Materials Science and Engineering A 528 (2011) 2192–2195

Contents lists available at ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Rapid communication

Novel technique for the synthesis of ultra-fine porosity metal foam via the inclusion of condensed argon through cryogenic mechanical alloying

Brian K. VanLeeuwen[a,*], Kristopher A. Darling[b], Carl C. Koch[a], Ron O. Scattergood[a]

[a] Department of Materials Science and Engineering, NC State University, 911 Partners Way, Room 3000, Raleigh, NC 27695-7907, USA
[b] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, RDRL-WMM-B, Aberdeen Proving Ground, MD 21005-5069, USA

ARTICLE INFO

Article history:
Received 13 October 2010
Accepted 18 November 2010

Keywords:
Metal foam
Cryogenic temperatures
Mechanical milling
Copper
Porosity

ABSTRACT

It was discovered that mechanical milling of metal powders in an ultra high purity argon atmosphere at cryogenic temperatures can result in argon being incorporated into the metal. This incorporated argon causes expansion by increasing the porosity when the material is annealed. The resulting annealed material can be classified as metal foam due to its highly porous nature. The most porous samples were measured to have nearly 50% porosity. This effect was observed in nominally pure copper and an alloy of 81 at% palladium and 19 at% zirconium.

Metal foams have a number of unique properties that make them interesting materials for a variety of applications. Most of these applications take advantage of the low density or the high specific surface area (surface area per unit volume) of metal foams. The low density of some metal foams can be significantly lower than conventional metallic materials and are therefore valuable for lightweighting applications [1]. There is, however, a compromise between weight and strength for any given metal foam which is a function of its porosity [2–15]. Metal foams are able to absorb large amounts of impact energy in compression [8,9] which makes them interesting materials for impact absorption applications, such as helmets, armor, vehicles, or other protective equipment. Because of their high specific surface area they can be useful for compact heat exchangers, catalysis, or catalyst substrates. Copper foam, for example, can be used as a catalyst to convert ethanol to acetaldehyde and hydrogen gas [16,17]. Since these properties have a dependence on porosity, pore morphology, pore distribution, and pore size, the applications can be limited by the methods of producing these materials.

Within a specific method, the changing of specified parameters gives control over the resulting material and its inherent properties, but only within a limited range and may need to be balanced against deleterious effects on other properties. For example, consider the most common industry method of producing metal foam: the liquid state foaming of aluminum. This is very efficient compared to most other methods and can produce foams of extraordinarily low density. It seems unlikely, however, that liquid state foaming could ever be used to produce foams with fine porosity which would be preferred for applications that use the large surface area of foams. The limitations of the methods of producing metal foam places limitations on the applications of metal foams. The discovery and development of new methods of producing these materials is therefore exceedingly important to expanding their potential applications.

The subject of this work is the recent discovery of a novel solid-state technique for creating metal foams through mechanical alloying at cryogenic temperatures. In the course of a previous investigation on the thermal stability of a nanocrystalline microstructure in mechanically alloyed $Pd_{81}Zr_{19}$ [18], it was discovered that condensed argon could be incorporated into a ductile metal during mechanical alloying at cryogenic temperatures. In the as-milled condition, the argon occupied a very small volume in the alloy as evidenced by the lack of optically resolvable pores on polished cross-sections. When these samples were annealed, they increased significantly in volume (approximately 50% by volume). Based on micrographs such as Fig. 1, it was hypothesized that the significant increase in volume was due to the expansion of argon "bubbles" in the metal. The incorporation of argon via the mechanical alloying process was confirmed by secondary ion mass spectroscopy. The work reported here is intended to show that the effect occurs with other metals, and is not unique to the $Pd_{81}Zr_{19}$ alloy.

* Corresponding author at: Materials Science and Engineering, Pennsylvania State University, 121 Steidle Building, University Park, PA 16802, USA.
Tel.: +1 919 412 9484.
E-mail address: bkv5016@psu.edu (B.K. VanLeeuwen).

0921-5093/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2010.11.057

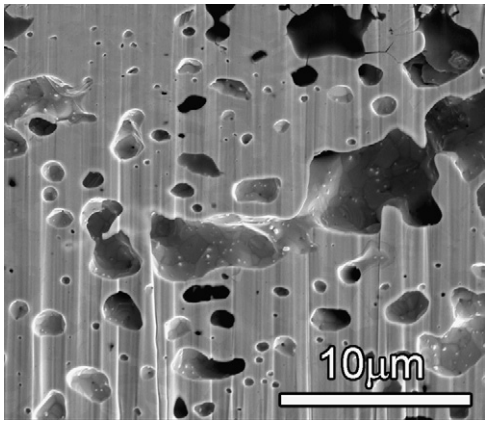

Fig. 1. FIB micrograph showing porous structure created by argon bubble expansion in mechanically alloyed $Pd_{81}Zr_{19}$ during annealing at 1000 °C.

Copper was selected because it is quite ductile and compacts at relatively low stresses. When nominally pure copper was processed under similar conditions to the $Pd_{81}Zr_{19}$ and then annealed at 1020 °C it expanded to about twice its initial volume. The mechanism of expansion is thought to be similar to that of metal foams produced by a solid-state foaming technique in which inert gas is trapped between powder particles during compaction and expands during annealing [14,19–36]. However, the foams produced here have a smaller pore size and more numerous pores then the foams created using the aforementioned technique.

