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In situ consolidation of ball milled metals

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ABSTRACT

Dry ball milling of face centered cubic metals can lead to a so-called in situ consolidation phenomenon by which relatively large, spherical particles of the milled material evolve. In this study the in situ consolidation of Ag, Al, Ni and Pd has been investigated. In particular the effect of different environments (milling media and atmosphere) on this process had been studied. A possible mechanism of evolution of the spherical particles has been revealed. The presence of a small amount of oxygen slows down the evolution of spherical particles; more oxygen results in a different morphology (flaky particles, instead of spherical ones). The occurrence of in situ consolidation is independent of the crystal structure of the metal concerned. It is concluded that the intrinsic strength of a metal determines the whether or not occurrence of spherical particles during ball milling.

1. Introduction

In the last decades, due to specific, superior features, the investigation of mechanical properties of nano-grained (grain size less than 100 nm) materials is in the focus of materials science. Mechanical attrition or ball milling (BM) is a widely used simple and efficient method to produce nano-grained powders[1] [3–5]. However, in order to utilize these materials and/or to investigate their mechanical properties, the milled powders have to be consolidated [6,7]. The remaining pores in the consolidated, bulk product significantly affect the mechanical properties (e.g. yield strength), as e.g. fracture can nucleate from the pores [8].

In order to get "truly dense" products (density higher than 96% of the theoretical value) high temperature densification (i.e. sintering) is often applied. Upon sintering grain growth may take place as a side effect. Grain growth leads to loss of the mechanical strength of the consolidated material. Therefore, the high temperature necessary to realize sintering is undesired.

Mechanical milling of ductile, particulate materials usually takes place as follows [9,10]: in the first stage plastic deformation causes particle flattening, then due to the cold welding process the particles tend to stick together and the average particle size increases [11,12]. In this stage the evolving particles usually have lamellar grain morphology. Later, as a consequence of work hardening, the particles become more brittle and thus the probability of fracture increases. Finally, a more or less steady-state emerges.

Several studies reported a so called *in situ consolidation* during BM of different ductile metals and alloys [13–16]. In this process low temperature milling or a "process control agent" is used to get fine particles of a ductile metal and then in a subsequent room temperature milling the particles are consolidated due to severe cold welding. Porosity-free Cu [11,15,16], Al and Zn [14] spherically shaped particles up to a diameter of 8 mm were consolidated with this technique. The formation of spherical particles was also reported for several alloys, such as Ti-Al [17–19], Nb-Al [18] and Ti-Cu [19]. In situ consolidated Cu has a very high tensile strength and a relatively high ductility [13,16]. In situ consolidation has become a processing method to produce "bulk" nano-grained metals. However, its mechanism is not well understood. It has been claimed in several studies, that in the first stage of BM flake-shaped particles evolve and later these particles would tend to stick together to form spherically shaped particles [11,12], but to our knowledge no convincing description has been offered for the initial formation of the spheres. In this article we demonstrate a possible method for and interpretation of the evolution of spherical particles due to BM. It is shown that the degree of sticking of the milled material to the milling media (i.e. vessel and balls) is of cardinal importance for the

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[1] For example, the analysis of x-ray diffraction-line broadening of ball milled metals clearly demonstrates their nanocrystalline nature [1,2]. Thus each particle of the ball milled product (e.g. a flake or more or less a sphere) can consist of very many crystallites.

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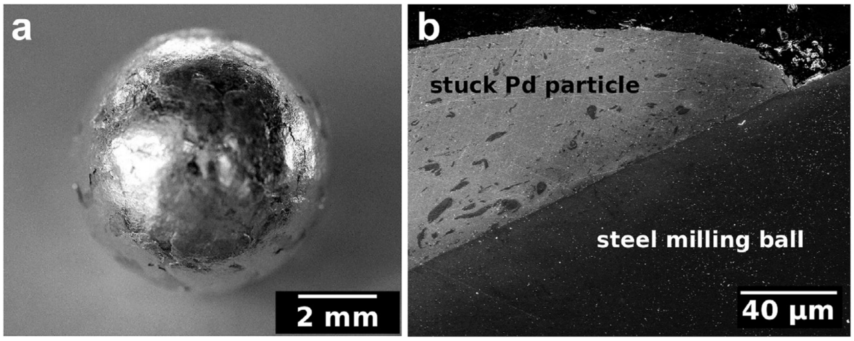

Fig. 1. Light micrograph of a 10 mm diameter steel milling ball covered with silver (a) and SEM micrograph of a cross-section of a 10 mm diameter steel milling ball with a Pd particle on its surface (b).

whether or not occurrence of spherically shaped particles.

