

Article

Microstructure and Mechanical Properties of Ultrafine-Grained CrMnFeCoNi High-Entropy Alloy Prepared via Powder Metallurgy

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Abstract

We studied the microstructural evolution and mechanical properties of ultrafine-grained CrMnFeCoNi high-entropy alloys fabricated by mechanical alloying of various additives and spark plasma sintering. The additives were 1 wt.% process control agent (stearic acid) + 1 wt.% graphene nanofiber (GNF) (PG) or 1 wt.% Y₂O₃ + 1 wt.% GNF (YG) to modify the constituting phase of the sintered alloy. The PG and YG powders exhibited a single FCC phase. The YG powders had a larger powder size and a smaller crystallite size than the PG powders. Ultrafine-grained FCC matrices with average particle sizes of 0.57 μm and 0.71 μm , respectively, were formed through the SPS process of PG and YG powders. The absence of PCA in YG alloys resulted in a bimodal distribution of fine and coarse grains (due to incomplete mechanical alloying) and formation of a lesser and finer Cr₇C₃ phase (due to reduced C content). The sintered PG alloy contained coarse (~60 nm) spinel Mn₃O₄ oxides along grain boundaries, whereas the YG alloy exhibited coarse Mn₃O₄ and fine (~17 nm) Y₂O₃ oxide particles along grain boundaries. Additionally, the YG alloy contained tiny (~5 nm) Y₂O₃ oxide particles with a cube-on-cube orientation relationship within the FCC matrix. YG alloy exhibited higher hardness and compressive yield strength than PG alloy, mainly due to the oxide dispersion strengthening of finely dispersed Y₂O₃ particles. The addition of Y₂O₃ reinforcing particles had a minimal effect on the ultimate compressive strength and fracture strain of the sintered alloy.

Keywords: high-entropy alloys; spark plasma sintering; microstructure; oxide dispersion strengthening; transmission electron microscopy



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1. Introduction

Over time, alloy development has progressed from relatively simple elemental combinations toward more complex alloy systems through the addition and integration of multiple elements in order to enhance mechanical performance or achieve targeted properties [1]. Within this evolutionary framework, high-entropy alloys (HEAs), which are composed of five or more principal elements in equiatomic or near-equiatomic ratios, have been developed as an alternative alloy design concept based on compositional complexity [2–5]. Owing to their diverse chemical compositions, HEAs often form simple solid-solution phases, predominantly with FCC or BCC crystal structures, and have been reported to exhibit a favorable combination of high hardness, good ductility, and thermal stability [3–6]. Among various HEAs, the equiatomic CrMnFeCoNi alloy, commonly

referred to as the Cantor alloy, forms a stable FCC structure [7] and exhibits excellent toughness and fracture resistance, particularly at cryogenic temperatures [7,8]. Accordingly, various processing routes and alloying or reinforcing elements have been employed to improve the mechanical performance of the Cantor alloy. For example, a previous study [9] reported that the addition of C and Ti to cast CrMnFeCoNi alloy followed by heat treatment led to the precipitation of plate-shaped TiC, resulting in an increase in yield strength of approximately 60 MPa.

Mechanical alloying (MA) or milling is a solid-state powder processing technique in which repeated fracture and cold welding of powder particles induce severe plastic deformation and effective elemental mixing [10]. This process enables significant grain refinement, extended solid solubility, and the formation of non-equilibrium microstructures without complete melting. For multi-principal element alloys, mechanical alloying provides a viable route to achieve compositional homogeneity while avoiding segregation commonly associated with melting-based processes [11]. Spark plasma sintering (SPS) enables rapid heating and short dwell times, allowing effective densification while suppressing excessive grain growth. Based on the beneficial effects, SPS processing has been applied to various metallic alloys, such as steels [12], Ni-based superalloys [13], and HEAs [14,15]. For AlSi4340 steel, high-energy ball milling followed by spark plasma sintering resulted in a refined microstructure with an average particle size of approximately 2.4 μm . The processed material exhibited excellent mechanical properties, including a hardness of 711 MPa and a yield strength of 1953 MPa [12]. Similar powder metallurgy approaches based on mechanical alloying have also been extended to high-entropy alloys, where phase evolution during milling and subsequent consolidation has been systematically investigated [14]. For the CrMnFeCoNi alloy, mechanical milling was reported to increase the compressive yield strength of the sintered alloy from 307 MPa to 886 MPa due to grain refinement and the formation of reinforcing carbides and oxides [15].

