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High-strength bulk nano-crystalline silver prepared by selective leaching combined with spark plasma sintering

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ABSTRACT

In this work, we propose a novel technique to prepare bulk nano-crystalline metals or alloys using selective chemical leaching and spark plasma sintering. The bulk nano-crystalline silver was successfully prepared by this technique. The average grain size of the bulk material was 50 nm. The Vickers hardness, compressive yield strength, ultimate compressive strength and maximum compressive strain of the nano-crystalline silver were 155 HV 0.04, 520 MPa, 620 MPa and 20%, respectively. Micro-crystalline and coarse-grained silver were also prepared as reference materials. The bulk nano-crystalline silver prepared by the novel technique exhibited the highest hardness and compressive strength reported to date. The mechanical properties of the material from this work are compared to those from other works using the Hall–Petch relationship, and the relevant properties are discussed in relation to the preparation technique and structural characteristics of the materials.

1. Introduction

Nano-crystalline materials are polycrystalline materials with grain sizes below 100 nm. Such materials can be classified as either nano-crystalline materials or nano-crystalline powders. Nano-crystalline materials are bulk materials with structural constituents (grains or phases) less than 100 nm in size, whereas nano-crystalline powders contain either ultrafine particles with diameters less than 100 nm (nanoparticles) or coarse particles whose internal structure is nano-crystalline [1–4]. Nano-crystalline materials have been extensively studied in the past few decades because they possess unusual mechanical properties such as ultra-high strength together with a high plasticity [5]. Nano-crystalline Al alloys were reported to have tensile strength levels of approximately 1.5 GPa; for comparison, the strength of commercial high-strength Al alloys is limited to 600 MPa [6]. Nano-crystalline copper was reported to have a tensile strength of almost 500 MPa, while the strength of annealed copper is only 200 MPa [5]. The high strength of fine-grained materials results from dislocation pile-up at grain boundaries, which is generally expressed as the Hall–Petch (H–P) relationship. However, nano-crystalline materials are characterised by a large volume fraction of grain boundaries that play a role in the deformation processes. Therefore, the nanocrystals may significantly alter the material properties compared with their conventional micro- or coarse-grained counterparts. Several mechanisms have been proposed to explain the anomalous deformation behaviour of nano-crystalline materials. These include grain-boundary sliding, grain-boundary diffusion along with the presence of nanopores and impurities [7–14]. By decreasing the grain size to a critical value of approximately 10 nm, the yield strength and hardness of the material tend to increase. However, the strength appears to decrease with further grain refinement when the grain size is less than the critical value. The H–P relationship is no longer valid, and an inverse H–P behaviour is observed. The role of grain boundaries in the deformation process predominates over dislocation processes in nano-crystalline materials that have grain sizes below 10 nm [11,12].

Many techniques can be employed to prepare bulk nano-crystalline materials. The severe plastic deformation (SPD) techniques such as equal-channel-angular pressing (ECAP), accumulative roll bonding (ARB) or high-pressure torsion (HPT), can transform initially coarse-grained materials to nano-crystalline materials.

Another group of techniques includes compaction of nano-crystalline powders. Powders with a nano-crystalline internal structure can be prepared by rapid solidification techniques such as melt atomisation and melt spinning followed by ribbon-milling [15]. Novel fabrication technologies for nanoparticles include a wide range of vapour, liquid and solid-state processing routes.

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Vapour processing routes include physical and chemical vapour deposition or aerosol spraying [16,17]. Liquid processing routes involve sol–gel and wet chemical methods [18]. The solid-state processing route takes place via mechanical milling or mechano-chemical synthesis [19]. The selective leaching method used in this study was originally developed for the preparation of catalysts, and it involves the chemical reaction of an alloy with an appropriate solvent. One component of the alloy is selectively dissolved, and the remaining residue is dispersed in the liquid solution in the form of nano-crystalline powder [20]. The advantage of this method is the capability of producing relatively large amounts of nano-crystalline powders with an extremely fine structure. A prior study [20] has demonstrated that selective leaching could be used to prepare nano-crystalline nickel with grain sizes of a few nanometres.

Processing nano-crystalline powders into fully dense nano-crystalline bulk products is difficult in practice. Due to high specific surface areas, nanoparticles exhibit a high reactivity and strong tendency to agglomerate, which make handling very difficult. In addition, maintaining the microstructure of the particles at a nanometre scale after the consolidation process could be problematic [2]. Ultrafine-grained structures have a great tendency to coarsen at elevated temperatures at which most of the compaction processes occur. Therefore, compaction should be performed quickly and at the lowest possible temperatures. Common powder metallurgy routes such as hot pressing, hot isostatic pressing (HIP) and cold pressing combined with hot extrusion have been proposed to process nano-crystalline powders [21–23]. By carefully adjusting compaction parameters, bulk nano-crystalline materials can be successfully prepared.

