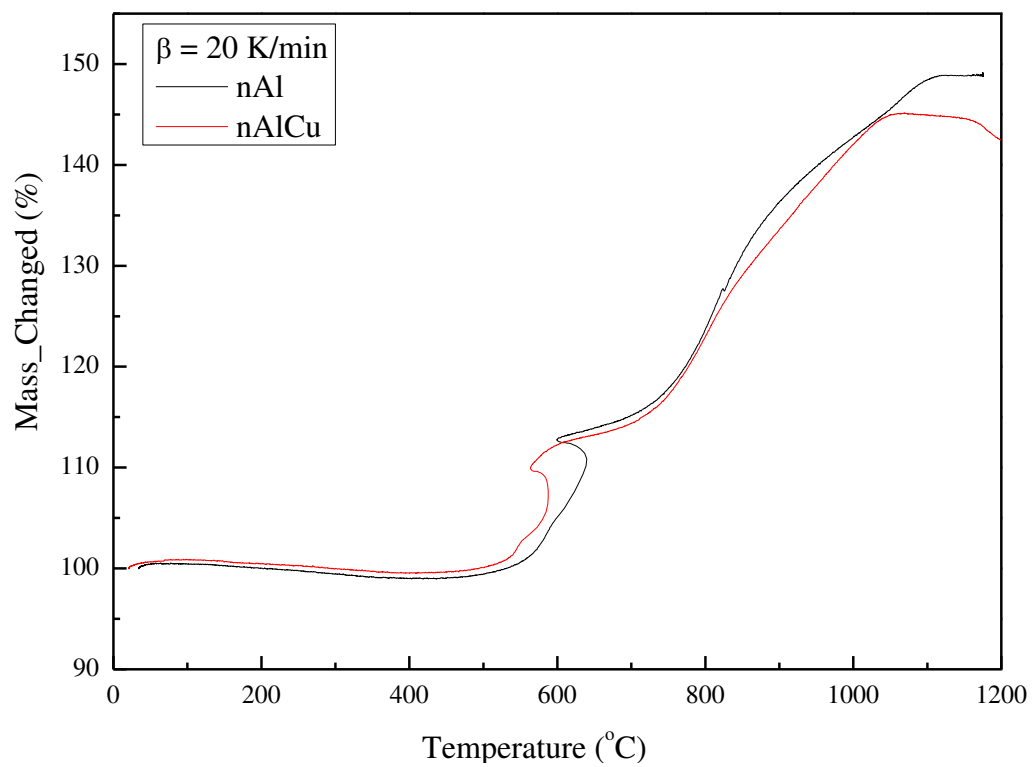


Fig. 4. Comparative thermogravimetric data for aluminium nanoparticles and aluminium-copper nanoalloy at high heating rate (20 K/ min).

