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# DEVELOPMENT OF AN EXTREMELY HIGH ENERGY BALL MILL FOR SOLID STATE AMORPHIZING TRANSFORMATIONS*

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## Summary

In order to characterize the process of solid state amorphization by mechanical alloying, we have developed a rotating-arm ball mill that has a large grinding capacity, a range of rotating-arm velocities from 0 to 500 rev $\text{min}^{-1}$, and peripheral equipment to measure the attrition temperature inside the tank and the torque applied to the rotating arm. For mechanically alloyed cobalt-rich alloys, the torque, $P$, increases with increasing rotational speed, $R$. For $R$ between 80 and 300 rev $\text{min}^{-1}$, which is a customarily used rotational speed, $P = AR^{0.3}$, where $A$ is a constant. For $R$ from 300 to 500 rev $\text{min}^{-1}$, $P = AR^{1.6}$. The mechanical alloying of elemental crystalline powders of cobalt and zirconium using $R = 450$ rev $\text{min}^{-1}$ was studied by monitoring the torque and the attrition temperature as a function of attrition time. The torque shows a peak at $t \approx 30$ min. The attrition temperature shows a peak at $t \approx 1.5$ h. This peak corresponds to an exothermic reaction in the powder and is identified with a solid state amorphizing transformation. For powders with average composition $\text{Co}_{85}\text{Zr}_{15}$, an increase in rotational speed from 300 to 450 rev $\text{min}^{-1}$ leads to a reduction in the attrition time necessary to complete the amorphization from 8.5 to 3.5 h, and to a decrease in the average particle diameter from 37 to 7 $\mu$m.

## 1. Introduction

High energy ball milling is a well-known process for grinding engineering materials, such as submicron ceramic powders, and for the mechanical alloying of composite powders such as oxide-dispersed strengthened alloy

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powders. Furthermore, it has recently been recognized that ball milling is a promising technique for the synthesis of amorphous binary metallic powders [1]. This technique has potential for the mass production, near ambient temperature, of a variety of amorphous metallic powders of widespread applications [2]. This process does not only involve grinding and/or cold welding of the particles but also the formation of multilayers of the starting elements. A solid state amorphizing reaction is thought to occur at these interfaces assisted by the extensive mechanical deformation and the increase in temperature [1]. Therefore, there is a need for a ball mill that optimizes the conditions for the efficient production of these amorphous powders, which are necessary for the development of high performance materials. Here we report a high energy ball mill that has a large grinding capacity and which enables us to control the process parameters (rotational speed, temperature inside the mill) in order to study the mechanical alloying process and optimize the yield.

## 2. Experimental procedure

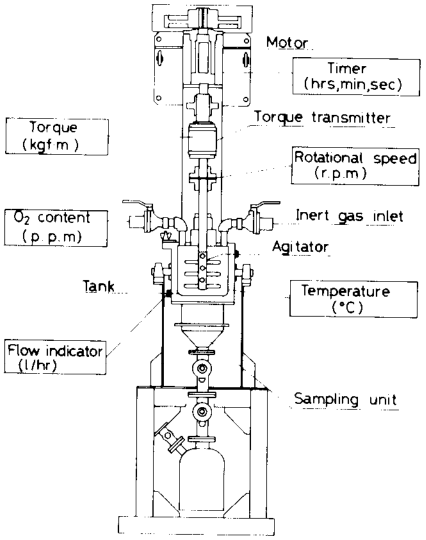
Powder mixtures of $Co_{100-x}Zr_x$ with $x = 7$ and 15, $Co_{100-x}Ti_x$ with $x = 15$ and 20 were mechanically alloyed under an argon atmosphere using a newly developed high energy ball mill with angular velocities ranging from 83 to 500 rev $min^{-1}$. X-ray diffraction and differential scanning calorimetry (DSC) were used to characterize the mechanically alloyed powders. The size distribution of the mechanically alloyed amorphous powders was measured using a light scattering method (Microtrac SPA).