During mechanical alloying, the use of a process control agent (PCA) can lead to the introduction of carbon and oxygen into the powder system, which may result in the formation of carbides and oxides during subsequent sintering [16]. In Cr-containing alloys, carbon introduced by PCA can promote the formation of chromium carbides, while oxygen may contribute to the formation of Cr- and Mn-based oxides [15]. These secondary phases can influence the microstructure and mechanical properties of the sintered alloys.

To further enhance mechanical performance, ceramic particles such as Y_2O_3 can be introduced during milling to induce oxide dispersion strengthening [13,17]. For Ni–20Cr–1.2 Y_2O_3 alloys processed by high-energy ball milling followed by spark plasma sintering, finely dispersed Y_2O_3 particles within the Ni grains were reported to promote significant grain refinement. In addition to grain refinement, oxide dispersion strengthening by Y_2O_3 resulted in a high yield strength exceeding 1.5 GPa [13]. In addition, Tan et al. [17] reported that the addition of 0.5 at.% Y_2O_3 to CrMnFeCoNi high-entropy alloy powders, followed by mechanical milling and plasma arc additive manufacturing, resulted in ~60 MPa increase in ultimate tensile strength due to synergistic effects of grain refinement and dislocation strengthening, and oxide-dispersion strengthening.

Recent studies have reported that the mechanical properties of HEAs can be enhanced through the incorporation of carbon nanotubes (CNTs) or graphene-based reinforcements [18]. Bahrami et al. [19] reported that the addition of 1 wt.% CNT increases the hardness of AlCoFeMnNi HEA due to solid-solution strengthening of C (partial diffusion of CNT-derived carbon) and dispersion strengthening of CNTs [19]. However, the studies on the effect of graphene nanofiber (GNF) on the HEAs remain limited.

Therefore, in this study, ultrafine-grained CrMnFeCoNi alloys with additions of PCA/GNF and Y_2O_3 /GNF were manufactured by MA and SPS processes. The evolution

of microstructures, including grains, secondary phases, and oxides, and their impacts on the mechanical properties of sintered alloys were systematically investigated.

2. Experimental Procedure

Gas-atomized CrMnFeCoNi powder (MK Ltd., Changwon, Republic of Korea) was used as the base material. GNF (Carbon Nano-material Technology Co., Pohang, Republic of Korea, diameter: 50–200 nm, length: 10–30 μm , purity: >95 wt.%), Y_2O_3 (Aladdin, Shanghai, China, powder size: ≤ 40 nm, purity: 99.5%), and stearic acid (Thermo Fisher Scientific, Waltham, MA, USA, flakes or powder, purity: 98%) as a PCA of mechanical milling were used as additives. The CrMnFeCoNi powders with 1 wt.% PCA + 1 wt.% GNF and 1 wt.% Y_2O_3 + 1 wt.% GNF were referred to as PG and YG, respectively.

Mechanical milling of PG and YG powders (20 g) was conducted using a planetary-type high-energy ball milling apparatus (Fritsch, Idar-Oberstein, Germany, Pulverisette-6) under an Ar atmosphere. A 250 mL SKD11 steel container and Fe–Cr balls ($\Phi 10$ mm diameter) at a ball-to-powder weight ratio of 30:1 were used in mechanical milling. Mechanical milling was conducted at a rotation speed of 250 rpm in a cyclic mode consisting of 60 min of milling followed by 30 min of rest, with a total processing duration of 24 h. Milled PG and YG powders (16 g) were placed in a cylindrical graphite mold (inner: $\Phi 20$ mm diameter, 40 mm height) and consolidated SPS (ELTEK Korea Co., Yongin, Republic of Korea) under a vacuum atmosphere (<150 mTorr) and an applied uniaxial pressure of 50 MPa. During SPS, the powder compacts were heated to 1000 $^\circ\text{C}$ at a heating rate of 1000 $^\circ\text{C}/\text{min}$, held for 1 min, and subsequently cooled to room temperature at a rate of ~ 150 $^\circ\text{C}/\text{min}$. The mechanical milling and SPS process parameters used in this study were optimal conditions for achieving pore reduction and enhanced oxide dispersion [15,20]. Cross-section specimens for microstructure analysis and cylindrical specimens for compression tests were prepared from the sintered alloy (Figure 1).

