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Surface mechanical alloying of an aluminum plate

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Abstract

Surface mechanical alloying was applied to coat aluminum plates with PbO and WO_3 powders. The target was used as part of the wall of the milling container and the powders were ball-milled as usual. As the balls carry some powder onto the plate, a coating develops. A SPEX 8000 and a homemade vibratory mill were compared. The coatings were investigated by optical and electron microscopy and X-ray diffraction. Uniform coatings could be obtained, if uniform ball motion, low milling intensity, small powder charge, and many small balls were used. Chemical interaction between the target and the coating powder requires efficient mixing between the coating particles and the surface of the target.

Keywords: Mechanical alloying; Surfaces and interfaces; High-energy ball milling

1. Introduction

When a mixture of powders is processed by mechanical alloying, part of the milled powder forms a coating film over the milling balls and on the inside wall of the container [1]. It was recognized recently, that this phenomenon could be utilized as a flexible method to coat the surface of an object, such as a plate attached to the wall of the milling container [2–4]. In this process, the impacts of the milling balls activate and harden the surface [5]. They also deliver and attach the powder particles and sometimes also initiate chemical interaction between target and coating powder.

In order to develop the above principle into a practical coating technology, the details of the process have to be understood and controlled. An important step in this direction is to study the effect of milling conditions on the resulting coatings.

The coating of an Al surface with PbO and WO_3 powders was selected for this investigation. Al reduces these oxides according to the equations:

$$3\mathrm{PbO} + 2\mathrm{Al} \rightarrow 3\mathrm{Pb} + \mathrm{Al_2O_3} + 1017\,\mathrm{kJ/mol} \qquad (1)$$

$$\mathrm{WO_3} + 2\mathrm{Al} \rightarrow \mathrm{W} + \mathrm{Al_2O_3} + 833\,\mathrm{kJ/mol} \qquad (2)$$

The driving force of these reactions is rather large. In fact, if both reactants are powders, ball milling initiates mechanically induced self-sustaining reaction (MSR) in either system [6]. MSR is not possible in this case, but the large driving force makes gradual reactions between target and powder likely in both systems.

2. Experimental

Some coatings were prepared using a SPEX 8000 Mixer Mill and flat-ended vial. Either the entire milling container was made of aluminum (alloy 6061) or the end plate of the steel vial was replaced with an aluminum alloy disc. Two combinations of milling balls were used: 2L + 5M stands for 2 large (L, 1.27 cm) and 5 medium (M, 0.95 cm) balls; 30S + 80V means 30 small (S, 0.635 cm) and 80 very small (V, 0.476 cm) balls. The balls fill only a fraction of the vial volume (7 and 13%) in both cases.

Similar coatings were prepared using a homemade vibratory mill. Its frequency was about 50 Hz, and the amplitude of vibration 4 mm. The axis of the cylindrical milling container was horizontal and the aluminum disc samples were attached to its vertical end surface. At this orientation, a large fraction of the impacts happened at an oblique direction. Five 8 mm plus 100 g of 3.5 mm and smaller balls were used, filling about 54% of the volume of the container. As hard balls can only be packed to a fill ratio slightly above 60%, there is little empty room for the balls to move and the vibration of the vial creates a “gas” of the milling balls.

The coated aluminum discs were inspected by optical and scanning electron microcopy (JEOL JSM-5600) and their phase composition was investigated by X-ray diffraction (XRD). A Philips Expert diffractometer and a URD-6 (DDR) system were used, both with Cu Kα radiation.

3. Results and discussion

Visual inspection of the coated surfaces often reveals substantial nonuniformity. Fig. 1 presents a typical example. Milling of

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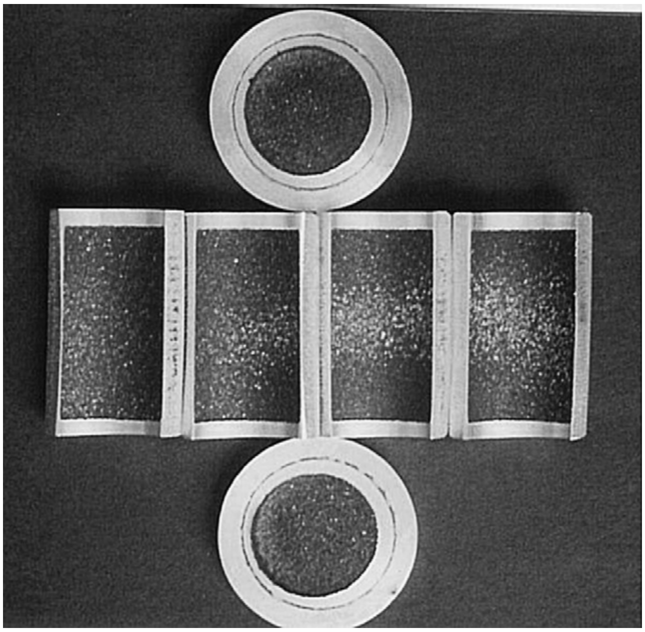

Fig. 1. Folded-out aluminum vial used with a SPEX mill for 60 min. The charge was 1 g of WO_3 powder and 2L + 5M balls. The cut in the middle is at the lower side of the vial.

