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Microstructures and mechanical properties of mechanically alloyed and spark plasma sintered $Al_{0.3}CoCrFeMnNi$ high entropy alloy

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HIGHLIGHTS

- $Al_{0.3}CoCrFeMnNi$ high entropy alloy was prepared using Spark Plasma Sintering.
- Optimum density and grain size is obtained at 900 °C sintering temperature.
- Microstructure consisted of fcc matric, ordered bcc (B2) and chromium carbides.
- Alloy showed high compressive strength of 979 MPa and failure strain of 39%.

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ABSTRACT

The present study focuses on phase evolution in $Al_{0.3}CoCrFeMnNi$ high entropy alloys (HEAs) during mechanical alloying and after spark plasma sintering. Aluminium addition hardens and induces ordered precipitates in a soft *fcc* alloy based on CoCrFeMnNi. Mechanical alloying of the alloy powders resulted in a single *fcc* phase. However, ordered B2 precipitates and chromium carbide precipitates were observed after spark plasma sintering. Sintering temperature optimization was done and maximum densification and hardness were obtained at 900 °C. High compressive yield strength of 979 ± 20 MPa and compressive ductility of 39 ± 3% were observed for the SPS processed alloy. Significant contributions from grain boundary strengthening coupled with dispersion strengthening via carbides and B2 particles appear to be major contributors to alloy strengthening. These hard intermetallic particles not only keep the grain growth in check but also increase the cumulative (fcc + B2) strength of the material.

1. Introduction

High-entropy alloys (HEAs) is a new class of metallic alloys, defined by Yeh et al. [1] as alloys consisting of five or more metallic elements ranging from 5 to 35 at.%. As the name suggests, high-entropy alloys have high configurational entropy, which favors the formation of solid solution instead of intermetallic compounds. Properties that attract interest towards HEA research include but are not limited to high strength, thermal stability, wear resistance, and corrosion resistance, among other interesting properties.

Of the myriad possibilities HEA systems offer, CoCrFeMnNi is one of the more intensively researched alloy system, due to its physical properties such as cryogenic mechanics [2], thermodynamic stability [3], malleability, to name a few. Originally reported by Cantor et al. [4], the microstructure was known to consist of a single *fcc* solid solution.

Although this alloy has many interesting traits, its initial mechanical properties were quite low [5]. Most studies on this alloy have been based on synthesis via conventional melting and solidification. Benefits attributed to this method include complete densification, since no gases are trapped within the slab and contamination of other elements can be removed. However, melting tends to create coarse grains (>4 μm) with heterogeneous grain structure during cooling [6]. To improve mechanical

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properties, different methods that have been applied include rolling at room, cryogenic and elevated temperature; high pressure torsion [3] and swaging [7] after arc melting.

Alternative methods of synthesizing HEAs are by powder metallurgy, mechanical alloying (MA) and spark plasma sintering (SPS). Target material in the form of powder is subjected to repetitive cold welding, fracturing, and re-welding to achieve solid state alloying. The alloyed powders are then subjected to pressure and are rapidly heated, thereby consolidating the powders. Previous research confirmed that CoCrFeMnNi follows the Hall-Petch equation [8]. The powder metallurgy process enables achieving nanosized grains, which in turn improve mechanical properties.

Comparing arc melting and powder metallurgy reveals that powder metallurgy is the more superior process. During the powder metallurgy process, grain refinement is obtained during mechanical alloying, while spark plasma sintering can maintain these small grains; whereas in arc melting, the grains are coarse and inhomogeneous.

The addition of aluminum may increase mechanical properties by further increasing the lattice distortion effect due to its larger size. A study by He et al. [9] confirmed that limited addition of Al will increase yield strength, decrease density due to solid solution strengthening and the formation of a harder bcc phase with further addition of aluminum [10,11]. Furthermore a study by Gwalani et al. [12] showed the effect of various ordered precipitates (L12 and B2), stabilized by addition of Al, on the tensile properties of CoCrFeNi HEA system.

This study focuses on the microstructures and mechanical properties of $Al_{0.3}$CoCrFeMnNi HEA produced by mechanical alloying and spark plasma sintering.

2. Experimental

A sequence of processing steps was followed to make the Al0.3CoCrFeNi alloy. High purity powders of Al, Co, Mn, Ni of <15 μm, Cr of <45 μm (Kojundo Co, Ltd.), Fe of <25 μm, were used (expressed in molar ratio) in the planetary ball mill (Pulverisette 5/4, Fritzsch) for 36 h for mechanical alloying. Stainless steel vials and Ø 1.1 cm stainless steel balls were used with a milling speed of 200 rmp. A ball-to-powder mass ratio of 15:1 was maintained and process was done in argon atmosphere with addition of n-heptane as process control agent (PCA) to reduce cold welding. As-milled powders were then consolidated using spark plasma sintering (Dr. Sinter Lab. SPS-515S) at 800, 900, 1000 °C in medium vacuum atmosphere (1.5×10^{-5} Bar) for 10 min under 50 MPa uniaxial pressure with a heating rate of 100 °C/min.

