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Preparation of superfine-grained high entropy alloy by spark plasma sintering gas atomized powder

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ABSTRACT

In this work, nanocrystalline CrMnFeCoNi HEAs were prepared by powder metallurgy. It was found mechanical milling can further refine the microstructures and morphologies of the gas-atomized powder, and increase the sintering ability. The HEAs sintered from the mechanically milled powder have much finer microstructures than that from the gas-atomized powder. The original morphology and defects in both the gas-atomized and the mechanically milled powders can be inherited to the bulk forms after the SPS. The SPSed HEAs have a tensile strength as high as 1000 MPa at room temperature and reasonable ductility. The strengthening mechanism can be attributed to the nanocrystalline microstructures, in which grain boundaries block the movement of dislocations. Powder metallurgy can be taken as a promising way for preparing HEAs with high mechanical properties.

1. Introduction

High entropy alloys (HEAs) have recently drawn more and more attentions from worldwide material scientists [1,2]. HEAs usually contain 4 or 5 metallic elements with nearly equiatomic ratios, but can crystallize as a single phase. Due to the high configuration entropy, HEAs shows novel properties, for example, high fracture toughness, high corrosion and wear resistance [2–6]. HEAs are mostly prepared by vacuum arc melting [7,8]. Since the alloys contain multiple elements, the compositional segregation of high-melting point elements and the evaporation of low-melting point elements are hard to avoid [9]. Moreover, HEAs ingots have coarse dendritic structures with the precipitations of some brittle intermetallic phases [5,10]. Usually, HEAs ingots are hot worked, and followed by the solid solution treatment, to make sure a fine, single phase and homogeneous structure can be obtained [11,12].

HEAs can also be made by mechanical alloying and subsequent consolidation process [13]. Firstly, HEAs powder was prepared by mechanical alloying (MA) different elemental powders of equiatomic ratio. Since HEAs contain 4 or 5 elements, the alloying and homogenization process take a long time of milling, for example, 30–60 h [14,15]. Furthermore, due to the long time of high energy milling, the powder can easily be contaminated by the milling materials and the environment. The mechanically alloyed HEAs powder has a fine or nanocrystalline microstructure, so a rapid consolidation process is necessary to preserve the non-equilibrium microstructures. Spark plasma sintering (SPS) is an activated densification process, in which both pulsed and direct currents are exerted on the powder [16]. Powders can be fully consolidation in few minutes to tens of minutes, and thus, the microstructural coarsening can be suppressed [16,17]. Recently, through the combination of MA and SPS, some bulk HEAs were processed. Gas atomization is a widely used way for making metallic powders by the rapid solidification process, in which the cooling rate can be in the range of 10^5–10^6 °C/s [18]. The rapid cooling rate helps to prevent the compositional segregation, to refine the microstructure and to stabilize the single phase or the amorphous phase. Compared with mechanically alloyed powder, gas-atomized powder is of higher purity and more homogeneous both in the composition and the morphology. Therefore, gas-atomized HEA powder is a good candidate for making bulk powder metallurgical (PM) materials. There have already been many reports on gas-atomized amorphous powder [19–21], but few on the HEAs powder. Due to the fine and nanocrystalline structure, PM HEAs show very high hardness and

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compressive strength [22], however, there are few data on the tensile mechanical properties of PM HEAs. The microstructural evolutions from powder to the bulk form in the PM process are essential for mechanical properties. For example, the primary particle boundaries (PPB) of gas-atomized powder can be inherited in the bulk form, and influence the microstructural homogeneity [23]. In SPS, the consolidation process is too fast to eliminate PPBs.

In this work, CrMnFeCoNi HEA powders were prepared by high pressure Ar gas atomization, and consolidated by SPS. In order to delete PPBs and to activate the sintering process, the gas-atomized powders were mechanically milled before the SPS. The microstructural evolutions and the mechanical properties of both the powder and the bulk alloy were investigated.

2. Experimental

High purity Cr, Mn, Fe, Co and Ni of an equiatomic ratio were melted in an induction-heated vacuum furnace. The melt was them drop through a ceramic tube, and atomized by high purity Ar. The atomization pressure was 4 MPa. The liquid droplets filed in the atomization chamber, cooled down and solidified to powder. The powder was collected and sieved. The gas-atomized powder was put into a stainless steel vial with stainless steel balls, and the ball-to-powder ratio is 10:1. The vial was then assembled on a planetary high-energy milling equipment with a speed of 250 rpm under argon atmosphere. In order to prevent the welding of powder in the vial, a process control agent, stearic acid, was added. The milling process was stopped and held for 5 min after running for every 20 min. The milling time was from 4 h to 15 h.

Both the gas-atomized and the as-milled powders were put into a graphite die with a diameter of 40 mm. SPS was conducted in a HP D 25/3 SPS equipment with a vacuum of 1×10^{-3} Pa. The powders were heated to 1000 °C, and held for 480 s at a pressure of 30 MPa. After the sintering, the alloys were cooled down to room temperature in the furnace.

