INL/JOU-14-33403
Accepted Manuscript

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September 2015

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

Prepared for the U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

An efficient and cost-effective method for preparing transmission electron microscopy samples from powders

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Abstract

The preparation of transmission electron microcopy (TEM) samples from powders with particle sizes larger than ~100 nm poses a challenge. The existing methods are complicated and expensive, or have a low probability of success. Herein, we report on a modified methodology for preparation of TEM samples from powders, which is efficient, cost-effective, and easy to perform. This method involves mixing powders with an epoxy on a piece of weighing paper, curing the powder-epoxy mixture to form a bulk material, grinding the bulk to obtain a thin foil, punching TEM discs from the foil, dimpling the discs, and ion-milling the dimpled discs to electron transparency. Compared with the well-established and robust grinding-dimpling-ion-milling method for TEM sample preparation for bulk materials, our modified approach for preparing TEM samples from powders only requires two additional simple steps. In this article, step-by-step procedures for our methodology are described in detail, and important strategies to ensure success

are elucidated. Our methodology has been applied successfully for preparing TEM samples with large thin-areas and high quality for many different mechanically milled metallic powders.

Keywords: TEM; Sample preparation; Powders; Epoxy; Dimpling; Ion milling

Brief title: Method for preparing TEM samples from powders

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1. Currently available methods to prepare TEM samples from powders

It is often important to study the microstructures of powders, as powder particles themselves have numerous important applications (Shipway, et al., 2000; Katz & Willner, 2004), and under many circumstances they are also precursors for bulk materials, e.g., bulk metals and ceramics can be fabricated via consolidation of powders (Chen & Wang, 2000; Li, et al., 2006; Witkin & Lavernia, 2006). In the case of nanostructured powders, TEM is an indispensable tool for studying the microstructure of the powders. It is a prerequisite to prepare TEM samples from the powders. Despite the availability of many methods for preparation of TEM samples from powders, this seemingly simple experimental task remains challenging, especially for powders with particle sizes larger than ~100 nm.

For powders with particle size smaller than ~100 nm, since the powder particles are electron-transparent, their TEM samples can be prepared by dispersing them, with the aid of ultrasound, in an ethanol suspension and then depositing droplets of the suspension on a Cu grid coated with a holey amorphous carbon film (Ayache, et al., 2010). However, if high-resolution TEM (HRTEM), ultrahigh resolution scanning TEM (STEM), or electron energy loss spectroscopy (EELS) is to be performed, the powder particles may require further thinning, since these techniques require extremely thin TEM samples (thicknesses well below ~50 nm) to achieve high-quality structural analyses or compositional measurements. For powders with particle sizes larger than ~100 nm, direct observation of the powder particles by TEM without any thinning leads to poor quality of TEM images, because the particles are not electron transparent, and accordingly only very basic and limited information about particle size and morphology may be obtained. Nevertheless, because of its simplicity and convenience, this method has been applied for TEM imaging of powders with particle sizes larger than ~100 nm (Wen, et al., 2007; Xiao, et al., 2008; Danaie & Mitlin, 2009; Benslim, et al., 2010; Hashemi-Sadraei, et al., 2011). Under some circumstances, a small fraction of the powder particles can be less than ~100 nm in thickness even though the other dimensions are larger than 100 nm, and therefore TEM images of fair quality can be acquired; the particles are, however, still too thick for high quality TEM imaging (Hashemi-Sadraei, et al., 2011).

One logical method that can be used for TEM sample preparation for powders involves compaction of the powders using pressure to form a bulk material, followed by the procedures applied for TEM sample preparation for bulk materials, e.g., grinding, dimpling and ion milling. If a low pressure is applied, however, during compaction, only

weak bonding between powder particles is acquired, and consequently the powder compact may be easily broken during subsequent grinding or dimpling. Conversely, if a high pressure is applied during compaction, a fairly strong bonding between particles may be achieved for metallic powders through plastic deformation and subsequent welding between particles; the high pressure, on the order of 1 GPa, is, however, likely to alter the microstructure of the powder particles. Moreover, in the case of ceramic powders, satisfactory bonding between particles can not be attained even with the application of a very high pressure (e.g., >1 GPa). Despite the potential to change the microstructure of powders during compaction, this method was used in some research to prepare TEM samples from Al, Al-Mg, Cu and ceramic powders; the pressure applied during compaction was on the order of 1 to 3 GPa (Huang, et al., 2003; Liao, et al., 2003a; Liao, et al., 2003b; Zhou, et al., 2003a; Xu, et al., 2008).