Crystal structure of the milled powders and sintered alloys were examined by X-ray diffractometer (XRD, Rigaku D/Max-2500) with CuKα radiation. Microstructural characterization was done using Scanning Electron Microscopy (SEM, Phillips XL30SFE) and Transmission Electron Microscope (Tecnai G2 F30 S-Twin). Densities of the sintered alloys were measured using the Archimedes principle. Hardness of the sintered alloy samples was measured by the Vickers hardness testing machine (Mitutoyo HM-124). Compressive properties were measured using INSTRON 5583 with Ø3 mm × 6 mm cylindrical specimens at 0.2 mm/min crosshead speed. Samples from the SPS processed alloys were prepared for Atom probe Tomography (APT) using Focused Ion Beam (FIB). Standard lift-out techniques were used for APT sample preparation in the FIB before mounting the small sections of the samples on suitable holders for analysis. APT experiments were conducted on a CAMECA local electrode atom probe 3000X HR instrument. All experiments were performed in the temperature range of 40–60 K with target evaporation of 0.5% and pulse fraction of 20% of a steady-state applied DC voltage. APT data reconstruction and analysis were carried out using CAMECA IVAS® 3.6.8 software.

3. Results and discussion

3.1. SEM and XRD results during MA

Fig. 1 (a) shows secondary electron (SE) SEM images demonstrating the change in size scale and morphology of the powder agglomerates as a function of milling time during mechanical alloying. The mixtures of elemental powders of Al, Co, Cr, Fe, Mn, and Ni were cold-welded together by the repeated collisions of milling media. The average size of the powder agglomerates increased rapidly in the early stages of milling up to 6 h. After 6 h, agglomerate size did not grow any further due to the balance between cold-welding and fracture of the milled powder. Fig. 1(b) shows the effect of milling time on crystallinity of the $Al_{0.3}$CoCrFeMnNi powders. Initially, elemental peaks of the respective elements were observed. However, as milling time increased, intensity of elemental peaks decreased, thereby denoting the alloying process. After 36 h of milling, only FCC peaks were observed. These FCC peaks of low intensity and relative broadening indicate a decrease in crystallite size according to the Scherrer formula. Crystallite size vs. milling time plot is shown in Fig. 2. Associating crystallite size and XRD plot validates the inference that the alloying process was complete after 36 h of milling. Thus, high entropy alloy phases in the alloy can be obtained by MA.

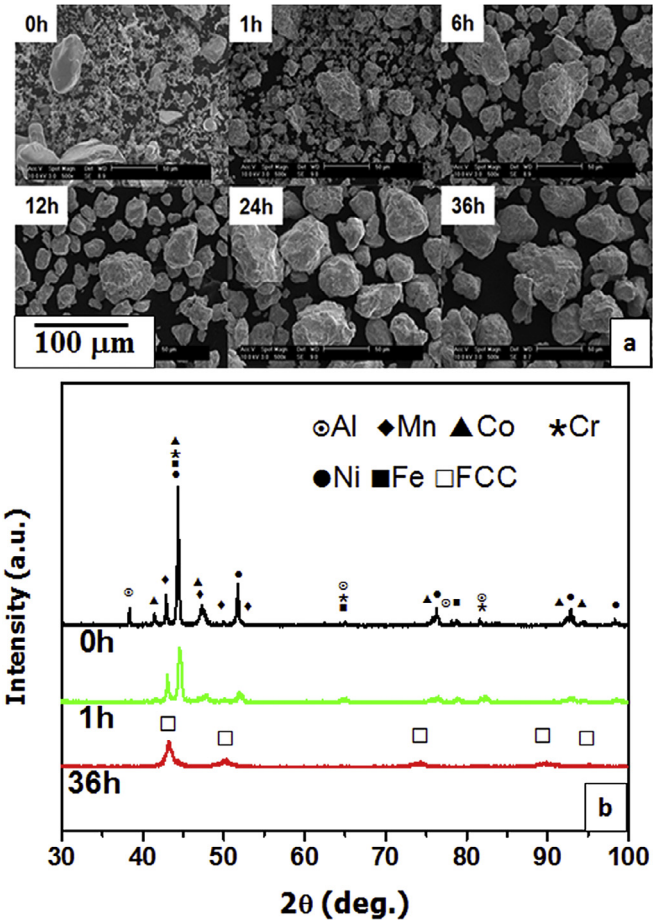

Fig. 1. (a) SEM micrographs of $Al_{0.3}$CoCrFeMnNi powders as a function of milling time. (b) XRD peaks of $Al_{0.3}$CoCrFeMnNi as a function of milling time.