Ball temperatures during mechanical alloying in planetary mills

Young-Soon Kwon[a], Konstantin B. Gerasimov[b],*, Sok-Keel Yoon[a]

[a]*Regional Research Center, ReMM, School of Materials Science and Engineering, University of Ulsan, Ulsan 680-749, South Korea*
[b]*Institute of Solid State Chemistry and Mechanochemistry, Kutateladze 18, Novosibirsk-128, 630128 Russia*

Abstract

A simple calorimetric technique was used to estimate the temperature of balls during mechanical alloying (MA) in an AGO-2 planetary ball mill. Temperatures up to 600 °C were realized for balls in the case that compact layers of milled powder are formed on the surface of the balls and the wall of the vial. Though free powders in the vial would decrease the temperature of the balls, it was found that a difference in temperature between the balls and the vial still exists. This should be taken into account in the analysis of temperature effects during MA. An influence of the temperature of the balls on the MA process of $Mg_{67}Ni_{33}$ and $Ni_{50}Al_{50}$ powder blends was demonstrated.
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1. Introduction

According to recent reviews [1,2] 'limited science content' is one of the main reasons that hamper further development of mechanical alloying (MA). Although it is known that MA is a versatile route of synthesis of novel materials, it is not very clear how this technique works. This is because MA is a complex stochastic process and the number of variables determining its evolution is too high. Amongst other things, the milling temperature is one of the most indeterminate parameters for ball milling.

Two kinds of temperature effects during MA are usually taken into account: local temperature pulses due to ball collisions and the overall temperature in a vial. The local temperature pulses have approximately the same duration as the collision time (10^{-5} s). The experimental determination of the local temperature and the size of the heated regions is a very arduous task and some different theoretical models are used for their estimation (see, for example, Refs. [3–6]).

Only a few investigations have been reported in which the overall temperature of the milling has been varied. Dripping of liquid nitrogen on the vials and electrical heating are usual methods to lower or to increase the temperature [7,8]. The temperature usually was monitored with a thermocouple inserted into the wall of the vial [8,9].

Modern mills often have a high power. A simple estimation gives values of several degrees for the temperature difference between outer and inner sides of a vial of stainless steel when the surface of the vial walls is 100 cm^2, the wall thickness is 5 mm and the dissipated power is 100 W. Considering that the temperature rise during milling is mainly due to ball-to-ball, ball-to-powder, ball-to-wall collisions and friction and that the balls make only point contacts with the vial, it becomes clear that temperature differences between the ball and the vial must be of much importance.

In the case of MA of ductile metals, compact layers of metals are often formed on the balls and the vial wall and there is almost no free powder in the vial until brittle products are formed (see, for example, Refs. [9,10]). For such a situation, the ball temperature may have a decisive role on the structure of the products and on the rate of MA.

In this investigation, temperatures of the ball were estimated for an AGO-2 planetary ball mill under various operating conditions. The effects of the ball temperature on MA of Ni–Al and Mg–Ni blends are also analyzed.

*Corresponding author. Present address: Research Center for Machine Parts and Materials Processing, University of Ulsan, P.O. Box 18, Ulsan 680-749, South Korea. Tel.: +82-52-259-2108; fax: +82-52-259-2109.
E-mail address: rrc@uou.ulsan.ac.kr (K.B. Gerasimov).

2. Experimental

MA was carried out in an AGO-2 planetary ball mill. During operation the vials were cooled by running water. The hardened steel balls used for experiments were 3, 5, 7 and 9 mm in diameter. The mill has two vials with capacity of 150 cm^3 each and an inner radius of 3 cm (the wall thickness is 0.5 cm). The radius of the planet carrier (distance from mill axes to vial axes) is 5.2 cm. The mill has three steps of operation mode, see Table 1.