For hard and brittle ceramic powders, soft and ductile metals such as Al and Cu have been used as a matrix/binder to embed/bind the powders into a bulk material through plastic deformation of the metals, and then the procedures for conventional TEM sample preparation can be applied. Ceramic powders can be bound by Al or Cu powders via ball milling together with those metallic powders during which large balls or fragments are formed due to cold-welding of the metallic powders (Huang, et al., 1994b; Yang, et al., 2001). In some research, ceramic powders are mixed with Cu powders and the mixed powders are pressed at a pressure of 1GPa into a thin pellet (Xu, et al., 2008). Thin metal sheets can also be used as the embedding matrix, and a small amount of the ceramic powders are placed between two Al or Ag sheets, which are then pressed using a low pressure until the cold-welding between the two metal sheets is achieved (Montone

& Antisari, 2003). All different varies of this method are typically limited to hard ceramic powders, since for metallic powders, large plastic deformation will be introduced into the metallic powders during the cold-welding process, which is likely to alter their microstructure.

Metallic or ceramic powders can be embedded in a thin metallic layer deposited on a substrate by electrochemical deposition (Lim, et al., 1992; Yang, et al., 2002) or electroless deposition (Yoshioka, et al., 1997). The resulting composite is then subjected to conventional TEM sample preparation. However, the deposition of a proper metallic layer requires careful control of the chemical or the electrochemical conditions. In addition, in the case of insulating powders, the process can be tedious and difficult (Montone & Antisari, 2003).

Ultramicrotomy has been utilized to prepare TEM samples from powders, in which powders are embedded in an epoxy and then ultrathin slices (30-100 nm thickness) are sectioned by an ultramicrotome equipped with a diamond knife (Wei & Li, 1997; Litynska-Dobrzynska, et al., 2010; Hoffmann, et al., 2012). Nonetheless, this technique has a number of limitations. Firstly, because the diamond knife deforms and fractures the sample, many defects are introduced into the material during cutting, which changes the microstructure of the sample and renders TEM image interpretation challenging (Williams & Carter, 1996; Williams & Carter, 2009; Ayache, et al., 2010); this limitation applies especially to metallic materials. Secondly, ultramicrotomy can be applied to only a limited range of materials, because it requires the material to be both sufficiently hard and plastic, so that during cutting fracture can readily occur and then spread without fragmenting the sample (Ayache, et al., 2010). Thirdly, ultramicrotomy may be difficult

to perform, and many problems may be encountered during cutting (Ayache, et al., 2010). Additionally, after cutting the thin slices or flakes are floated onto water or an appropriate inert medium, and it can be challenging to collect them on a TEM grid (Williams & Carter, 1996; Williams & Carter, 2009).

Dual-beam focused ion-beam (FIB) milling has been implemented to prepare TEM samples from powders, utilizing the lift-out method (Kitano, et al., 1995; Prenitzer, et al., 1998; Rea, et al., 2005; Ipus, et al., 2010; Lin, et al., 2012). This technique is powerful and can be applied to both metals and ceramics. It has, however, several major disadvantages. Firstly, the equipment is very expensive and not available at many universities or institutes; even if access to an instrument is available, the cost per hour for using the equipment is high. Secondly, the FIB lift-out technique requires considerable skill and therefore a long training period, and much practice is required to master it. Thirdly, this technique can be time-consuming as only one sample can be obtained from one lift-out and subsequent thinning. Fourthly, it requires care to handle the sample when transferring it to a TEM grid or membrane box or TEM microscope sample holder.

