

Preparation of Coatings by Mechanical Alloying

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Abstract

Conventional mechanical alloying (MA) is used to process mixtures of powders and generates a product that is also in powder form. MA can also be adapted to the preparation of coatings. For example, if a plate is attached to the wall of the milling container, the impacts by the milling balls activate the surface of the plate, deliver particles from the powder charge and pound them onto or into the surface. The structure and properties of the coating depend on the milling conditions and the properties of the components. In this paper, some aspects essential to the preparation of coatings are discussed. In particular, the importance of the relative hardness of the components is demonstrated by comparing the deposition of aluminium on steel and nickel on aluminium. Mechanical deposition is a promising method that may be utilized to produce a variety of coatings, but its successful application requires detailed understanding and control of the process.

INTRODUCTION

Traditionally, mechanical alloying (MA) and mechanochemical processing are carried out between powders, or between a powder and a liquid or gaseous component, generating a product that is also in powder form [1, 2]. Usually MA is performed in ball mills that utilize the impact of balls to cause alloying and chemical changes. Repeated impacts by balls are also used to treat surfaces. Shot peening [3] and surface mechanical attrition treatment [4] result in the nanocrystallization of the surface, leading to increased hardness. They also create higher activity toward surface treatment processes performed in a separate step. In the process called mechanical plating, mild impacts by small glass beads aid in coating the small parts with zinc and other soft metals in a tumbled slurry [5]. During MA the balls and the wall of the container become coated with a thin layer of powder that decreases contamination from the milling tools [6].

The deposition of powder on the internal surfaces of a ball mill can also be used as the basis for a general coating method [7]. Several arrangements are possible, depending on the size and shape of the part to be coated. Small, rounded objects can be mixed to the milling balls in a tumbler mill. A plate can be configured as a wall of the milling container and coated that way. The mill is operated with only the coating powder or liquid precursor as the charge. Activation and deposition take place simultaneously, thus the increased activity of the surface is fully utilized, promoting chemical reactions and bonding between target and powder. If post-annealing is required, it can be performed at a lower temperature due to the mechanical activation [8, 9]. Different types of ball mills – shaker mills, vibratory mills, tumbler mills – can be adapted to the deposition of coatings. The impacting balls also clean the surface, making preliminary surface preparation unnecessary.

In this paper, some general comments will be made concerning the possibilities offered by the mechanical deposition of coatings and the questions that need to be addressed in order to make the method a reproducible and controllable technology. Examples will be presented to illustrate some points.

POSSIBILITIES AND CHALLENGES

In its simplest form, coating by MA involves the deposition of powder onto a surface with no mixing of the components at the interface. This simple physical process is anticipated when the coating powder is much softer than the surface to be coated, such as the deposition of Al on steel, as discussed later. The *in situ* cleaning and activation of the surface is beneficial even in this case. Depending on the chemical nature of the components, an alloy or compound may form at the interface, aided by the enhanced diffusion between the activated surfaces [10].

If the coating particles are harder than the target, they get pressed into the surface and substantial mixing between the two components becomes possible. Coating an aluminium plate with SiO₂ [8], PbO and WO₃ [11] are such cases. Even if the intermixing is purely physical, surface hardening is achieved by the inclusion of a dispersion of hard particles. Mixing the fragmented particles into the surface provides large interface area where reactions between the components are possible. Chemical changes may take place during a post-annealing step [8] or during the deposition process itself [11]. The reaction kinetics and the microstructure of the coating are sensitive to the mechanical and chemical properties of the components. They also depend on the type of the mill and the milling conditions.

While some material always accumulates on the container walls and on the balls, using this phenomenon for depositing a uniform coating requires clear understanding and control of the deposition process. Much is already known about the mechanical processing of powders [1, 2] and that knowledge is a useful starting point. Nevertheless, there are issues that are specific to the coating process and require further investigation from a somewhat different point of view.

When a powder mixture is processed in a ball mill, the charge is mixed and moved around within the volume of the milling container. What happens in the powder trapped between two colliding balls is important, but where it happens within the container is irrelevant; uniformity is assured by the continuous mixing of the charge. If deposition of a uniform coating on a section of the container wall is desired, assuring a spatially uniform distribution of impacts becomes necessary. This adds a new dimension to modeling the ball motion in a ball mill, as the distribution of impact sites becomes a matter of concern. Assuring uniform distribution of impacts also becomes a requirement in equipment design. For example, while the SPEX 8000 mill offers high intensity in a compact size, the distribution of the impact points is very uneven, making it less suitable as a coating instrument than less energetic vibratory mills [12].