WO_3 was carried out in a cylindrical container made from aluminum. Then the container was cut up and folded out to inspect the inner surface. The obviously uneven coverage of the sides is a result of the swinging motion of the vial. Also notice the uneven wear of the end discs. Better uniformity was achieved with the vibratory mill. The larger number and consequently more uniform distribution of balls and the simpler motion of the vial are probably the main reasons.

When interpreting XRD data, one must keep in mind the nonuniformity of the samples. Also, due to the strong absorption of X-rays by Pb and W, most of the information provided by the spectra originates from the top 3 μm of the samples. Fig. 2 presents some typical XRD results on PbO-coated plates.

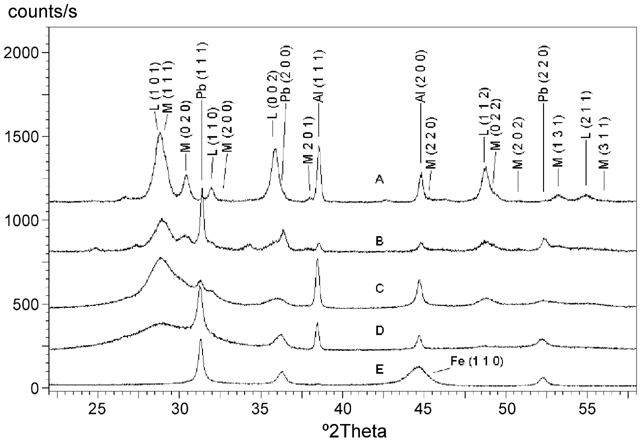

Fig. 2. XRD patterns of Al plates coated with PbO in a SPEX mill: (A and B) 1 g powder, 2L + 5M balls, 10 and 60 min of processing; (C–E) 130 mg powder, 30S + 80V balls, 10, 20, and 60 min of processing. L and M stand for the Litharge (tetragonal, 05-0561) and Massicot (orthorhombic, 38-1477) forms of PbO.

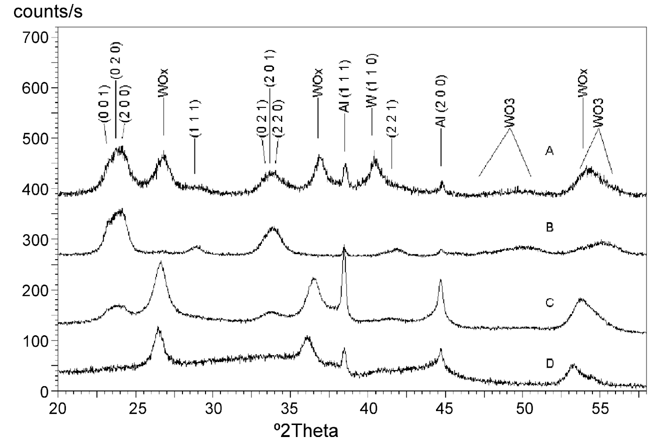

Fig. 3. XRD patterns of Al plates coated with WO_3 in a SPEX mill: (A) 1 g powder, 2L + 5M balls and (B) 3 g powder, 30S + 80V balls, both with 60 min processing time; (C and D) 130 mg powder, 30S + 80V balls, 10 and 60 min of processing. The indexed lines and the overlapping groups of lines around 49° and 54.5° are from orthorhombic WO_3 (20-1324); WOx is an unidentified oxide phase, related to a cubic structure with $a = 0.351$ nm.

Patterns A and B were prepared with a large powder load. As a result, the deposited oxide did not change much as a result of milling. Some mixing into the surface of the plate and reaction according to Eq. (1) took place. When the charge contains only 130 mg of PbO, the crystallinity of the powder decreases even when milled with much smaller balls and reaction (1) progresses much more quickly. After 60 min, Pb metal dominates the pattern and much Fe contamination from the milling tools is visible.