The vials were designed to allow pumping and subsequent filling with gases up to pressure of 1.0 MPa. A calorimetric method was used for the measurements of the ball temperatures. The mill was cooled with water from a thermostat. The water flow was kept constant with an accuracy of ±2%. To decrease the heat exchange between the mill and ambient, the mill case was thermally insulated by microcellular rubber. The difference in temperature of the cooling water before and after milling was recorded with an electric bridge circuit with two temperature-sensitive resistors embedded in the pipes of the cooling water. The dissipated power and the temperature of the external side of the vial walls were calculated from this difference. Measurements were done after the temperature difference reached a steady state (approximately 15 min). The temperature of the cooling water was matched, so that the temperature of the external side of the vial wall was close to ambient.

When the mill is turned off, redistribution of heat between the balls and the vials will occur. However, the total heat accumulated in vial and balls remains unchanged during some time. The vials might become heated above ambient temperature due to the heat dissipated by the ball, which needs some time. According to our measurements, the heat content of the vials changed by an only negligible amount during 30 s after switching-off the mill. Thirty seconds is enough time to transfer the vials from the mill into calorimeters. Dewar vessels with mixers and thermometers were used as calorimeters. Distilled water was the calorimetric liquid.

From the change of temperature of the cooling water, we calculated the dissipated energy. From this value and the heat conductivity of the vial material (33 W m^{-1} K^{-1}), the temperature of the inner side of the vial walls, the average temperature of the vials and their heat content during milling were calculated. This heat content was subtracted from the heat content of the vials and the balls, which was determined in the calorimeter. The difference was used for the calculation of the ball temperature. Usually the heat content of the vial was smaller than 10% of total heat accumulated in the balls and the vials during milling.

To reduce the influence of surface oxides, the use of fine dispersed powders was avoided in this work. Commercial powders of iron, nickel and copper with particle sizes larger than 0.2 mm were used for the experiments. Titanium and zirconium were taken in the form of coarse filing (about 0.5 mm) obtained from a crystal bar made via the iodide process. Aluminium was prepared from wire (diameter 0.4 mm) cut into pieces about 2 mm long.

3. Results

3.1. Temperature of the balls for the case of absence of powder in the vial (bare balls)

Fig. 1 shows the ball temperatures as a function of milling time for different diameters of the balls. From the initial slopes of the plots, it is concluded that about 80% of the energy generated in the mill is consumed to heat the balls. The temperature of the balls increased as the ball diameter increased (the total surface area of the balls with the same total mass decreases). 7 mm balls and 9 mm balls showed almost the same time dependencies of the temperature. Two competing effects can explain this fact. It is rather straightforward to say that bigger balls acquire higher temperatures. Further increase in diameter of the balls, however, leads to decrease of ball speed due to decrease of the effective vial diameter [12] (difference between diameter of vial and diameter of the ball) and so the dissipated energy. In theoretical kinematics of motion

Table 1
The parameters of operation modes of AGO-2 mill

Number of steps	Rotation frequency, rpm (angle frequency, s^{-1})		Ball speed[a] (m s^{-1})
	Planet carrier	Vials	
I	630 (66.0)	1290 (135.1)	4.79
II	890 (93.2)	1820 (190.6)	6.76
III	1090 (114.14)	2220 (232.5)	8.24

[a] The ball speed was calculated according to formulae (7) and (15) of Ref. [11] for 5 mm diameter balls. The effective vial radius [12] (differences between the inner radius of vial and the radius of ball) was taken as r_v.
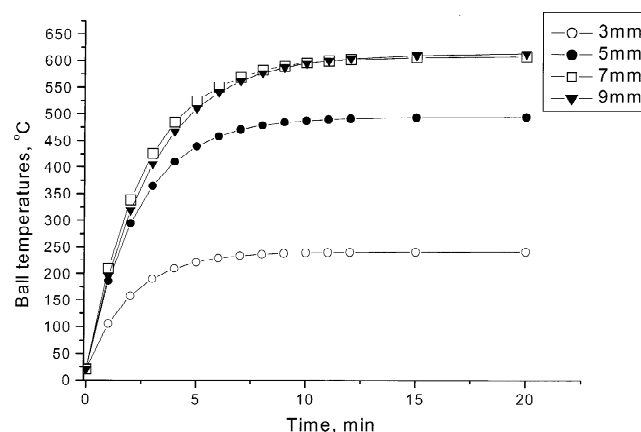

Fig. 1. Time dependences of the ball temperatures for the case of absence of powder in the vials (bare balls). Step III of operation mode, 0.1 MPa of Ar in vials, balls charge is 200 g per vial.