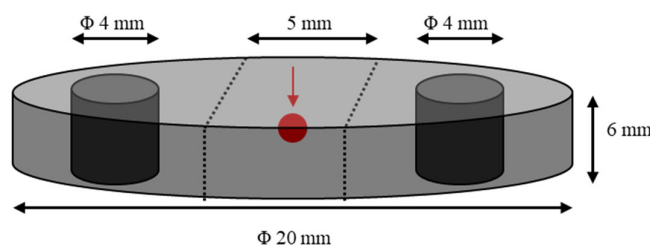


Figure 1. Schematic illustration showing the location of the specimens for microstructural analysis and compressive testing of the sintered alloy. The red dots indicate the locations where the measurements were performed.

X-ray diffraction (XRD, Shimadzu, Kyoto, Japan, XRD-6100) with a $\text{Cu K}\alpha$ target ($\lambda = 1.5406$ $\text{\AA}$) was used to examine the microstructure of milled powders and sintered alloys. The 2θ range of 20 – 100° was scanned at a scanning rate of $2^\circ/\text{min}$, step size of 0.02° , accelerating voltage of 40 kV, and a current of 30 mA. The phase analysis was performed using CrystalDiffract software (CrystalMaker Software Ltd., Oxford, UK, CrystalDiffract version 6.9.4) [21] and the corresponding phase reference CIF file. The crystallite size of the milled powder was analyzed by applying the Williamson–Hall relationship to four FCC reflections (111, 200, 220, and 311) [22]. The sintered alloys were examined by optical microscopy (OM; Nikon EPIPHOT 200, Tokyo, Japan) at a magnification of $\times 200$ to evaluate the densification behavior after sintering. The bulk densities were measured seven times using the Archimedes method. The relative densities (R.D.) were calculated by normalizing the measured bulk densities with the corresponding theoretical densities, which were estimated using the rule of mixtures based on the final sintered composition of each alloy.

(PG: 7.998 g/cm³ and YG: 8.004 g/cm³). The microstructures of the powders and sintered alloys were observed using a scanning electron microscope (SEM, HITACHI SU3900 and HITACHI SU-70, Tokyo, Japan). The powder size of milled powders was measured on SEM images captured at $\times 300$ using the ImageJ software (National Institutes of Health, Bethesda, MD, USA, ImageJ 1.54g) [23]. Electron backscatter diffraction (EBSD, HITACHI, Tokyo, Japan, SU-70) was employed to analyze the FCC matrix and secondary phases. The EBSD analysis was performed on SEM images taken at $\times 20,000$ with a step size of 10 nm, and the obtained data were analyzed using TSL OIM Analysis 9 software. The crystal structure and size distribution of carbides, oxides, and the FCC matrix were characterized by transmission electron microscope (TEM, FEI Talos F200X G2, Thermo Fisher Scientific, Waltham, MA, USA) and energy dispersive X-ray spectroscopy (EDS) operated at 200 kV. TEM specimens were prepared by a focused ion beam (FIB) technique in an SEM (Thermo Fisher Scientific, Waltham, MA, USA, Helios G5).

For mechanical properties, Vickers hardness was measured at the center of the cross-section of sintered alloys using a TIME TH-715 (Beijing, China) under a load of 1 kgf with a dwell time of 15 s. Compression tests were conducted in accordance with ASTM E9/E9M [24] using cylindrical specimens with a diameter of 4 mm and a height of 6 mm on an Instron 5569 testing machine (Norwood, MA, USA) at a nominal strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. Each alloy condition was tested twice to ensure reproducibility. The compressive yield strength was determined from the stress–strain curves using the 0.2% offset method.

3. Results and Discussion

3.1. Powder Evolution

Figure 2a–c show SEM images of the unmilled CrMnFeCoNi alloy powder used as a base material and milled PG and YG powders. The base powder exhibited a spherical morphology with an average powder size of $14.4 \pm 10.1 \text{ }\mu\text{m}$ (Figure 2a). The milled PG (Figure 2b) and YG (Figure 2c) powders displayed irregular morphologies, which are associated with the repeated fragmentation and cold welding occurring during the mechanical milling process. The size of the milled PG and YG powders was measured to be 14.8 ± 7.0 and $27.9 \pm 17.6 \text{ }\mu\text{m}$. The addition of Y₂O₃ nanoparticles is reported to have a refining effect on the milled powders by mechanically embedding into the welded powder interface and thus promoting particle refinement [25,26]. However, in the present study, the milled YG powders exhibited an increased powder size with a broader size distribution. This can be attributed to enhanced particle agglomeration during mechanical milling due to the absence of an effective PCA, which offsets the powder refinement effect of the Y₂O₃ nanoparticles. Figure 3a,b show XRD pattern of milled PG and YG powders, exhibiting a single FCC phase with a lattice constant of 0.3625 and 0.3639 nm. The crystallite sizes of milled powders can be estimated using Williamson–Hall method [22]:

$$\beta \cos \theta = C \sin \theta + \frac{K\lambda}{D} \quad (1)$$

where β denotes the full width at half maximum (FWHM) of the XRD peak, θ is the Bragg angle of the diffraction peak expressed in radians, ε represents the microstrain, C is the strain coefficient fixed at 4, K is the shape factor taken as 0.9, λ is the X-ray wavelength (1.5406 Å), and D corresponds to the crystallite size. It should be noted that the crystallite size obtained from XRD represents the coherent diffraction domain size and does not directly correspond to the powder or agglomerate size observed in SEM [27]. The crystallite sizes of the milled PG and YG powders were estimated to be 14.2 and 6.8 nm, respectively, which is much smaller than that of the unmilled CrMnFeCoNi alloy powder (89.0 nm [15]).

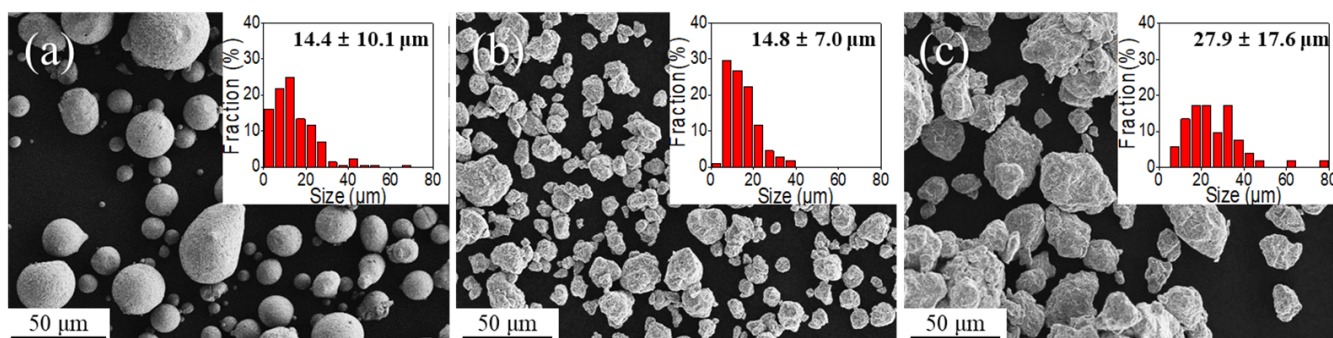


Figure 2. SEM image and powder size distribution for (a) unmilled CrMnFeCoNi alloy powder and milled (b) PG and (c) YG powders.

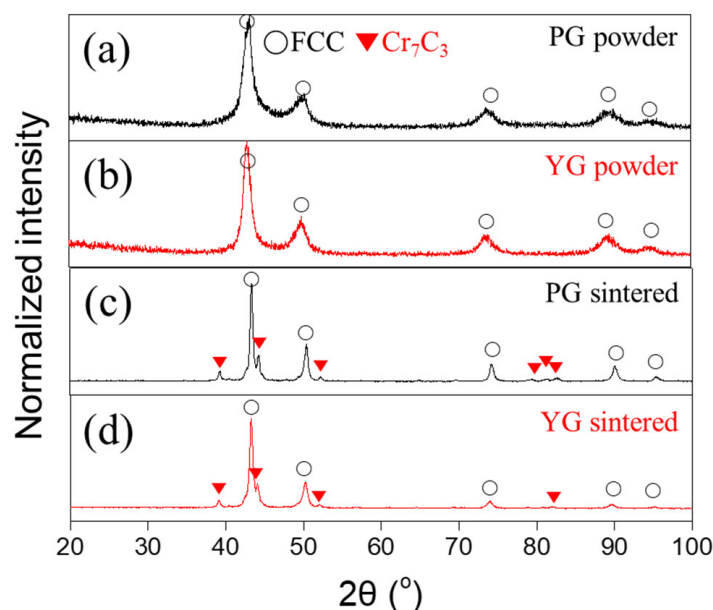


Figure 3. XRD pattern of (a,b) milled powders and (c,d) sintered specimens for (a,c) PG and (b,d) YG alloys.