It is a viable method to use epoxy to bind powder particles, and subsequently prepare TEM samples from the powder-epoxy mixture. Gatan Inc. has purchased from EPO-TEK a special epoxy and rebranded it as G-1 epoxy, for TEM sample preparation (Gatan Inc.). The G-1 epoxy contains a resin and a hardener, which are mixed when used, and it is stable during ion milling and when exposed to the electron beam in a TEM. In their book on TEM, Williams and Carter describe a method for preparation of TEM samples from powders based on the use of an epoxy (Williams & Carter, 1996; Williams & Carter, 2009), and Gatan Inc. describes the same method in their instructions for using

the G-1 epoxy (Gatan Inc.). Firstly, the G-1 resin is mixed with the G-1 hardener to form the G-1 epoxy, and powders are mixed with the G1-epoxy in a teflon cup. Then the powder-epoxy mixture is transferred into a brass tube, 3 mm outer diameter, and the epoxy is cured by heating. Finally, the brass tube is sectioned into multiple discs, and the discs are ground, dimpled and ion milled to electron transparency, following the standard procedures for preparing TEM samples from bulk materials. This method, which we denote as the *tube method* hereafter, has been utilized for preparing TEM samples from Al, Al alloy, Ni and Ni alloy powders (Zhou, et al., 2001; Chung, et al., 2002; He, et al., 2003; Zhou, et al., 2003a; Zhou, et al., 2003b; He, et al., 2004; Thornton, et al., 2007). In some research, stainless steel tubes instead of brass tubes were utilized (Chung, et al., 2002; He, et al., 2003; He, et al., 2004).

Despite the utility of the *tube method,* it has some limitations. Firstly, it can be difficult to transfer the powder-epoxy mixture into a brass or stainless steel tube tens of millimeters in height, due to its small inner diameter (~2 mm). In order to place the mixture into the tube and occupy as much space in the tube as possible to minimize porosity, a good fluidity of the mixture is required, and therefore the powder load must be low, which leads to problems during the later stage of ion milling, as evident in the later discussions of this article. If the powder content is high, it is very difficult to transfer the powder-epoxy mixture into the tube. One can force the mixture into the tube by pressing with a wire or a tooth pick. However, a portion of the powder mixture tends to adhere to the wire or tooth pick, and therefore only a low packing density in the tube can be achieved, which results in a high porosity in the tube. After curing the epoxy and cutting the tube into discs, many large pores can be seen with the naked eye in most, if not all, of

the discs; a fraction of the discs are not intact, with a large portion missing, making them unusable. The high porosity in the discs leads to problems during grinding, dimpling and ion milling. A strategy to alleviate this problem is to section the tube into short tubes with a height of ~1 mm before transferring the powder-epoxy mixture into it, and use these short tubes (Chung, et al., 2002); it is significantly easier to place the mixture into a short tube than into a long one. Nevertheless, it remains difficult to fill with the powder-epoxy mixture the short tubes with small inner diameter and achieve a low porosity in the tubes. The second limitation associated with the *tube method* is that de-bonding between the powder-epoxy mixture and the tube is likely to occur during grinding, especially when the disc is <100 μm thick. In summary, although it is viable for TEM sample preparation from powders, the *tube method* has some major disadvantages.

In addition to the *tube method*, there are some other methods in which epoxy is used to bind powder particles (Carr, 1985; Huang, et al., 1994a; Guilemany, et al., 1997; Tang, et al., 2007). For example, a special mold made of epoxy is fabricated, and epoxy-powder mixture is placed in the mold and centrifuged, followed by curing of the epoxy; after curing, the epoxy-powder mixture is removed from the mold and ground (Carr, 1985). In a different method, a piece of 3 mm-diameter metal net with net aperture 300 mesh is embedded into the epoxy-powder mixture and flattened; the epoxy is allowed to cure, and the metal net loaded with the epoxy-powder mixture is then mechanically ground until both faces of the metal net are revealed (Huang, et al., 1994a). In another method, powder particles are mixed with the epoxy in a special silicone mold; after the epoxy is cured, the bulk material is sectioned with a diamond saw to thin slices (Guilemany, et al., 1997). In all these methods, special molds or holders are used, which adds complexity to the

methods and makes them not easy to perform.