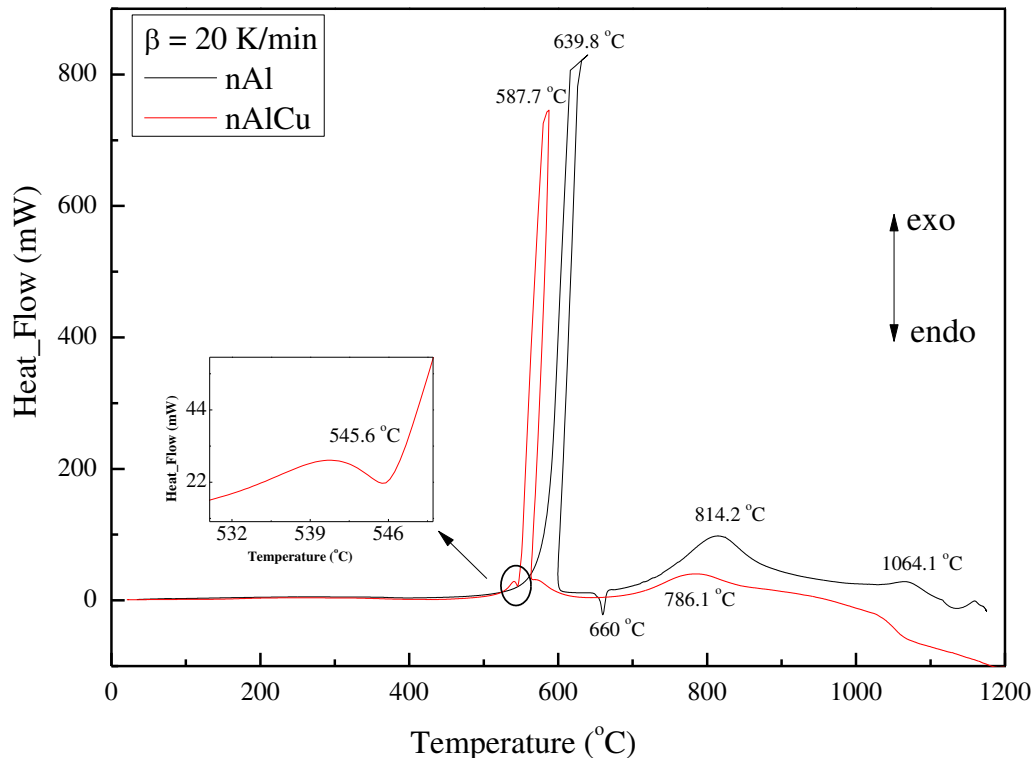


Fig. 5. Comparative DSC trace for aluminium nanoparticles and aluminium-copper nanoalloy at high heating rate (20 K/ min)