3.2. Microstructure of Sintered Alloy

Figure 3c,d show XRD patterns of the sintered PG and YG alloys, having an FCC matrix with a lattice constant of 0.3611 and 0.3620 nm, respectively, which are lower than those of the milled powders. Additional XRD peaks of the Cr_7C_3 phase (mp-19855, $Pnma$, space group No. 62; $a = 0.453$ nm, $b = 0.697$ nm, $c = 1.221$ nm [28]) were observed in both alloys, with the PG alloy exhibiting higher intensity. Figure 4 shows the equilibrium fraction of Cr carbide and FCC matrix of PG and YG alloys in the temperature range of 600–1100 °C calculated using FactSage 8.3 software and FSstel database [29]. Previous studies [20] confirmed that the addition of 1 wt.% stearic acid (i.e., PCA) can increase the C content of sintered alloy to ~0.7%, which corresponds to the theoretical value. The GNF, which consists only of carbon, increases the C content of the sintered alloy, whereas Y_2O_3 has no effect on the C content. Thus, the C contents of the sintered PG and YG alloys were estimated to be 1.7 and 0.7 wt.%, respectively. Thermodynamic calculations reveal that the Cr_7C_3 phase is stable at the sintering temperature of 1000 °C in both PG and YG alloys. The equilibrium fraction of the Cr_7C_3 phase of the PG alloy (18.2%) is higher than that of the YG alloy (10.3%), which is consistent with the XRD results.

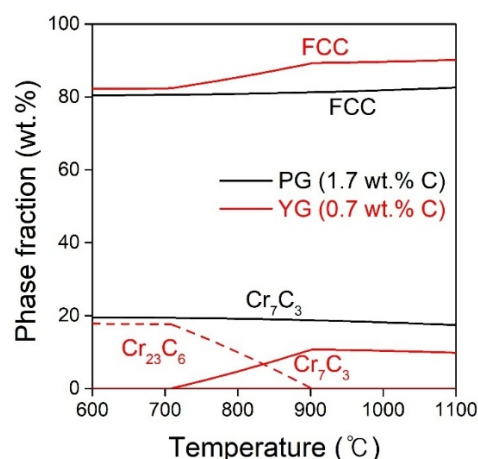


Figure 4. Change in the equilibrium fraction of Cr carbide and FCC matrix of PG and YG alloys in the temperature range of 600–1100 °C.

Figure 5 shows OM images of sintered PG and YG alloys. This indicates that both alloys exhibit dense and homogeneous microstructures without observable residual porosity, indicating that near-full densification was achieved during spark plasma sintering. This observation is consistent with the high relative densities (>99%) of the PG and YG alloys.

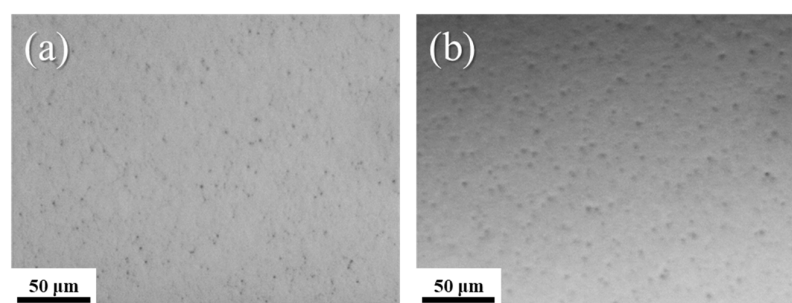


Figure 5. OM images of (a) PG and (b) YG sintered alloys.