Ball diameter (mm)	Operation step		
	I	II	III
3	130	189	240
5	261	352	494
7	304	424	607
9	308	430	613

Ar, 0.1 MPa.

of balls in planetary ball mill, balls are taken as point bodies (see Ref. [11]) and effective vial diameter should be used to calculate speed of the balls.

The measured temperatures of the balls at a steady state (after 20 min of operation) are cited in Table 2 for different operation steps and ball diameters with 0.1 MPa pressure of argon in the vials. Fig. 2 illustrates dependence of the steady state temperature of the balls on the pressure of the argon and helium gases in the vials.

From the data of Fig. 2 and Table 2, it becomes clear that the main mechanism of heat transfer between balls and vial in a planetary ball mill is a forced convection. In accordance with this mechanism the ball temperature increases with the milling power and decreases with increasing total surface of the charged balls, heat conductivity and pressure of the gas in the vial. A simple estimation shows that heat transfer by irradiation is also important at high temperatures (500 °C and more). Decrease of the ball temperature by several tens of degrees was observed for specially blackened balls.

3.2. Ball temperature during MA

Two different cases can be dealt with separately. In the first case, compact layers of the powders are formed on the milling media and the wall of the vial. This is usual at the initial stage of milling ductile metals having large affinity to materials of balls and vials [10]. There are no free powders in this case until brittle products are formed. Such cases were observed at initial stages of MA of the Zr–Co, Ti–Al, Zr–Ni, Cu–Fe and Ni–Al systems. It must be stressed that formation of strong coverage depends on the quantity of brittle surface oxides. The second case is that compact covering is not formed due to brittleness of the initial powders or only small affinity to the balls and vials. In the first case the ball temperature is approximately the same as for the case of absence of powder in the vials. Unconnected powders decrease the ball temperature (Fig. 3).

An intermediate type of behavior took place for MA of Mg–Ni blends. Some part of the powders formed coatings on the balls and the vial, while the rest of the powder formed large pellet-like agglomerates with lamellar structure. The agglomerates had diameters up to 5 mm and thicknesses up to 0.3 mm. In this case, the ball temperature was lower than in the case of compact covering but higher than in the case of more dispersed powder. Ball temperature at the initial stage of MA of $Mg_{67}Ni_{33}$ blends (after 10 min of milling at step III of an operation with 7 mm diameter balls under 0.1 MPa of Ar in vials) was 360 °C. This is to be compared with 607 °C for balls without powders (or compact covering case, see Table 2) and 190 °C for a large amount of corundum powder in the vial (see Fig. 3).