2. Our modified methodology for preparation of TEM samples from powders

Our method for preparation of TEM samples from powders also involves the use of Gatan's G-1 epoxy, which is similar to the *tube method*. We do not, however, use tubes or transfer the powder-epoxy mixture into tubes. Instead, we mix the powders with G1-epoxy on a piece of weighing paper, and cure the powder-epoxy mixture on the paper, without transferring the mixture to any kind of *holder*. After curing, the paper can be removed and the powder-epoxy mixture becomes a free-standing bulk material. Our modified approach overcomes all the disadvantages of the *tube method* and is efficient and easy to perform, with a high probability of success. We have used this modified methodology to prepare successfully TEM samples from many different metallic powders (Wen, et al., 2010; Wen, et al., 2011; Zheng, et al., 2011; Liu, et al., 2012; Wen & Lavernia, 2012; Wen, et al., 2013; Ma, et al., 2014), but the detailed procedures have not been reported heretofore. In this article, we describe our step-by-step procedures in detail, and elucidate important strategies for each step to ensure success.

We use cryomilled Cu powders to illustrate the step-by-step procedures for preparing TEM samples. Cryomilling is a mechanical milling technique in a cryogenic liquid, such as liquid nitrogen, which usually results in a nanocrystalline grain diameter and micron-scale particle diameter for metallic powders (Witkin & Lavernia, 2006). Mechanical milling or alloying in general is a widely used technique to synthesize novel non-equilibrium powder materials with nanostructures, supersaturated solid-solutions or metastable phases, etc. (Suryanarayana, 2001; Witkin & Lavernia, 2006). Therefore, it is

important to prepare TEM samples for mechanically milled powders and then study the microstructures of the powders by TEM.

2.1 Obtaining thin foil of powders

The first step is to use G-1 epoxy to bind powders into a bulk material and then grind the bulk material to obtain a thin foil. G-1 epoxy contains two components, a resin and a hardener, which should be mixed with a volume ratio of 10:1 (Gatan Inc.). We place 10 drops of resin and 1 drop of hardener on a piece of weighing paper, and then mix them uniformly with a tooth pick. Cu powders are placed on top of the epoxy, and mixed homogenously with the epoxy using a tooth pick. There is no exact ratio of the powders to the epoxy, since an appropriate ratio is dependent on the properties of the specific powders, e.g., wettability of the powders by the epoxy. However, one important principle is that an as high as possible weight or volume ratio of the powders to the epoxy should be achieved, while simultaneously ensuring that there is adequate epoxy to bind the powders. The powder-epoxy mixture should have a solid load as high as possible, being a “paste” instead of a “suspension”; meanwhile, the mixture should be sticky rather than loose, and the powders in the mixture should not be dry to ensure that the powder particles are sufficiently bound by the epoxy. The reasons why this requirement should be met are that sufficient binding of the powder particles by the epoxy is critical for ensuring success during subsequent grinding and dimpling of the powder-epoxy mixture, and that a high load of powders in the mixture is crucial for the last step of ion milling of the mixture. Figure 1(a) shows the powder-epoxy mixture immediately after the mixing. The mixture should be naturally aged for one night or a few days, so that bubbles originally in

the epoxy and subsequently in the mixture can migrate to the surface and break, thereby reducing the porosity in the mixture. This step is not crucial but beneficial. Figure 1(b) displays the powder-epoxy mixture after being naturally aged overnight.

The epoxy in the powder-epoxy mixture needs to be cured to acquire strength for the mixture. If the mixture is aged naturally for several days, then the epoxy will be cured at room temperature. For extremely temperature-sensitive powders, the long-time natural aging is desirable. Nevertheless, most metallic or ceramic powders are not extremely sensitive to low-temperature heating. To avoid waiting several days for the epoxy to cure at room temperature, the powder-epoxy mixture on the weighing paper is heated using a hot plate at a temperature <100 ^{o}C for ~20 min to permit the epoxy to cure. One can simply touch the mixture during heating to judge if the epoxy has been cured; after complete curing, the mixture becomes both hard and strong. Figure 1(c) shows the powder-epoxy mixture after curing the epoxy by heating. The mixture is now a bulk material with a fairly high strength, and the weighing paper can be removed.

