

ESTIMATION OF PEAK TEMPERATURE REACHED BY PARTICLES TRAPPED
AMONG COLLIDING BALLS IN THE BALL-MILLING PROCESS USING
EXCESSIVE OXIDATION OF ANTIMONY

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Since the works of Koch et al. (1) and Ermakov et al. (2) amorphization by using the high-energy ball milling technique has been observed in many binary or ternary systems. However, the mechanism of glass formation is not yet fully understood. In particular, the effective temperature present in the powder during the milling process is surrounded by controversy. Ermakov et al. (2) suggested that each time two balls collide, the powder particles which are trapped between them are subjected to frictional glide and plastic deformation, which in turn heats local regions of the powders above their melting temperature. If the melts solidify sufficiently fast through heat conduction, the amorphous structure could be preserved.

Schwartz et al. (3) concluded that this process does not involve the formation of melt and that the local peak temperature must be below the crystallization temperature of the amorphous phase, or else the powder would have crystallized. The temperatures must be high enough that a solid state interdiffusion reaction can occur as an important contribution to amorphization in the ball-milling process.

However, Schwartz and Koch (4) estimated by calculation that the peak temperature increase in the powder particles trapped between colliding balls does not exceed about 38 K, which means that only the accumulation of point lattice defects which arise during milling must be responsible for the glass formation.

In 1988, Schultz (5) showed that if ball milling is continued beyond the completion of the glass formation, amorphous powders begin to crystallize, which must be due to excessive heating during the milling.

Eckert et al. (6) showed that the milling intensity strongly affects the amorphization process. A partial crystallization can occur during the alloying of several Ni-Zr samples at high milling intensities and must be an effect of excessive heating during milling. The temperature increase of the individual particle during alloying must be at least high enough to cause crystallization ($T > 400^{\circ}\text{C}$).

Based on the concentration variation of Ni in Zr as a function of the milling time and using a simple interdiffusion model, Schulz et al. (7) estimated an effective local temperature of 180°C . Recently, Trudeau et al. (8) showed that the crystallization in their milling experiments seemed to be related more to the alloy chemical composition than to its crystallization temperature. Therefore, the relation between the crystallization temperature and the local powder temperature during milling should be done with great caution.

During a series of experiments performed in our laboratory using the ball-milling technique (9,10) we found it necessary to ball-mill elemental antimony. We used the ball-milling procedure as reported recently by Stubičar and Dužević (9). The milling was done in an agate vial (125 ml of

the volume) mounted on a laboratory centrifugal ball mill (Heidelberger Colloidmühle, Vetter K.G., Heidelberg, Germany). The authors (9) reported that using a single agate, steel and WC-Co ball, or more balls of different diameters for milling Ni-Ti and Ni-Al powders they found that the best results in alloying and amorphisation were achieved using twelve WC-Co balls (four balls of 16 mm diameter, one ball of 12 mm diameter and ten balls of 10 mm diameter) with a total mass of 160 g. The rotational speed used was 380 rev min⁻¹. These were the experimental conditions we also used in our milling experiments.

Pure antimony powder (Balzers 99.999%) of about 2.5 g of mass was put into the agate vial together with twelve WC-Co balls and submitted to ball milling in air at room temperature. After the desired time intervals, small amounts of the powder were taken out and examined by means of X-ray diffraction using copper K alpha radiation. We observed an excessive oxidation of antimony which proved to be of great help in the evaluation of the local temperature rise during our milling experiments.

Figures 1a-1f show the diffraction patterns after different milling. After 1.0 h of milling Sb diffraction peaks showed line broadening (Fig. 1b). Peaks of the oxide phase became clearly visible after 2 h of milling, and the peaks of Sb began gradually to disappear without showing further line broadening (Fig. 2c). The oxidation was quite pronounced after 12 h of milling (Fig. 2d). After 16 h the Sb peaks were no longer detectable on the diffraction patterns; the oxide phase was the only phase present, with milling remaining unchanged for up to 40 h of milling time (Fig. 1f). It may be worth noting that the temperature of the outer walls of the agate vial never exceeded 50°C during the milling procedure.

The oxide phase was revealed to be the high-temperature orthorhombic Sb₂O₃ phase (11), which is stable above 570°C, but decomposes to the low-temperature cubic Sb₂O₃ phase below 570°C (11). We rechecked these data. By annealing at temperatures of 610°C we obtained only very sharp lines of high-temperature orthorhombic Sb₂O₃, but when annealing at temperatures below 570°C, the orthorhombic phase decomposed into the low-temperature cubic Sb₂O₃ phase (Figs. 1g-1h).

The annealing time, below 570°C, needed for a complete transformation from high- to low-temperature oxide was much shorter than the milling time used in our experiment. This means that in the milling procedure local temperatures exceeded 570°C at any times, or else high-temperature oxide, once formed, would have decomposed to low-temperature oxide.

In conclusion we may say that excessive oxidation of antimony during the ball-milling process indicated that the local temperature which appears in our milling procedure is rather high, exceeding 570°C. This also means that in models explaining structural transformations in the ball-milling process the interdiffusion reaction must be taken into account.

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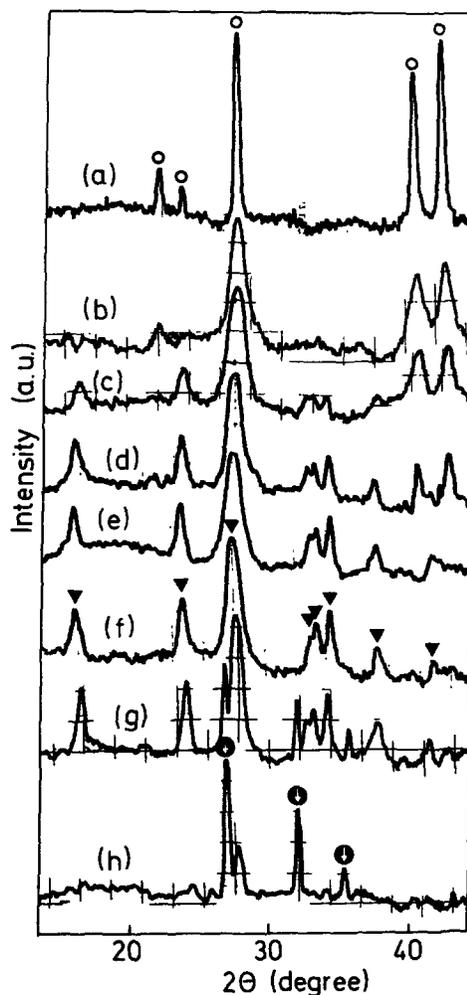


FIG. 1.

X-ray diffraction patterns for Sb treated by MG: (a) before milling, (b) after 1 h milling, (c) after 2 h milling, (d) after 12 h milling, (e) after 16 h milling, (f) after 40 h milling, (g) powder of (f) annealed in vacuum at 300°C for 24 h, (h) powder of (f) annealed in vacuum at 410°C for 4.5 h. (○) rhombohedral Sb, (▼) high-temperature orthorhombic Sb_2O_3 , (⊕) low-temperature cubic Sb_2O_3 .