The structure of the coatings critically depends on the mechanical properties of the target and the powder. Simple deposition is likely when a softer material is deposited on a hard surface *e.g.* for corrosion protection, while hard particles can be pressed into the surface of a softer target. The repeated impacts of the balls can result in mixing of the components to a depth of a few tens of micrometers. Too many impacts can also result in surface damage. It is important to choose the impact energy and treatment time carefully. If a chemical reaction is possible, its kinetics depends on mixing and microstructure also.

Chemical interactions – diffusion, alloying, and the formation of new phases – take place at the interface between the target and the coating particles. Similar processes take place during the MA of powders, but they happen at multiple locations under different conditions and between particles with different history. In the case of coatings, the important microscopic processes take place at the interface, where they can be located and studied more easily, making this process more suitable for fundamental studies of reactions between activated materials.

The amount of powder has to be chosen carefully. Too much powder results in a thick but loose coating while decreasing the amount

of powder increases contamination from the balls. Optimizing the process requires detailed understanding of how the powder moves around inside the container. While some powder is carried onto the surface to be coated, the balls and the wall of the milling container also get covered with powder. If a small charge is used, most of the powder becomes attached to the available surfaces and only a small fraction remains loose. Matter gets transferred between surfaces during impact. Exactly how that happens is crucial to the coating process, although it is less studied for traditional powder-powder MA.

EXPERIMENTAL EXAMPLES

Coatings were prepared using a SPEX 8000 Mixer Mill. The end plate of a flat-ended steel vial was replaced with a disc made of the target material. A mixture of 12 9.5-mm and 406.35-mm milling balls were used. The amount of coating powder was 100 mg. The coated aluminium discs were inspected with a scanning electron microscope (JEOL JSM-5600) and their phase composition was investigated by X-ray diffraction using a Philips X'Pert diffractometer with $\text{CuK}\alpha$ radiation.

In a series of experiments, steel targets were coated with aluminium using different treatment times. This combination represents the deposition of a soft coating material on a harder surface. Little mechanical mixing was expect-

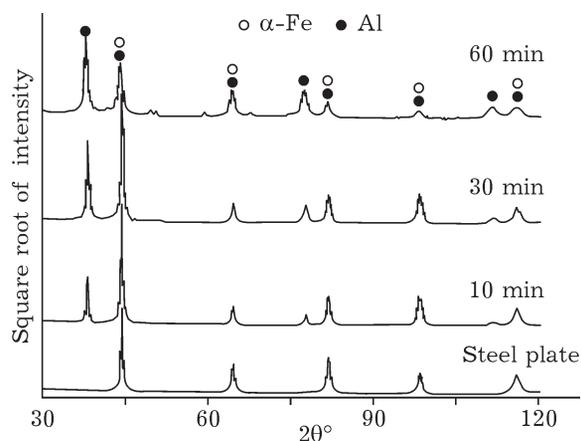


Fig. 1. X-ray diffraction patterns of a steel plate coated with aluminium after the given milling times.

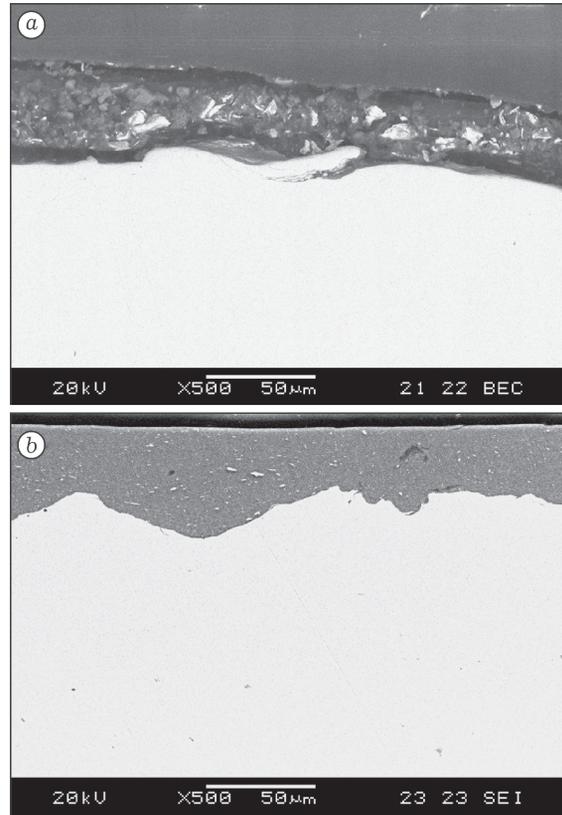


Fig. 2. Typical cross-sectional SEM images of steel plates coated with aluminium after 10 (a) and 60 min (b) of milling.

ed in this case. As a result, interdiffusion and the possibility of forming compound phases were restricted to a thin boundary layer between target and coating. As it makes up a negligible volume fraction of the sample, X-ray diffraction (Fig. 1) reflects the thickening of the Al coating with increasing milling time, but no phase other than *bcc* Fe and *fcc* Al is visible.