## 3. Results and discussion

### *3.1. Performance of the high energy ball mill*

Figure 1 illustrates the high energy ball mill (Mitui Miike Attritor, model MA1D–X) developed especially for the synthesis of amorphous powders by mechanical alloying. This ball mill has a large motor which makes it possible to raise the arm rotating speed $R$ to 500 rev $min^{-1}$. The torque transmitter enables us to measure the applied torque $P$. The customarily used maximum speed of the standard commercial ball mill (Mitui Miike Attritor, model MA1D) is 300 rev $min^{-1}$. Figure 2 shows the torque acting on the agitating media *vs.* the angular velocity for various testing temperatures between 30 °C and 250 °C. We can see that the torque increases with rotational speed. In the ranges from 83 to 300 rev $min^{-1}$, and from 300 to 500 rev $min^{-1}$, the torque increase can be fairly well expressed by a power law:

$$P = AR^n \tag{1}$$



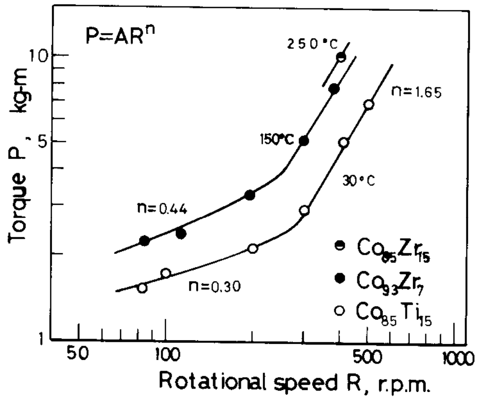


Fig. 1. Schematic diagram of the high energy ball mill for the synthesis of amorphous powders by mechanical alloying.

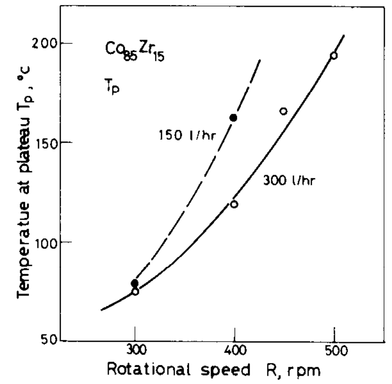
Fig. 2. Torque acting on the agitating arm *vs.* revolving velocity at various testing temperatures for some mechanically alloyed cobalt-rich alloys with titanium and zirconium.

where $n$ is an exponent and $A$ is a constant. The exponent is found to be approximately 0.30 for $83 < R < 300$ rev min$^{-1}$ and 1.65 in the newly extended range from 300 to 500 rev min$^{-1}$. Equation (1) indicates that the motion of the balls, even for $R > 300$ rev min$^{-1}$, is random (normal grinding) and not a collective motion which would result in a reduction in the torque with increasing rotation speed. Figure 2 shows that a rise in the attrition temperature causes a considerable increase in the torque, corresponding to an increase in the constant $A$ of eqn. (1).

At the same time, the use of a rotational speed above 350 rev min$^{-1}$ leads to a fast rise in the plateau attrition temperature $T_p$ (which we define in the next section) when using a relatively low flow rate of cooling water as shown in Fig. 3. In our mill, the flow rate of cooling water is varied from 0 to 1500 l h$^{-1}$, so that we can control the agitating temperature $T_p$ to optimize the rate of solid state reaction. Furthermore, our mill provides a system to control the atmosphere inside the attritor, as shown in Fig. 1.