The copper powder used in this study was spherical, −100 + 325 mesh, acquired from Alfa Aesar with a 99.9% purity. Using an argon filled glove box with less than 1.0 ppm O_2, 5.0 grams of Cu powder was sealed in SPEX high-energy shaker mill steel vials with 32 stainless steel balls in each as milling media (16 with 1/4″ diameter and 16 with 3/8″ diameter). This is a ball-to-powder weight ratio of about 15:1. Each vial was loaded into a SPEX shaker mill modified for cryogenic milling. Each vial was milled for 1, 2, or 4 h, following a 15 min cool down period. Liquid nitrogen coolant was used for the full duration of the milling. The $Pd_{81}Zr_{19}$ alloy from the work on thermal stability of nanocrystalline microstructures [18] was processed in a similar way.

Cryomilling [18,37–47] is sometimes used instead of the more common room temperature milling to achieve smaller grain sizes, to yield finer powder, to reduce cold welding, and to inhibit reactions. Sometimes cryomilling refers to ball milling directly in the cryogenic coolant, usually liquid nitrogen or liquid argon [38,40,42,43,45–47] and sometimes it refers to ball milling in sealed vial containing an inert gas atmosphere, usually argon, while the vial is being cooled externally [18,37,44,47]. The cryomilling performed for this work refers to the latter.

At atmospheric pressure, liquid nitrogen boils at −195.85 °C [48]. At the same pressure, gaseous argon condenses at −185.9 °C and then freezes at −189.20 °C [48]. This suggests that if the contents of the vial reach thermal equilibrium at or near the boiling point of the liquid nitrogen coolant, solid or liquid argon may be present in the vial. As a well sealed vial is effectively a closed system with a rigid boundary, the pressure in the vial should be much lower than atmospheric pressure when it reaches thermal equilibrium and since the phase transition temperatures decrease with decreasing pressure, it cannot be stated with certainty which state, liquid or solid, the argon is in without further analysis and investigation.

The cryomilling of the copper powder resulted in a yield of nearly 100%; an insignificant amount of copper was lost to the walls and milling media. The powder yield consisted of roughly circular flakes with diameters on the order of 0.5 mm. This diameter decreased with increasing milling times. The powder was pressed into disk shaped compacts in 3.0 mm and 10.0 mm diameter tungsten carbide dies under an applied uniaxial pressure of 2.0 GPa. 3.0 mm compacts used about 75 mg of material. These samples were used for microscopy but were not sufficiently massive to perform accurate density measurements using Archimedes' method. 10.0 mm compacts used about 2.0 g of material. These larger samples used were used to accurately measure the densities. All of the copper samples were annealed in a standard tube furnace at 1020 °C for one hour in a reducing atmosphere (Ar with 5 at% H_2) unless otherwise specified. The temperature of the samples was monitored during annealing via a K-type thermocouple probe adjacent to the Al_2O_3 crucible containing the samples. The temperature reached equilibrium after about 15 min. Samples of as-received copper powder were also compacted and subjected to the same annealing conditions as a means of controlling for variables in the as-received powder.

It was found that when the powder source was changed from Afla Aesar to electrolytically purified copper powder from Fisher Scientific, the "control" samples that were made from the as-received powder were observed to increase in porosity. The control samples made from the Alfa Aesar copper powder had a porosity of 8.9 ± 0.3% as-pressed and 9.5 ± 1.7% after annealing at 1020 °C. The samples made from powder from Fisher Scientific, however, had an as-pressed porosity of 10.0 ± 0.8% and a porosity of 25.2 ± 6.0% after annealing. It seems likely that the electrolytically refined powder from Fisher Scientific contained impurities and therefore only Alfa Aesar powder was used in this study.

A standard Archimedes' method setup was used for determining density of the samples. For the 10 mm diameter samples, the error in density measurement should be less than 0.1%, calculated from the ±0.1 mg precision of the digital scale used for these measurements. A thin layer of vacuum grease was applied to the surfaces of each sample to seal off any open porosity. By comparing the measurements made with and without a vacuum grease layer, it was determined that the majority of the porosity is closed or too small to allow water to infiltrate under the experiment's conditions. The average pore size in these samples is extremely fine so it is difficult to assess the degree to which these pores are open, closed, or networked. When the samples were mounted in a resin, they appeared to show complete infiltration which suggests that the porosity is open, but this would need to be confirmed by further investigation.

Traditional methods of metallographic cross-sectional preparation caused smearing which masked the porosity. To avoid this, copper foam samples were cross-sectioned with a focused ion beam (FIB). The resulting cross-section was observed with FIB microscopy and scanning electron microscopy (SEM).

Fig. 2 shows a 3 mm compact which was imaged using a dual beam FIB/SEM. This sample was annealed for one hour at 1020 °C during which the porosity increased from 9.6% to 47.4%, as measured by Archimedes' method. The surfaces were observed to be flat prior to annealing but they appear textured following the anneal. Further analysis revealed that the "bumps" observed in Fig. 2 were individual flake-shaped particles prior to annealing. These have distorted to a more equiaxed shape after annealing. Fig. 2A shows the surface of a single particle. The voids on this surface suggest that the porosity may be open, although the degree to which the pores are networked internally is not known. Inset B shows a small cross-section made with the FIB to reveal some of the internal porosity.

Fig. 3 shows the sample section from Fig. 2 at higher magnification. The image on the right was taken using the electron beam. The image on the left shows exactly the same region but was taken using the ion beam. The ion channeling contrast shows the grain structure. Using ImageJ analysis software, the cross-sectional areas of 200 pores were measured from micrographs