The composition of the gas-atomized powder was analyzed by chemical methods. The oxygen content was determined by the fusion method on a Leco O/N analyzer. Microstructures were observed by using a Leica optical microscope (OM) and an FEI Nova Nano230 scanning electron microscope (SEM) equipped with an Energy dispersive X-ray (EDX) analyses. The thin foils for transmission electron microscopy (TEM) observations were electrochemically polished. TEM investigations were conducted in an FEI Tecnai 20 at 200 KV. X-ray diffractometer (XRD, Rigaku D/MAX-2250) with a Cu Kα radiation was used to identify the phase constitutions. The real density was measured by Archimedes method, and the relative density was measured by the imaging processing of porosity in the cross section of the samples under the optical microscope.

Dog-bone samples of a gage size of 6 mm × 6 mm × 15 mm were cut from the SPSed pancake, and underwent tensile tests on an Instron 3369 testing machine. The loading speed is 10^{-3}/s. The engineering stress–strain curves can be drawn according to the recorded data. The microhardness of both the powder and the bulk form was measured on the optical microscope with a load of 50 N.

3. Results and discussions

Table 1 shows the chemical analyses of the gas atomized HEA powder. The results are in good agreement with the nominal composition. The content of oxygen is as low as 720 ppm, indicating no obvious oxidation during the gas-atomization. Under the current technical parameter, the mean gas-atomized particle size d50 is 45.2 μm with a distribution from several microns to more than 100 μm, as shown in Fig. 1. The powder size and its distribution can be further tailored by adjusting the synthesizing parameters such as the atomization pressure. Fig. 2(a)-(c) show the morphology and microstructure of the gas-atomized powder. The powder is spherical in shape with some satellite structure. During the gas atomization, smaller melt droplets experienced a higher cooling rate and solidified in a shorter time. They can easily stick to the surface of large droplets which are still in a mushy state and formed the satellite structure. The internal structure of HEA powder is very fine. The magnified image in Fig. 2(c) shows that the microstructure consists of cellular and pore structure at submicron scale, which is due to the shrinkage during the solidification process [24]. These kinds of casting defects are difficult to eliminate which may due to that the HEA melt is highly viscous. The morphologies of powders milled for different time are shown in Fig. 2(d)-(f). After being milled for 4 h, the powder was deformed to be plate-like. Previous study [2] showed that CrMnFeCoNi HEA has a very high toughness, therefore, the alloy powder can withstand long time of deformation without fracture. After being milled for 10 h, the morphology of the powder changed to be nodular. With the accumulation of the milling energy in the powder, the powder deformed severely and may break at this stage. On the other hand, the local temperature due to high energy collision and large deformation can be as high as 500–600 °C [25]. Therefore, it's easy for the broken powder weld with each other. Through rapid fracture and welding, the thickness of the powder can increase and the shape changes. After further milling for 15 h, the particle size of the powder increased further, as shown in Fig. 2(f). Fig. 3 shows the XRD patterns of the gas-atomized and as-milled powders. The gas-atomized powder is of pure FCC structure. After being mechanically milled, the phase constitution of the powder does not change, but the width of the diffraction peaks increases with the milling time, which is due to the refinement of grains and the severe plastic deformation. Previous work on mechanical alloying of HEAs has indicated that the powder can have a grain size as fine as tens of nanometers [26,27]. Furthermore, microhardness of the powder increases significantly with the milling time. Comparing with the gas-atomized powder, the powder milled for 15 h has a more than doubled microhardness, as shown in Table 2. In the HEAs prepared by mechanical

Table 1
Chemical compositions of gas atomized CrMnFeCoNi HEA powder.

Elements	Cr	Mn	Fe	Co	Ni
at.%	19.1	20.9	19.5	18.4	22.1

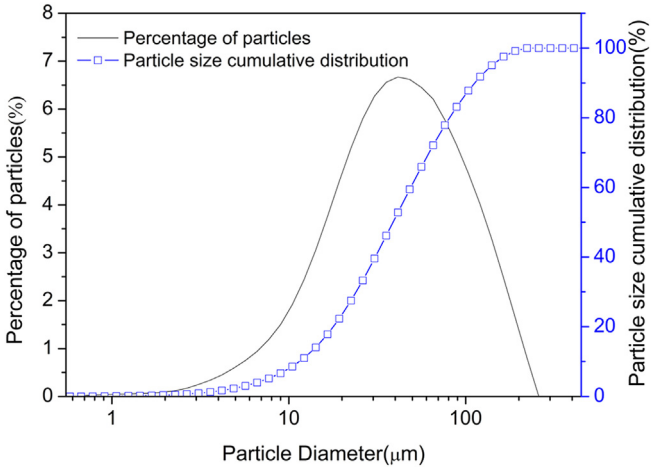

Fig. 1. Particle size distribution of the gas-atomized CrMnFeCoNi HEA powders.