2. Experimental

Powders of Ag (99.99 wt%) and Pd (99.99 wt%), Ni (99.8 wt%) and Al (99.5 wt%) supplied by Alfa Aesar, (initial particle sizes of 125 μm, 75 μm, 50 μm and 150 μm, respectively) were milled in a Fritsch Pulverisette 6 planetary ball mill in different vessels (steel, nickel, alumina) with different balls (steel - 10 mm diameter, alumina - 25 mm diameter and nickel - 5 mm diameter) with, for all cases, the ball to powder ratio of 10:1 and at milling speeds of 150 and 500 rpm. The milling was interrupted after every 30 min and a 30 min break was made in order to minimize heating of the specimens. Milling experiments were carried out both in a high purity Ar atmosphere (O content lower than 1 ppm) and in air. The sealing of the steel and nickel vessels from the outer atmosphere (a rubber sealing ring was applied between the vessel and its lid and an outside metal cage was utilized to hold together the vessel and the lid, thereby giving airtight sealing) were such that the slight overpressure (2–3 mbar) of pure Ar in the vessel could be maintained for at least a couple of weeks. Therefore millings in the steel and nickel vessels were carried out in a practically oxygen free atmosphere. For the alumina vessel a less perfect seal (with a teflon ring and laboratory parafilm) had to be accepted (see also Section 3).

The milled products were investigated by optical and scanning electron microscopy (SEM; Zeiss (LEO) 1530 FEG SEM, operating at 5–20 kV). For the cross-section SEM micrographs a small amount of the milled product was embedded in a conducting resin cutted with a diamond blade saw and polished with SiC polishing paper. The final polishing step was carried out with 0.25 μm diamond paste.

The oxygen contamination of the specimens was determined with carrier gas hot extraction.

3. Results and discussion

The type of mill is not crucial for the occurrence of in situ consolidation. In situ consolidation has been observed in vibratory [11,18,19], shaker [13,20], tumbler [12], magneto [21] and also in planetary mills ([22] and this study).

It was found that, if the Ag, Al, Ni or Pd powder was milled in a metallic vessel (steel, nickel) with metallic balls (steel, nickel), in the first stage of BM the powder forms globules, which then stick to the milling balls and the wall of the milling vessel (for Ni, see later in this section). Upon the continuous collisions the powder consolidates to a dense layer on the milling balls and in some cases also on the wall of the vessel. A 10 mm diameter steel milling ball covered with Ag and a 10 mm diameter steel ball with a stuck Pd layer are shown in Fig. 1. It is obvious that the Ag layer is not homogeneous; small parts may peel off during subsequent collisions. In the case of Pd milling the thickness of the layer stuck to the milling balls varies between 20 and 120 μm. As BM proceeds, parts of this stuck layer break away from the milling ball forming bended flake-shaped particles of different size. Due to the continuous circular movement of the vessel[2] the edges of these flake-shaped particles begin to convolve and doughnut-like particles evolve (see the schematic illustration and corresponding experimental results shown in Fig. 2). The evolution of doughnut-like particles was already observed for pure Cu [11] although the mechanism of the formation of this morphology was not clarified. According to the evolution process proposed here, further BM leads to the closing of the hollow middle part of the particles (Fig. 2) and eventually small spheres have developed. Once spherically shaped particles have evolved smaller flakes may weld to the surface of these spheres, as suggested by Fig. 3, where one can see that small flakes (highlighted by white rectangles in the figure) stack on the surface of a relatively large sphere. Due to the latter cold welding process the diameter of the large spheres increases with time of BM at the expense of small particles, as demonstrated in Fig. 4 where the particle-diameter distribution of Pd after different amounts of milling time has been plotted together with fitted log-normal distributions.

A couple of large, *hollow*, spherical particles were also formed, as for example shown in Fig. 5 for Ag processed in the steel milling vessel after 10 h of milling. An independent earlier study also showed frequent formation of hollow spheres during in situ consolidation [20]. There the mechanism proposed for the growth of these spherical particles was the cold welding of the already formed hollow particles leading to larger particles with multiple cavities inside. However, although the current study also showed evidence of cold welding of several particles, this mechanism seems to be rather rare: no particles containing multiple cavities were observed. The so called Russian doll effect [20], a large hollow particle containing much smaller inner particle(s), was occasionally observed in the current study: see the particle on the right-side of Fig. 5. In an earlier study the evolution of this striking morphology was suggested to be a spalling mechanism [24], involving that small pieces of the inner wall of the hollow particle peel off and form spherical particles inside the larger hollow particle. However, considering the roughness of both the inner particle and the inner wall of the large particle and also the slight opening of the large particle (at the top side of the particle), it is strongly suggested here that the evolution of this special, rare morphology is simply the

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[2] The movement of the vessel is only roughly circular; see e.g. Ref. [23].