### *3.2. Process characterization of the solid state amorphization*

We describe here the mechanical alloying process of $Co_{85}Zr_{15}$ which becomes amorphous [3] when using a rotational speed $R > 400$ rev min$^{-1}$. Figure 4 shows the attrition temperature and the torque *vs.* milling time in the case with $R = 450$ rev min$^{-1}$. The torque shows a sharp increase at early attrition time, concomitant with an increase in attrition temperature, and then, following a maximum at 0.5 h, a decrease. For longer milling time,



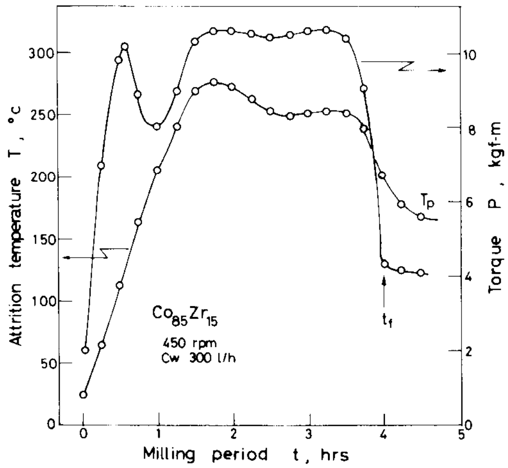


Fig. 3. Plateau attrition temperature as a function of rotational speed for mechanically alloyed $Co_{85}Zr_{15}$.

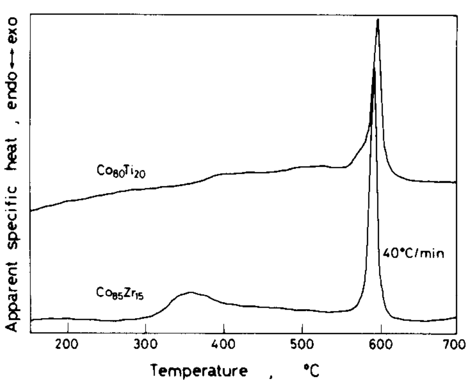
Fig. 4. Torque and attrition temperature *vs.* milling time for a rotational speed of 450 rev $min^{-1}$. Measurements taken during the mechanical alloying of $Co_{85}Zr_{15}$.

the torque increases again at around 1 h and undergoes a sudden drop at 4 h. At the same time, the attrition temperature rises and then undergoes a drastic decrease, approaching the constant level $T_p \approx 170$ °C. At this stage, the powder is completely amorphous as confirmed by the differential scanning calorimetry traces shown in Fig. 5.

The initial sharp increase in torque up to the first maximum can be coupled with a sharp increment in average particle size and the formation of powder agglomerates by the cold welding of elemental powder particles [4]. The continuous decrease in torque from this maximum is attributed to the formation of a multilayer structure. The temperature increase after the first peak in the torque results from an exothermic solid state reaction between cobalt and zirconium. The subsequent sudden drop in the torque is considered evidence for the completion of a solid state amorphizing transformation. Thus, $T_p$ measures the attrition temperature during a normal agitation after amorphization, without the exothermic reaction. Note that the torque is sensitive to changes in the powder structure and the attrition temperature is an appropriate variable by which to monitor the kinetics of the solid state amorphizing transformation.

### *3.3. Effects of rotational speed on glass formation and powder size*

Figure 6 shows changes of the attrition temperature *vs.* milling time for various rotational speeds and flow rates of cooling water. A higher water flow rate tends to suppress the exothermic reaction, (compare the curves for 400 rev $min^{-1}$ and water flows of 150 and 380 l $h^{-1}$) but the temperature rise does not have a strong effect on the attrition time necessary for the



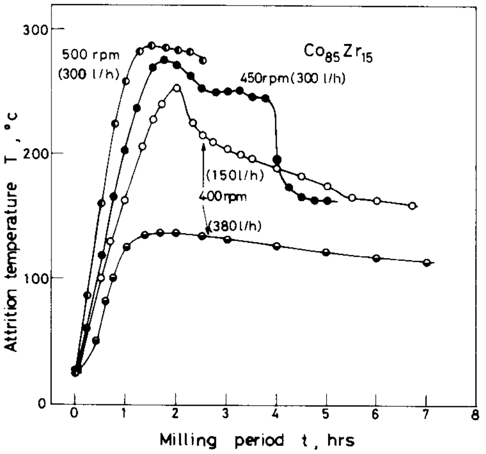


Fig. 5. DSC traces of mechanically alloyed amorphous $Co_{85}Zr_{15}$ and $Co_{80}Ti_{20}$.