Nevertheless, SEM images of the cross section (Fig. 2) exhibit several interesting features. The interface between the steel target and the coating is quite irregular, showing that the impacts result in substantial roughening of the surface. After 10 min of treatment, the coating consists of Al particle agglomerates (dark) and fragments of steel contamination from the milling tools (bright). Contamination is quite substantial, of the order of 10 at. %, as very small amount of powder – 100 mg – was used as the powder charge, and consequently the steel tools could abrade each other easily. The typical size of the larger steel particles is 10 μm . The microstructure is very similar after 30 min

of milling. The uniform appearance of the coating after 60 min of milling shows that the Al melted completely, and solidified back into a uniform, fine-grain material that forms a flat and smooth coating evening out the roughness of the steel surface. This is a somewhat surprising result, as it indicates that the local temperature exceeded the melting temperature of aluminum. Typically, the temperature of the milling balls remains below 100 °C in the SPEX 8000 Mill with flat-ended vial [13], therefore the temperature in the thin aluminium layer was at least 560 °C higher than the average temperature in the mill. The steel contamination broke up into particles smaller than 5 µm, the majority below 1 µm.

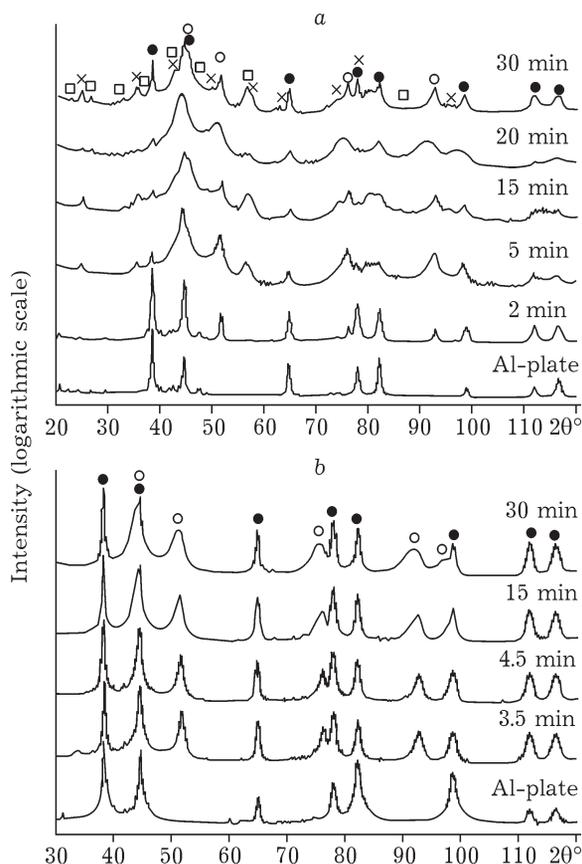


Fig. 3. X-ray diffraction patterns of an Al alloy 2024 (a) and 6061 (b) plates coated with Ni after the given milling times: 1, 2 – Ni and Al metal, 3, 4 – tetragonal (JCPDS card 21-008), and 5 – cubic (card 9-097) modifications of AlNi_3 .

The deposition of Ni onto Al plates is a more complicated case. Two series of experiments were carried out, using discs made of alloys 2024 and 6061 as targets. The main difference between the two alloys is that 2024 contains a significant amount of copper (up to 5 mass %) and it is harder than 6061. The X-ray diffraction patterns of the untreated plates are shown as the lowest patterns of Fig. 3, a, b. Alloy 2024 (see Fig. 3, a) contains a small amount of Al_2Cu (JCPDS card 25-12) and traces of other compound phases, while no second phase is detected in alloy 6061.

The phase compositions are surprisingly different for the two sets of targets. Al–Ni intermetallic compounds form on alloy 2024, while only alloying of Al into the Ni coating is observed on alloy 6061. The exact reason for the difference is not clear yet. Nevertheless, the results show that minor differences in the target significantly affect the properties of the coating. Plastic properties, *i.e.* hardness, determine the amount of mixing and the morphology of the microstructure, while the presence of alloying elements and secondary phases influence diffusion and the nucleation of new phases. More detail on this problem will be given elsewhere [14].

CONCLUSION

The preparation of coatings by mechanical means is a promising area that will lead to practical applications, although further studies are needed to achieve better understanding and control of the deposition process. Many elements of the method are similar to the traditional MA of powders, but some issues, such as the distribution of impact points or understanding the transport of powder in the mill, require further studies. Investigations of the coating process will also contribute to understanding the MA of powders.

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