3.3. Influence of ball temperature on MA, some examples

3.3.1. MA of $Mg_{67}Ni_{33}$ blends
MA of $Mg_{67}Ni_{33}$ powder blends with formation of the Mg_2Ni intermetallic compound was already investigated in a number of works [13–15]. In this paper the rates of Mg_2Ni formation for maximal difference in ball tempera-
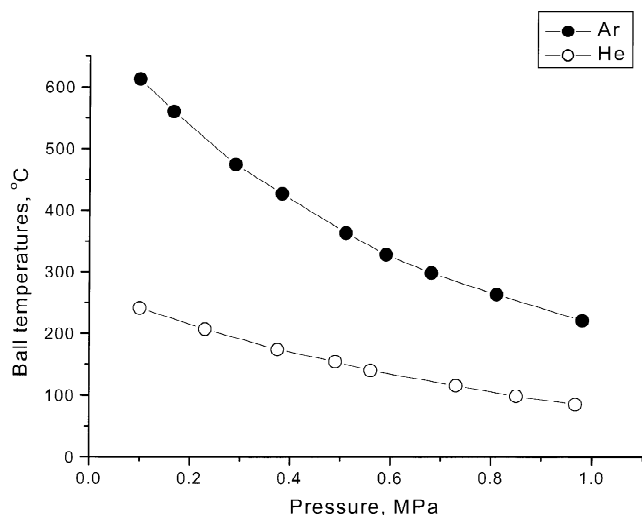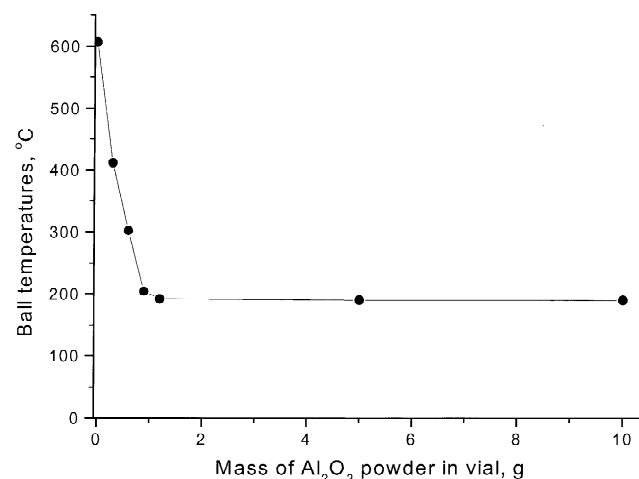

Fig. 2. Steady state ball temperatures as functions of gas pressure in the vials for bare 9 mm balls, step III of operation mode and 200 g ball charge.

Fig. 3. Steady state ball temperatures as function of the mass of Al_2O_3 powder in the vial for III step of operation mode, 0.1 MPa of Ar in the vials and 200 g charge of 7 mm balls.

tures and the same other milling conditions were studied. The milling conditions were as follows: step III of the milling operation, 200 g steel balls of 7 mm diameter, 5 g of powder blends of Mg and Ni per vial, 0.1 MPa of Ar gas for the case of high ball temperatures and 1.0 MPa of He gas for the case of low ball temperatures. The progress in Mg_2Ni formation was monitored by measurements of the content of ferromagnetic Ni in the powders, using a Gui balance. The milling process was interrupted at selected times. All treated powders were taken off the vials. Each preparation started with a fresh batch of powder. The preparations and measurements were re-produced three times for each selected time.

Fig. 4 shows obtained time dependences of the Ni content. The S-shaped form of the curves was even more pronounced than in Ref. [15]. During the induction period, the Ni content remain almost constant and after that decreased rapidly. At the end of the induction period, the ball temperatures were 360 °C for 0.1 MPa of Ar and 81 °C for 1.0 MPa of He in vials. After completion a formation of brittle Mg_2Ni, the steady-state ball temperatures were 180 °C for argon and 73 °C for helium. From the data in Fig. 4 it is clear that the ball temperatures have a strong influence on the induction period while the rate of rapid decrease in Ni content is approximately the same (within the experimental error) for both cases.