The bulk material obtained by curing the powder-epoxy mixture is glued to a sample holder or any bulk material with a flat surface and appropriate dimensions to permit handling, and then ground using silicon carbide grinding paper. The powder-epoxy bulk material may be thick (e.g., ~1-3 mm thickness), and therefore a coarse grinding paper (e.g., grit size 120) and a high grinding speed can be used when commencing grinding. If there are powder particles dropping out from the surface or if the entire sample collapses during this stage of grinding, too many powders or too little epoxy was used when mixing the powders with the epoxy during the first step of the procedure. The thickness of the powder-epoxy mixture can be adjusted to several

hundred microns immediately after mixing the powders with the epoxy by carefully spreading the mixture paste on the weighing paper using a tooth pick. A grinding paper with a grit size of 800 or 1200 should be used for the final stage of grinding and polishing of the powder-epoxy bulk material to obtain a relatively smooth surface on both sides of the sample. The powder-epoxy bulk material can be ground to a thin foil ~50 μm thick in ~30 min, even if it was initially ~3 mm thick. The thin foil obtained after grinding is shown in Figure 1(d). The area of the foil is now smaller than that of the original powder-epoxy bulk material, due to uneven grinding of a fairly large sample and therefore loss of some portion during grinding. Small pores can be observed in some areas of the foil. However, the porosity is low and the foil is generally dense.

In contrast with the *tube method* in which it is difficult to obtain low porosity samples with a high powder content, Section 1, it is evident that a dense thin-foil with a high powder load can be easily obtained using our method. After obtaining a thin foil, numerous 3 mm diameter discs can be punched from it. A small fraction of the discs containing pores, especially at the centers of the discs, can be discarded, whereas the rest of the discs can be dimpled. Some representative discs are displayed in Figure 2(a). Using our method, numerous dense discs with a high powder load can be obtained in one set of grinding, whereas the *tube method* requires multiple sets of grinding if multiple samples need to be prepared, Section 1. Therefore, our method is significantly more efficient than the *tube method*. In summary, compared to the *tube method*, our method is notably easier to perform and significantly more efficient, producing dense and strong discs with a high powder content, which is crucial for ensuring success during the subsequent steps of the TEM sample preparation.

2.2 Dimpling

After the 3 mm diameter discs are obtained, dimpling is performed using a South Bay D500i dimpler or a Gatan 656 dimple grinder. Because the discs prepared using our method are dense and strong with high powder content, the procedures for dimpling these powder-epoxy discs are exactly the same as those for dimpling discs of bulk metals, and in our experiences these discs rarely break or buckle during dimpling. For the first stage of dimpling, a coarse diamond paste or suspension with particle diameter of 3 μm can be used; in the final stage, a diamond paste or suspension with 1 μm particle diameter should be used, and dimple-polishing wheel with cloth or rubble should be utilized, so that a smooth surface with a small root-mean square roughness is obtained. We usually dimple only one side of the disc, and the nominal thickness after dimpling is ~10-15 μm. It typically requires ~20 minutes to dimple one sample; this time depends on the material and the exact thickness of the disc before dimpling. Figure 2(b) displays representative discs after dimpling.

It is noted that dimpling is a necessary step for TEM sample preparation from powders. When preparing TEM samples from bulk materials, some researchers grind the discs to ~20-30 μm and then ion mill them without dimpling. If a foil of a powder-epoxy mixture is ground to ~20 μm, it may buckle or become fragile, which renders it difficult to handle. Additionally, it only requires ~20 min to dimple a sample with an original thickness of ~50 μm to ~10-15 μm, whereas it may require additional time notably longer than 20 min to ion mill a ~20-30 μm thick sample than to ion mill a ~10-15 μm thick one.

Therefore, it is suggested that the thin foil is ground to ~50 μm thick, and then dimpling is performed on the discs punched from the foil.

2.3 Ion milling

The dimpled discs are now ready for ion milling. If during grinding, the foil is ground to a thickness <30 μm, after dimpling the discs may become fragile, and they should be glued, using Double/Bubble extra-fast set epoxy, to Cu TEM grids with 2 mm-in-diameter holes, so that the discs are supported on the Cu TEM grids. Discs having an original thickness of ~50 μm are usually sufficiently strong after dimpling, and therefore they do not need to be glued onto Cu grids. Ion milling is performed using a Gatan precision ion polishing system (PIPS), equipped with an optical microscope to monitor the sample during the ion-milling process. 4 kv Ar^+ ions are used. The angle employed during the initial 1-2 hr is 6^o, and then it is reduced to 3^o. The ion milling usually takes <4 hr. Liquid-nitrogen is used to cool the stage and therefore the sample during the whole process of ion milling.