Fig. 6. Attrition temperature *vs.* milling time for mechanically alloyed $Co_{85}Zr_{15}$ using rotational speeds of 400, 450 and 500 rev $min^{-1}$ at various flow rates of cooling water.

completion of the amorphization. However, the milling time $t_f$ at the completion of the solid state amorphizing transformation greatly decreases from 8.5 to 3.5 h if the rotational speed is increased from 300 to 450 rev $min^{-1}$ as shown in Fig. 7. It is suggested that a higher rotational speed, and the resultant higher torque as shown in Fig. 2, works as a driving force to shorten both the attrition time required to get a critical layer thickness for the onset of a solid state reaction and to complete the solid state amorphizing transformation under a relatively lower attrition temperature as shown in Fig. 3. A detailed analysis of the kinetics of the solid state amorphization as a function of the torque will be given elsewhere.

Figure 8 shows the logarithmic normal distribution of powder size of mechanically alloyed amorphous $Co_{85}Zr_{15}$, using both rotational speeds of 300 rev $min^{-1}$ and 400 rev $min^{-1}$. We find that increasing the revolving velocity from 300 to 400 rev $min^{-1}$ leads to a drastic decrease in the average

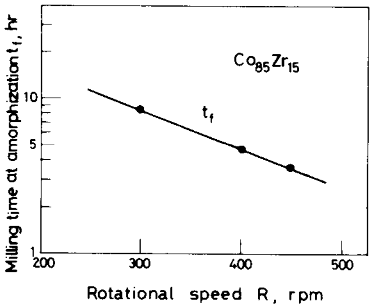


Fig. 7. Relationship between the milling time for the completion of the solid state reaction and the rotational speed, for solid state amorphized $Co_{85}Zr_{15}$.

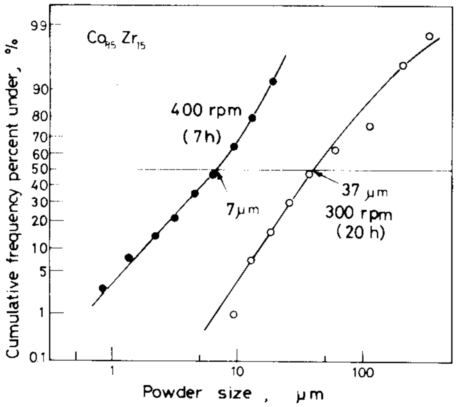


Fig. 8. Logarithmic normal size distribution of amorphous $Co_{85}Zr_{15}$ powders mechanically alloyed at the rotational speeds of 300 and 400 rev $min^{-1}$.

particle diameter from 37 to 7 μm. When considering that the occurrence of the plateau in the curve of average particle diameter against milling time after amorphization may be due to a balance between the rates of grinding and warm welding (consolidation) of the ductile mechanically alloyed amorphous powders [4], the increase in torque in eqn. (1) seems to result from the increase in the grinding force needed to shear off the amorphous powder particles.

## 4. Conclusion

We have developed a ball milling machine for the mechanical alloying of powders that has a large grinding capacity and which allows us to increase the rotational speed up to 500 rev $min^{-1}$. The torque acting on the stainless steel balls increases with increasing rotational speed. This increase is expressed by a power law of the form $P = AR^n$. The mechanical alloying process of elemental crystalline powders of cobalt and zirconium at a constant value of $R$ is characterized by an increase in the attrition temperature and a sudden drop in the torque; these events represent an exothermic solid state reaction of the starting powders. An increase in $R$ from 300 to 450 rev $min^{-1}$ leads to a reduction in attrition time for the completion of the amorphization, and a drastic decrease in the average particle diameter.

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