Cheng et al. [15] connected the induction period during the formation of Mg_2Ni by MA with the nucleation stage. The time needed for the formation of aggregates from the initial powder particles seems to us a more reasonable explanation. If it is really so, an increase in ball tempera-tures shortens the time of aggregate formation presumably by softening of the metals in blends. The weak dependence of the rate of Mg_2Ni formation on the ball temperature may be explained as follows. The formation of Mg_2Ni occurs upon ball collisions, and the ball temperature only weakly affect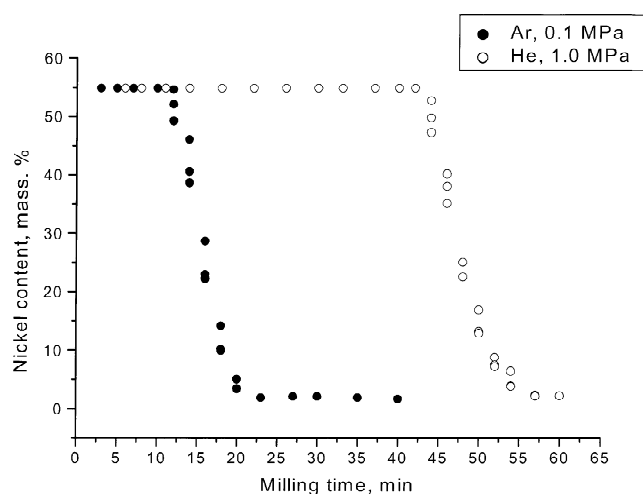s the local conditions developed in the aggregates during the collisions. For example, this may be the case if the local temperature upon ball collisions is essentially larger than the ball temperature.

3.3.2. MA of $Ni_{50}Al_{50}$. Self-propagating exothermic synthesis of NiAl intermetalics

For some highly exothermic reactant blends spontaneous compound formation can occur by a mechanically induced self-propagating reaction mechanism [9,16–20], which is analogous to that of the thermally ignited self-propagating high-temperature synthesis. The length of the induction period for such reactions depends on the milling condition and the exothermicity of the reactant blend. Self-propagat-ing explosive formation of NiAl during MA of nickel and aluminum was firstly observed by Atzmon [9]. In this work, the influence of the ball temperatures on the length of the induction period for MA of $Ni_{50}Al_{50}$ powder blends was ascertained.

The powder load was 10 g, the steel balls charge was about 200 g per vial. As was pointed out in Section 2, only coarse dispersed powders with small surface were used. Compact covering was always reached for such powders. The covering mass on the balls and on the vials walls was approximately equal. There was no free powder in the vials until reaction ignition. The exothermic formation of NiAl led to a spike-like increase in temperature of the cooling water (Fig. 5). The reproducibility of the lengths of the induction period was surprisingly good. The time spread was less than 8% for the same milling condition. Like in the case of MA of $Mg_{67}Ni_{33}$ blends, the length of the induction period essentially decreased with increasing ball temperatures.

Schaffer and McCormick have proposed [20] the follow-ing model to explain the induction period for self-prop-
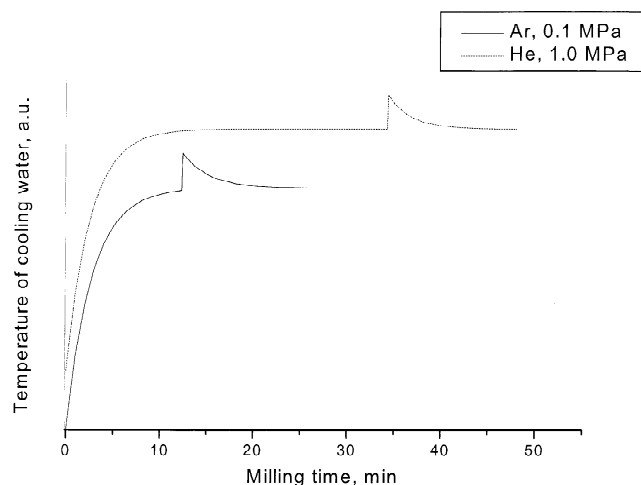

Fig. 4. Time dependences of nickel content during mechanical alloying of $2Mg+Ni=Mg_2Ni$. The milling conditions: step III of operation mode, 200 g charge of 7 mm balls; the powder mass is 5 g per vial. See text for details.