Some problems may arise during ion milling. The rate of ion milling of metals or ceramics can be significantly slower than that of the G-1 epoxy. Consequently, ion milling of the powder-epoxy mixture is non-uniform. Epoxy surrounding powder particles may be selectively removed, whereas the powder particles are only slightly ion milled. If the area fraction of epoxy is high, i.e., the solid load is small in the powder-epoxy mixture, the rapid removal of the epoxy will lead to powder particles falling out of the disc because they are poorly bound, after a significant fraction of the epoxy surrounding them is removed. This problem will result in failure of the sample

preparation. Therefore, during the first step of mixing powders with epoxy, it is critical to ensure that the solid content in the powder-epoxy mixture is as high as possible, with the precondition that the powder particles are sufficiently bound by epoxy.

Even if the solid content in the powder-epoxy mixture is high, ion milling of the mixture is very different from that of a regular bulk sample. Consequently, it is not trivial to determine the instant when the sample is ready and therefore when ion milling should be terminated. For a regular dense bulk sample, there are no pores in the sample prior to ion milling. Once a small orifice is generated during ion milling, the process should be terminated immediately, and electron-transparent regions are usually present along the edges of the orifice; otherwise, an excessively long time of ion milling may remove the thin areas. In contrast, in the case of the powder-epoxy mixture, some pores may exist before ion milling, Section 2.1. Additionally, since the epoxy is transparent to light, an area of epoxy may be mistaken as a pore or orifice. Figure 3(a) shows an optical micrograph of a disc before ion milling, which was taken with lights above and under the disc. There is a relatively large hole with irregular shape roughly in the center of the disc (note that the center of the disc does not coincide with that of the view-filed of the micrograph). This hole was generated during dimpling, due to two or three powder particles falling out of the disc by dimpling. In Figure 3(a), four nearly spherical pores are present. These pores originated from bubbles created during the mixing of powders with epoxy. In addition to the large hole and the spherical pores, some areas with irregular shapes appear transparent, Figure 3(a), corresponding to epoxy. The fraction of these areas is very small, indicating a high solid-content of the powder-epoxy mixture. Figure 3(b) displays an optical micrograph of the sample after 1.5 hr of ion milling,

which was recorded with light under the disc. The central hole is now significantly larger because of ion milling. With only the light under the disc, the small transparent areas with irregular shapes corresponding to epoxy are clearly seen. It is evident that most areas along the edges of the central hole are powder particles, due to the high solid-content in the powder-epoxy mixture. More careful examination of the powder particles along the edges of the central hole indicates that some powder particles have been significantly milled, which can be determined by monitoring changes in particle shapes during ion milling. Additionally, it can be seen in Figure 3(b) that some powder particles along the edges of the central hole have undulating edges with spikes, which may be electron-transparent areas, and the ion milling may be stopped. To increase the thin areas we decided to further ion-mill the sample for an additional 1 hr; Figure 3(c) is a micrograph of the sample after ion milling for 2.5 hr. The central hole has further expanded, compared to Figure 3(b), and has now an ~400 μm diameter. This hole can be seen clearly with the naked eye, Figure 2(c). During the last 1 hr of ion milling, one observes particles falling out of the sample, due to faster milling of the epoxy surrounding the particles compared to that of the particles. The detachment of particles is not critical, since most of the areas along the edges of the hole still contain powder particles. During the prolonged ion-milling, original thin areas may be removed and new thin areas are generated. A careful examination of Figure 3(c) reveals that some of the powder particles along the edges of the hole have undulating edges that are likely to be thin areas. Since the circumference of the hole is larger, there are more powder particles along the edges of the hole and the total thin-area of the powder particles increases relative to the case of a smaller hole; if the hole is too small, there may be only several

particles along its edges, and these particles may not have thin areas along their edges. Nevertheless, the hole should not be excessively large, because with increasing distance from the center of the dimple area, the thickness of the sample increases. During excessive ion milling, the thin areas generated earlier are likely to be removed, whereas it is difficult to generate new thin-areas because being far from the center of the dimple area, the regions along the edges of the large hole are too thick. Based on the preceding discussions, the general principle to determine when ion milling should be terminated is that along the edges of the central hole, there are many powder particles which appear to have thin areas; the appropriate hole size is larger than that for a regular bulk sample, but should not be excessively large.