A few typical XRD spectra of WO_3-coated plates are presented in Fig. 3. Metallic W forms only when milling with large balls, and its relative amount is low even in that case (pattern A.) It seems that it is difficult to create good contact between the hard WO_3 particles and the Al surface. Small balls were used to prepare samples B–D. When a very large powder charge was milled, only the deposition of a thick WO_3 layer took place. Milling a small charge results in gradual transformation, but into an unidentified oxide phase rather than metallic W. The first strong lines of this phase are close to the lines of a cubic lattice with $a = 0.351$ nm, but additional lines and shifted positions suggest a larger unit cell and probably monoclinic distortion. This phase is named WOx, as it may be an oxide slightly reduced from WO_3. A substantial amorphous oxide component develops after 60 min of milling, most clearly identifiable by the broad hump around 34° (pattern D.) If annealed, this component turns into crystalline WO_3.

The morphology of the coatings was investigated by optical and scanning electron microscopy both in plane view and in cross-section. In plane view, the sites of the latest impacts are often visible. It is also clear that some impacts remove a substantial piece from the coating, especially when the milled charge is large and the coating is thick but loose.

Optical micrographs of the cross-sections of PbO and WO_3 coatings are compared in Fig. 4. The difference is very characteristic: PbO and metallic Pb are soft, they mix with the aluminum plate in layers, folding and shifting over each other as the result

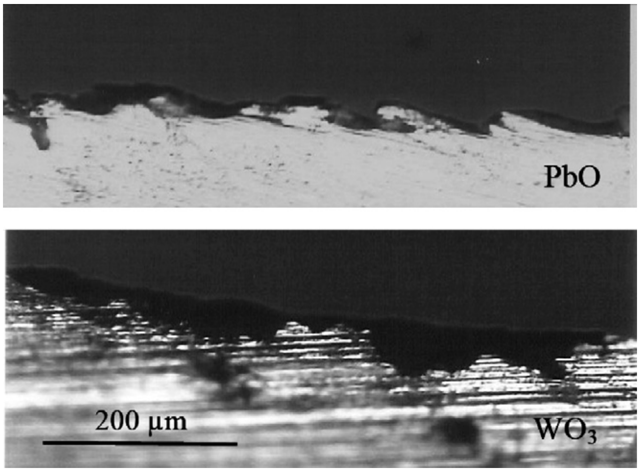

Fig. 4. Optical micrograph of the cross-section of aluminum plates coated with PbO and WO_3. One gram of powder was milled for 60 min with 2L + 5M balls.

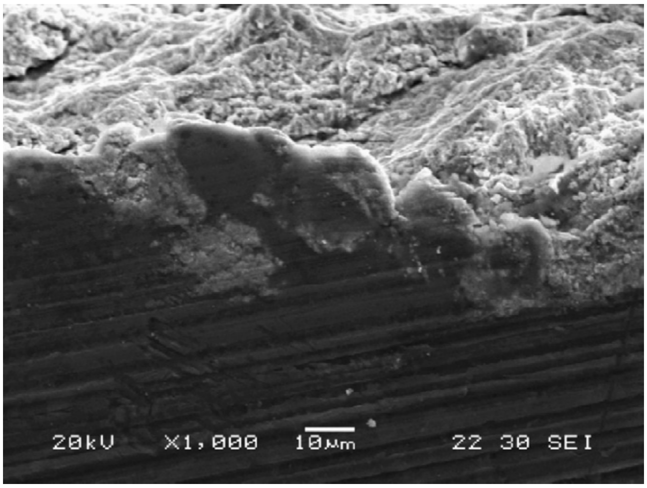

Fig. 5. The surface of an aluminum plate coated with WO_3. One gram of powder was milled with 2L + 5M balls for 60 min. The lower part shows embedded oxide particles in cross-section while the morphology of the free surface is seen above the edge.

of the impacts. Similar folding is never observed in WO_3 coatings. Instead, hard WO_3 particles get pressed into the surface, sometimes a few times 10 μm deep. Similar morphology is seen on a finer scale in Fig. 5. It also shows a partial view of the uneven top surface.

4. Conclusions

The deposition of a uniform coating by mechanical alloying is possible, but it requires good control of the ball motion so that the uniform distribution of impacts over the processed surface is assured. Controlling ball motion here is more important than in conventional powder–powder mechanical alloying, where the constant mixing of the charge diminishes the consequences of uneven ball motion.

Mechanochemical reactions in powder mixtures are promoted by the intense mixing during ball milling. Substantial reaction between the coating powder and the substrate requires mixing also when a powder reacts with the surface of a macroscopic object, but mixing also creates roughness. Proper balance must be found.

The hardness and ductility of the components affects the mixing mechanism and consequently the microstructure and chemical kinetics.

Several milling conditions – type and intensity of mill, geometry of the milling chamber, ball size and number, amount of powder, etc. – must be optimized.

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