Fig. 5. Temperature traces of cooling water during MA of $Ni_{50}Al_{50}$ powder blends. The milling conditions: step II of operation mode, 200 g charge of 7 mm balls, 10 g of powder was only in one vial (for the case of powder blends in both vials overlapping of two slightly shifted spikes was observed).

agating reactions during MA. The combustion reaction can occur if the temperature generated due to ball collisions, T_c, is higher than the ignition temperature, T_{ig}. The ignition temperature is a function of the enthalpy change and the microstructural parameters such as particle size and interfacial area between the reactants. Since the MA process refines the particle size and develops the interfaces, T_{ig} decreases with milling time. In contrast, T_c increases and reaches a steady state with increasing milling time. The time at which the T_{ig} and T_c curves intersect is the critical milling time or the induction period. To study influence of the ball temperatures on T_c, the following experiment was done. The milling process was stopped just before the spike-like increase in water temperature, and the vials were left in the mill under a flow of cooling water for 60 min or more. Then resumption of milling led to an exothermic reaction 20–60 s later. As the time needed to reach steady-state ball temperatures was essentially larger than 20–60 s (see Fig. 1), it was concluded that influence of the ball temperature on T_c was only negligibly small. This fact is direct evidence for T_c being much larger than the ball temperature.

4. Discussion

The temperature distribution during MA in ball mills is more complicated than a simple overall temperature in the vial and local temperatures due to the collisions. A really essential difference exists between the temperature of the vials and the temperature of the milling balls for all cases except for cryomilling when the attritor is put in a Dewar and liquid nitrogen is both in the attritor and in the Dewar [21]. During the MA process part of the milled powder is attached to the vial walls and, other part is attached to the balls. The remaining part is in a free state moving in the volume of the vial. All these parts have different temperatures. Apparently mass transfer between these powder parts occurs during milling.

The ball temperatures increase with increasing milling power and ball diameter. According to our knowledge, the AGO-2 planetary mill has the largest power per gram of ball charges (up to 3.0 W g^{-1} at third step of the operation mode and 200 g mass of ball charge) compared to other types of laboratorial planetary mills. Nevertheless, the Fritsch Pulverisette G5 planetary mill has up to 1.604 W g^{-1} power [22,23], approximately the same value as the AGO-2 mill in the second step of operation. The ball velocity for a Fritsch Pulverisette G5 mill is even more than that for AGO-2 mill (up to 11.24 m s^{-1} compared to 8.24 m s^{-1}). Therefore the ball temperatures for Fritsch Pulverisette G5 mill may be high too.

Concerning the balls diameter, the data are limited to 9 mm in this article. The curvature of the inner walls of the vials at mergence of sidewalls and bottom restricted us using of bigger balls. Appreciably bigger balls are often used for MA. For example, 12.7 mm steel balls were used in Refs. [24,25], a 50 mm steel ball was used in Ref. [26]. One can presume the development of high temperatures for such large balls even in the case of low milling power.

The ball temperature is especially high for the case of a compact covering of the balls and the walls of the vials. After formation of the powder products the ball temperatures considerably decrease. This may be the reason that crystalline intermetallics form as intermediate products during amorphisation by MA [10,27,28]. Indeed, the powder blends which are typically used for the production of amorphous alloys by MA often have a large affinity to the balls and the vial and lead to a compact covering during the initial stages of MA [10]. Crystalline products may form in the materials covering the balls due to high temperature. When free powder appears in the vial, the temperature of the balls decreases and the formation of an amorphous alloy is setting in.

5. Conclusion

The temperature of milling balls during MA essentially differs from that of the vials. Heat transfer between balls and vial occur under forced convection conditions. The ball temperature increases with increasing milling power and decreases with increasing total surface of the balls, heat conductivity and gas pressure in the vials.

With MA of $Mg_{67}Ni_{33}$ and $Ni_{50}Al_{50}$ as examples, it is demonstrated in the present work, that the course of MA essentially changes when changing the ball temperatures but keeping all other parameters of milling the same.

The difference between the temperature of the balls and the temperature of the vial is especially high for the case of compact covering of the balls and vials from the milled powders. Even in the case of the presence of free powder in the vials this difference is essential and should be taken into account in the analysis of temperature effects during MA.

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