The ion-milled sample needs to be examined using TEM to determine if thin areas are present in the sample. Our experience indicates that as long as the sample has been prepared following our method and strategies as detailed above, thin areas can always be found in the sample. In practice, it may not, however, be simple to locate thin areas in the sample, since the hole created by ion milling is large, and there are both powders and epoxy in the sample. Using a high magnification may result in a significant amount of time needed to locate thin areas, because at high magnifications it takes time to move the sample and examine the areas along the edges of the hole. On the contrary, using a low magnification will reduce the amount of time needed to examine the areas along the edges of the hole, but it may be difficult to distinguish real thin areas of powder particles and consequently they may be missed. An efficient and effective strategy to locate thin areas is to look for those regions with undulating edges and small spikes along the edges of the hole at a very low magnification, and then to increase the magnification to search

for thin areas. For example, Figure 4(a) is a low-magnification TEM image displaying a region characterized by undulating edges and small spikes along the edges of the large hole from ion milling. The rectangle area in the image was magnified and another image was taken at a higher magnification, Figure 4(b). Thin areas of powder particles are clearly seen in Figure 4(b). A large thin area ~5 × 2 μm^2 and smaller thin areas are indicated by arrows. The smaller thin areas are sufficiently large considering the nanocrystalline grain size of the cryomilled powders. Additionally, the area adjacent to the large thin-area of powder particle is epoxy, which appears featureless. At low magnifications, Figure 4(a), it is difficult to distinguish thin areas of powder particles from those of epoxy, and hence a higher magnification is required, Figure 4(b). Using our strategy, thin areas can typically be located within 10 min.

3. Examples of application of our method for preparation of TEM samples from powders

3.1 Cu powders

Figure 5(a) displays a SEM image of the cryomilled Cu powders, which we used as an example to elucidate the procedures for our method of TEM sample preparation. The average powder particle size is ~50 μm. Figure 5(b) displays a representative TEM image taken of the large thin area, Figure 4(b), in the TEM sample. Nanoscale grains with an average grain size of ~46 nm (Wen, et al., 2010) can be clearly observed, and deformation twins in some grains are evident; some are indicated by arrows.

3.2 Brass powders

We also utilized our methodology, Section 2, to prepare TEM samples from cryomilled brass (Cu-Zn-Al alloy) powders. A SEM image of the powders, Figure 6(a), indicates that the powder particles have an average diameter of ~150-200 μm. A representative TEM image, Figure 6(b), displays nanocrystalline grains in the powder particles, and it is evident that a high density of deformation twins or stacking faults, some of which are indicated by arrows, is present inside most of the grains. The average grain diameter is ~26 nm (Wen, et al., 2013). A HRTEM image, Figure 6(c), exhibits nanoscale twins with a twin thickness of ~1-4 nm in a nanocrystalline grain. The high density of twins and stacking faults is ascribed to the low stacking fault energy of this material (<7 mJ m^{-2}), and the low temperature and high strain rate during cryomilling (Wen & Lavernia, 2012). A second-phase particle with diameter of ~8 nm is displayed in another HRTEM image, Figure 6(d), which is identified as aluminum nitride or aluminum oxynitride (Wen, et al., 2013). The high quality of the HRTEM images indicates that the quality of the TEM samples prepared by our method is high. The thin areas of the TEM samples are probably <50 nm thick, and there is no contamination from the G-1 epoxy, which is stable when exposed to the electron beam in a TEM.