Maintaining the grain size in the nanometre scale after compacting is critical for retaining the mechanical properties of the nanomaterial. In the present study, we used the spark plasma sintering (SPS) technique to compact nanoparticles. This novel technique was originally developed for the compaction of ceramics, but a number of studies also used SPS to compact metallic nanoparticles or nano-crystalline powders [24–32]. In these studies, the SPS process has been found very suitable to prepare nano-crystalline materials. The SPS process is a combination of hot-pressing and pulsed current generation. The powder is placed in a conductive graphite chamber to be uni-axially compressed and exposed to high electric current pulses (up to 20 kA). Such high current pulses cause rapid heating of the powder (up to 1000 K/min) and, in combination with simultaneous compression, quickly compacts the powder. For most materials, the high sintering speed and low sintering temperature can effectively hinder grain growth and produce materials with a high-density and a fine grain structure. For these reasons, SPS can be used to produce nano-crystalline materials with significantly improved mechanical properties, microstructure and other special properties [24–32]. As an example, Al-based alloys having an ultra-high compressive strength of 1.2 GPa were prepared by this technique [27,32]. Although the exact mechanisms of densification during SPS have not yet been well explored, it is believed that they include various physical processes such as plastic yielding, creep, solid- and liquid-state diffusion, micro-arc and micro-spark discharges at particle contacts, local melting or even evaporation and the breakdown of oxide layers [25–27]. Some researchers also believe that the electric current accelerates diffusion processes between particles and particle bonding [25].

The purpose of our study is to demonstrate the feasibility of preparing bulk nano-crystalline materials using the selective leaching technique followed by spark plasma sintering for compaction. Nano-crystalline silver was prepared with this method, and the material was shown to possess the highest compressive strength among all bulk nano-crystalline silver materials reported to date.

2. Experiment

In this work, bulk nano-crystalline silver prepared from nanoparticles by the SPS process was investigated. Coarse-grained as-cast silver ($d=60\ \mu m$) and micro-crystalline silver ($d=13\ \mu m$) were also prepared as reference materials.

The silver nanoparticles were produced by selective leaching of a binary Al–30Ag (wt%) alloy. The alloy was prepared by conventional melting in an induction furnace with an argon protective atmosphere before being cast into a brass mould. The ingot was processed by mechanical machining to obtain fine particles with an average size of 1 mm that were suitable for dissolution. These particles were subjected to solution annealing in an argon atmosphere at 550 °C for 3 h before being subsequently quenched in liquid nitrogen to stabilise the solid solution of silver in aluminium. The prepared alloy was processed by selective dissolution in a sodium hydroxide solution (20 wt%) at 0 °C for 24 h. The amphoteric nature of aluminium resulted in its selective dissolution in sodium hydroxide to produce a suspension of very fine silver powder in the liquid solution. The dissolution of aluminium is described by the following equation:

$$2AlAg_X + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2 + 2XAg \quad (1)$$

The resulting silver powder was rinsed and decanted using distilled water and isopropyl alcohol, respectively. The isopropyl alcohol was then evaporated.

The micro-crystalline silver was prepared by compacting a gas-atomised silver powder ($-50+20\ \mu m$, $d50=35–40\ \mu m$) purchased from Safina CR. The as-cast silver ingot with a diameter of 10 mm was prepared by melting pure silver in a vacuum induction furnace and casting it in a graphite mould.

The nano-crystalline and micro-crystalline silver powders were uni-axially cold pressed at a pressure of 280 MPa (using an electromechanical LabTest 5.250SP1-VM machine). The prepared green bodies were then processed using the spark plasma sintering technique (Thermal Technology SPS 10-4), pressed with a pressure of 80 MPa and heated to a consolidation temperature of 500 °C (at a heating rate 100 °C/min). This temperature was maintained for 5 min.

The powders and compacted products were investigated using X-ray diffraction analysis (XRD, PANalytical X'Pert Pro, Cu anode), optical microscopy, scanning electron microscopy (SEM, TESCAN VEGA 3 LMU, W cathode), energy dispersive spectrometry (EDS, Inca 350 Oxford Instruments) and transmission electron microscopy (TEM, Jeol JEM 3010, LaB_6 cathode).

The mechanical properties of the prepared bulk samples were investigated with compressive tests. Cubic specimens with edge length of 3 mm were pressed at a strain rate of 0.18 mm/min at room temperature (LabTest 5.250SP1-VM). Vickers microhardness measurements using a 40 g load (HV 0.04, Zwick) were also performed.

3. Results

3.1. Structures of nano- and micro-crystalline powders

An SEM micrograph of silver nanoparticles prepared by the selective leaching technique is shown in Fig. 1a. The micrograph demonstrates a large cluster (several μm) of nanoparticles, and the particles are less than 50 nm in diameter. A more detailed structural examination was performed using TEM, and Fig. 1b shows the TEM view of the nanopowder together with a selected area electron diffraction pattern (SAED). One can observe that the particles are almost spherical in shape. The SAED pattern contains sharp diffraction maxima indicating that the nanopowder was