Solid-state reactions during high-energy milling of mixed powders

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Abstract

The phase formation of carbides and borides during high-energy ball milling has been investigated by measuring the gas temperature inside the vial and by X-ray diffraction studies of specimens taken at different stages of the milling process. The formation mechanism changes from a gradual process to an instantaneous, explosion-like reaction with increasing milling intensity and enthalpy of product formation. Finally, a model was developed to describe the milling process, and to determine the peak temperatures that are reached in the powder particles during ball collisions as well as the microstructure evolution. Using an effective coefficient of diffusion and calculating the evolution of the continuously growing diffusion layer, it was possible to determine whether and when rapid phase formation occurs. The model was tested by reproducing the milling times needed for rapid phase formation inside the mill.
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1. Introduction

Mechanical alloying, the high-energy milling of (elemental) powders, offers a cost-effective way to obtain amorphous or nanostructured materials [1,2]. The prolonged milling of powder mixtures can result in the formation of (supersaturated) solid solutions, (non-equilibrium) intermetallic compounds, or in the formation of stable or unstable carbides, borides, nitrides, silicides, etc. The kind of product formed during milling depends on the composition of the powders and the milling conditions and has been summarized in milling maps [3] for various systems.

In this paper we discuss the processes that occur in systems with strongly negative enthalpies of formation, such as the formation of titanium carbide from its elemental powders. In the 1990s, several approaches were published [4,5] that described the correlations between the various

factors influencing these processes. In this paper a different method is used to quantitatively describe the local collision events of milling balls based on geometrical considerations and the accompanying solid-state reactions. The developed model was used as an examplar to describe the milling process and to predict whether and when explosion-like phase formation occurs. The quantitative validity was tested by reproducing milling experiments.

2. Experimental results

The milling experiments were performed using mixtures of titanium powder (Goodfellow, <150 μm, 99.5% purity) with carbon ($d_{90} < 15$ μm) or boron ($d_{90} < 5$ μm) to study the formation of carbides and borides during milling or during subsequent heat treatment. The thermodynamic properties of the powders and the steel of the milling system are shown in Table 1. The milling system used was a planetary ball mill (Fritzsch Pulverisette P6) with a steel vial of 250 ml volume and steel balls with a diameter of 10 mm. The ball/powder ratio was 10:1 with a total powder mass of 19 g.

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Table 1
Thermodynamic properties of the powders used (data from Ref. [36]), numbers indicate at.%.

	Steel	Ti	B	Graphite	Ti (50) + C (50)	Ti (57) + C (43)	Ti (33)+B (66)
C (J kg^{-1} K)	500	523	1260	709	560	552	752
ρ (kg m^{-3})	7850	4500	2460	2260	3754	3891	3577
λ (W m^{-1} K^{-1})	17	22.6	27	140 (mean)	56.3	54.5	24.6
κ 10^{-6} (m^2 s^{-1})	4.8	9.6	8.7	86	27	25	9.1

Since the phase formation should give a temperature signal due to the exothermic reaction, a special wireless temperature and pressure monitoring system (GTM [6]), designed for the planetary ball mill vials, was used. The sensors allowed the pressure and temperature inside the vial to be measured at intervals of down to approximately 20 ms. From the data obtained, a pressure–temperature curve with milling time was produced. The idea was that the heat produced by the exothermic reactions in the powders is transferred to the gas atmosphere immediately and could hence be detected by the pressure sensor in real-time. Finally, as all heat becomes evenly distributed throughout the milling system (powder, balls and vial), and due to the relative masses (powder 20 g, balls 200 g, vial 2000 g), the heating of the milling container should be relatively small and delayed, giving a blurred temperature signal. As the quantity of material in, and the volume of, the vial is constant during the milling process, the gas temperature can be calculated using the law of ideal gases. With starting values of pressure and absolute temperature, this is given by:

$$T(t) = p(t)\frac{p_{start}}{T_{start}}. \tag{1}$$

A typical curve obtained during milling is shown in Fig. 1. At the beginning of the milling process, the temperature increases due to the heat produced in the system. Because of the heat transport to the outer atmosphere, the temperature reaches a constant level after some time. This level is reduced in our experiments by frequently interrupting the process. For milling intensities larger than 200 min^{-1} the pressure increases suddenly after some time of activation,
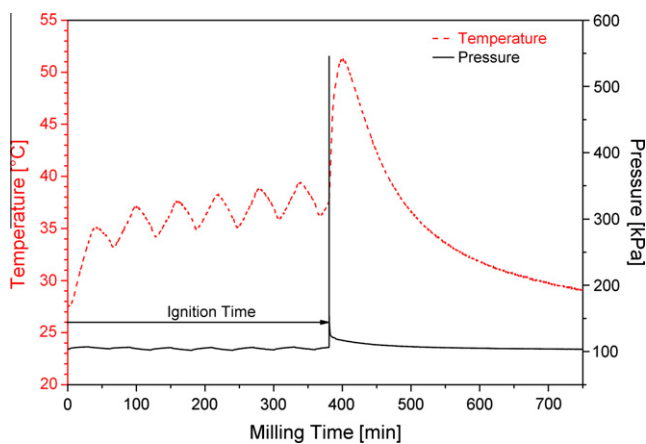
indicating explosion-like phase formation. For a milling intensity of 350 min^{-1}, the time until reaction (ignition time) could be reproduced with an accuracy of 2%. The pressure increases from 100 to 550 kPa within 50 to 250 ms. Using Eq. (1), the maximum temperature can be calculated to be about 1600 °C. The dependence of the time until ignition on the milling intensity and powder composition is shown in Fig. 2.

X-ray studies of specimens taken before the sudden reaction showed no partially reacted material. X-ray diffraction analysis (XRD) of a powder specimen taken shortly after the reaction showed no unreacted material, though light microscopy observation showed a small proportion of unreacted metal (up to 10%).

Decreasing the milling intensity below a critical value (about 200 min^{-1}) and milling for much longer times results in a continuous formation of the phases with all possible fractions.

The minimum temperature which has to be reached in the powder particles to trigger immediate product formation (ignition temperature) was determined through a rapid heating experiment. Powder specimens taken a short time before ignition were enclosed in brass capsules and dipped into liquid tin at different temperatures for a short time. XRD studies were used to detect whether or not formation of the carbide occurred. The ignition temperature of Ti–C was found to be in the range from 350 to 450 °C for milling intensities from 300 to 400 min^{-1}, and above 600 °C for Ti–B.

Fig. 1. Measured temperature and pressure during milling of a Ti–C powder mixture.
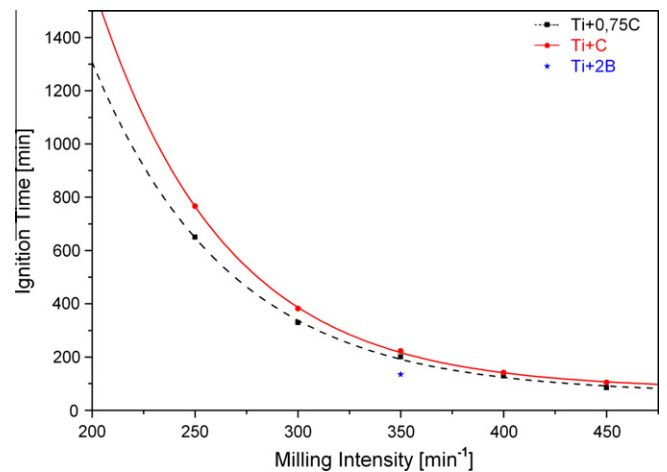

Fig. 2. Milling time until ignition vs. milling intensity; the lines show experimental fits for the measured data.