3.3 Al 5083 alloy powders

TEM samples of ball-milled Al 5083 alloy (Al-Mg-Mn-Cr alloy) powders, which were milled at room temperature under an argon atmosphere, were also prepared by our method, Section 2. In this case, the epoxy-powder mixture was cured at room temperature to avoid any possible microstructural evolution, since a curing temperature of 100 °C corresponds to a homologous temperature of 0.44 for an Al 5083 alloy. Figures 7(a) and

7(b) show representative low-magnification TEM images of the powders milled for 4 and 8 hr, respectively. Inspection of the TEM images reveals $> 4 \times 3\ \mu m^2$ thin areas in the TEM samples, which confirms that our method for TEM sample preparation for powders produces large thin-areas. From the TEM images, Figure 7, nanocrystalline grains are obtained in both powders; moreover, the powders milled for 8 hr have significantly smaller grain sizes than those milled for 4 hr.

4. Summary and Conclusions

- We have developed a modified methodology to prepare TEM samples from powders. This method involves mixing G1-epoxy with powders on a piece of weighing paper, curing the powder-epoxy mixture by heating at a temperature <100 ^{o}C or aging at room temperature to form a bulk material, grinding the bulk to obtain a thin foil, punching the foil to attain 3 mm diameter discs, dimpling the discs, and ion milling the dimpled discs to electron transparency. The step-by-step procedures for our method are described in detail, and strategies to tackle potential problems associated with each step are elucidated to ensure success.
- We have applied the modified methodology to prepare successfully high-quality TEM samples with large thin areas <50 nm in thickness from many different metallic powders.
- Our method is efficient, cost-effective and easy to perform, with a high probability of success. Compared to the well-established robust and universal method for TEM sample preparation from regular bulk samples involving grinding, dimpling and ion milling, our methodology for TEM sample preparation from powders only adds

simple steps of mixing the powders with G1-epoxy and subsequently curing the epoxy. Therefore, our method for TEM sample preparation from powders is anticipated to be also robust and universal. It is anticipated that the method will apply well to ceramic powders, since it is based on the well-established method for TEM sample preparation from bulk samples, and no step in our procedures involves a limitation imposed by the material type. Hence, our method can be applied to prepare TEM samples from any metallic or ceramic powders in any laboratory possessing equipment for conventional TEM sample preparation.

Acknowledgements

Financial support from the National Science Foundation (DMR-1210437) is gratefully acknowledged. Y.J. Lin thanks financial support from the One-Hundred Talents Project, Hebei Province, China and the Research Program of Department of Education, Hebei Province, China (Project No. 2011111).

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Figure captions

Figure 1. (a) Powder-epoxy mixture immediately after the mixing of Cu powders and G1-epoxy; (b) Powder-epoxy mixture after one-night natural aging; (c) Powder-epoxy mixture after curing the epoxy by heating at a temperature <100 ^{o}C for ~20 min; and (d) the thin foil ~50 μm thick obtained after grinding the cured powder-epoxy mixture.

Figure 2. (a) Some representative 3 mm diameter discs punched from the thin foil in Figure 1(d); (b) some representative discs after dimpling; and (c) a dimpled disc after ion milling.

Figure 3. (a) An optical micrograph of a disc before ion milling, recorded with lights above and under the disc; (b) an optical micrograph of the disc after 1.5 hr of ion milling, recorded with only a light under the disc; and (c) an optical micrograph of the disc after 2.5 hr of ion milling, recorded with only a light under the disc.

Figure 4. (a) A low magnification TEM image showing a region along the edges of a large hole produced by ion milling; (b) a magnified view of the rectangle area in (a). A large thin area and smaller thin areas of powder particles are indicated by arrows.

Figure 5. (a) A SEM image of the cryomilled Cu powders, which were used as an example to demonstrate our method of TEM sample preparation; (b) a representative TEM image of the Cu powders taken of the large thin area in Figure 4(b). Some deformation twins are indicated by arrows.

Figure 6. (a) A SEM image of the cryomilled brass powders; (b) a representative TEM image of the brass powders where some deformation twins or stacking faults are indicated by arrows; (c) nanoscale twins with a twin thickness of ~1-4 nm in a nanocrystalline grain; (d) a second-phase particle with diameter of ~8 nm.

Figure 7. Representative low-magnification TEM image of the Al 5083 alloy powders milled for 4 hr (a) and 8 hr (b).