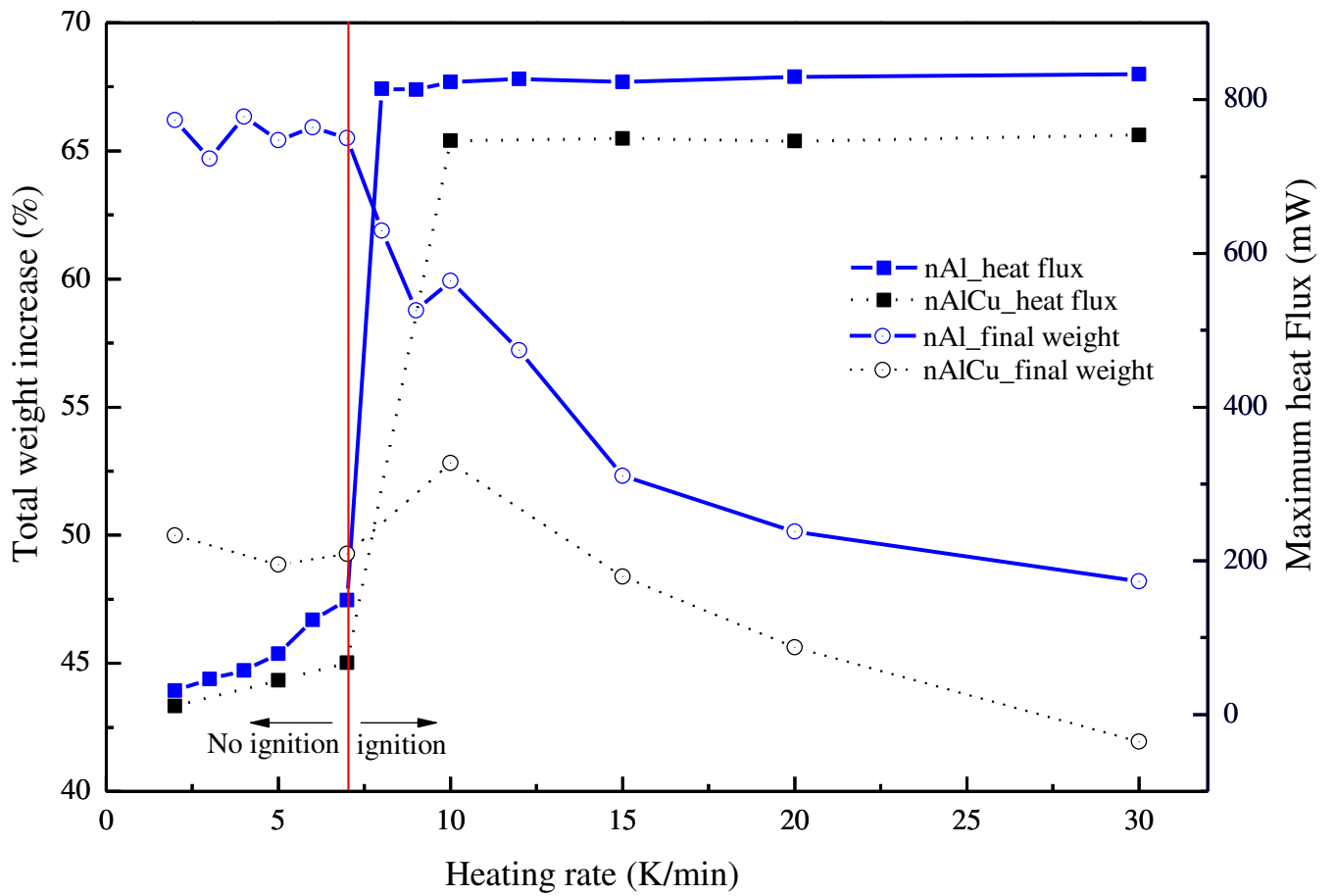


Fig. 6. Trend of weight increase and peak heat flux with ignition reaction

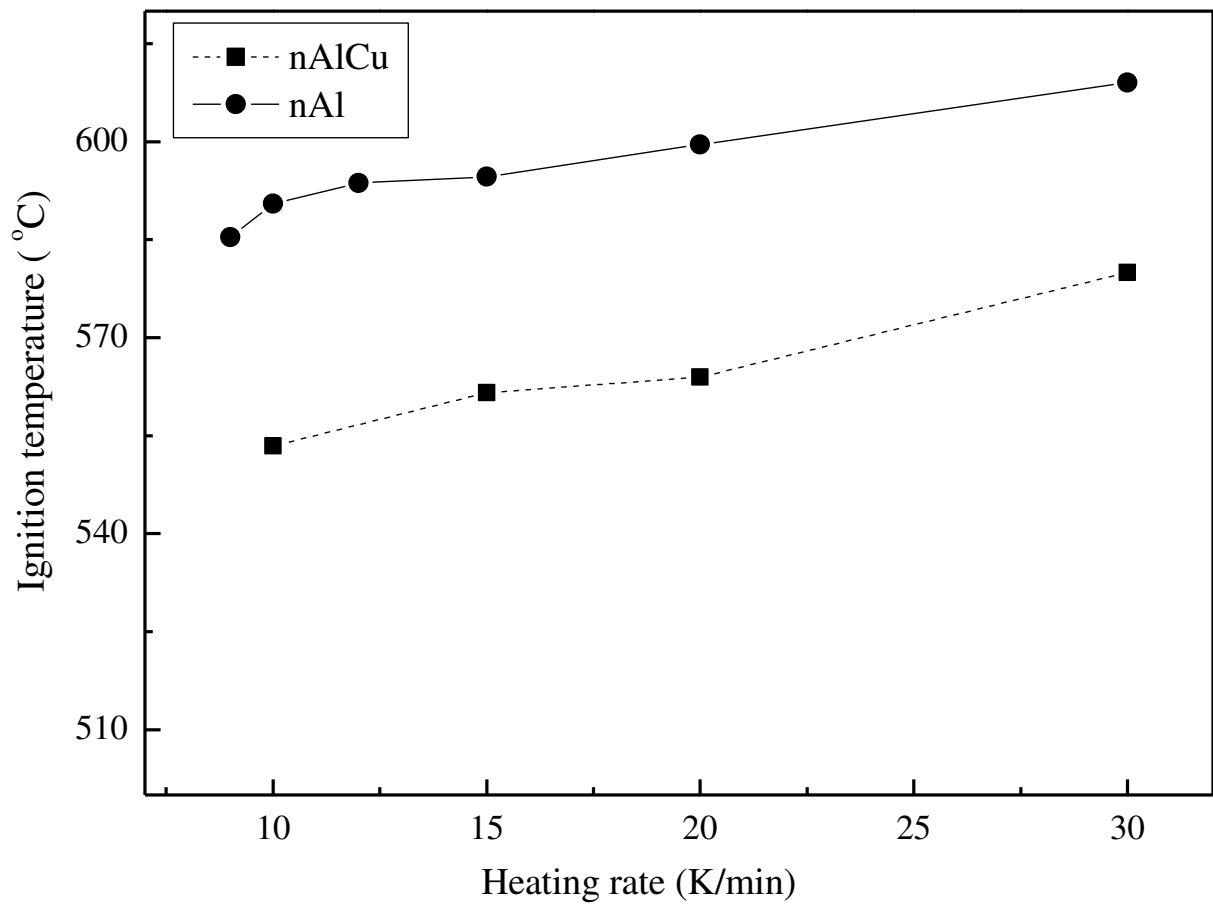


Fig. 7. Comparison of ignition temperatures of nAl with nano-AlCu under different heating rates