Figure 6a shows an SEM BSE image of the sintered PG alloy. There are dark particles, Cr-rich carbide phases with sizes of $\sim 0.4 \mu\text{m}$ and Mn-rich oxide phases with sizes of $\sim 50 \text{ nm}$. EBSD image quality (IQ), inverse pole figure (IPF), phase, and kernel average misorientation (KAM) maps (Figure 6b–e) indicate that the submicron-sized ($0.4 \pm 0.1 \mu\text{m}$) Cr-rich phase corresponds to the Cr_7C_3 phase with an area fraction of $\sim 10.5\%$. The FCC matrix is composed mainly of high-angle grain boundaries (HAGBs) with a grain size of $0.57 \pm 0.31 \mu\text{m}$. This indicates that ultrafine-grained HEA was obtained through MA and SPS processes. Fine Mn-rich oxide particles were not analyzed in EBSD measurements. Figure 6f–j shows SEM and EBSD results of the sintered YG alloy. The sintered YG alloy contained the smaller ($0.2 \pm 0.1 \mu\text{m}$) (Figure 6f) and lesser (8.0%) Cr_7C_3 phase (Figure 6i), compared to the PG alloy, which is attributed to the lower C content of the YG alloy. The FCC matrix consists of fine-grained ($\sim 0.2 \mu\text{m}$) regions and coarse-grained ($\sim 1.0 \mu\text{m}$) regions (Figure 6h), with an average grain size of $0.71 \pm 0.33 \mu\text{m}$. The fine-grained regions contained more low-angle grain boundaries (LAGB) with orientations less than 15° (Figure 6g,h). The presence of bimodal grain size distribution and aligned Mn-rich oxide particles in the YG alloy indicates that mechanical milling was incomplete due to the absence of PCA. Additional mechanical milling is required to homogenize the microstructure of the YG alloy. The YG alloy contained numerous Y-rich oxide particles, as shown in Figure 6f. The KAM values of PG and YG alloys were $0.51 \pm 0.36^\circ$ and $0.65 \pm 0.42^\circ$, respectively, indicating a

higher KAM value in the YG alloy containing a finer LAGB region. The dislocation densities of PG and YG alloys were obtained to be $6.69 \times 10^{14} \text{ m}^{-2}$ and $6.82 \times 10^{14} \text{ m}^{-2}$, respectively.

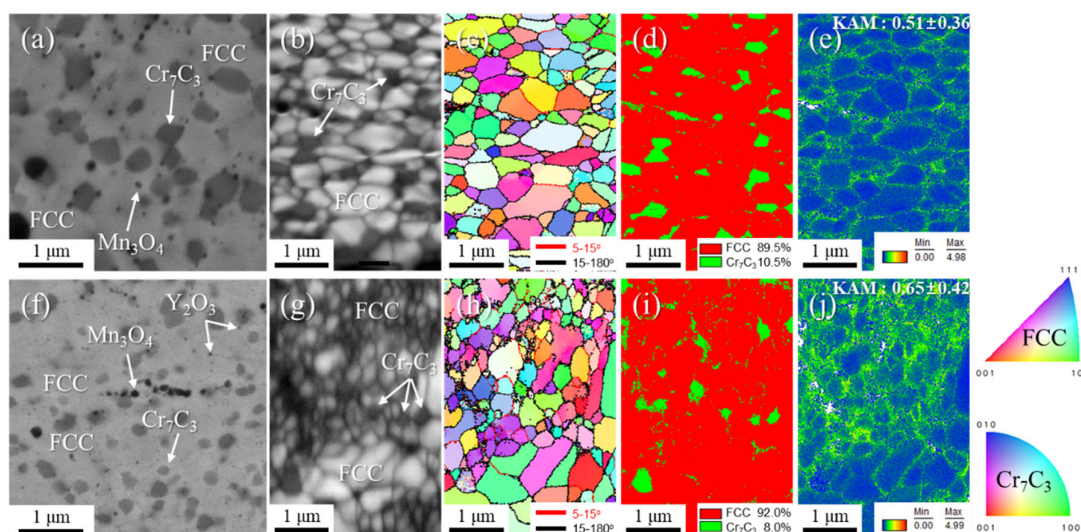


Figure 6. SEM BSE image, EBSD IQ, IPF, phase, and KAM maps of (a–e) PG and (f–j) YG alloys.

Figure 7a–c show bright-field scanning TEM (BFSTEM) images and EDS elemental mapping of the sintered PG alloy, which consists of submicron-sized FCC matrix and Cr_7C_3 phases and Mn-oxide phases along grain boundaries. The grain size of the FCC matrix was measured to be $485 \pm 286 \text{ nm}$, consistent with the EBSD result. The diameter of the Mn-oxide phases was measured to be $62 \pm 23 \text{ nm}$. High-resolution TEM (HRTEM) and fast Fourier transform (FFT) analyses of the Mn-rich oxide phase present along the LAGB are shown in Figure 8a. The Mn-rich oxide phase was identified as spinel-structured Mn_3O_4 (mp-28226, $\text{Fd}\bar{3}m$, space group No. 227; $a = 0.845 \text{ nm}$ for MnCr_2O_4 [30]) with a cube-on-cube orientation relationship (OR) (i.e., $[001]_{\text{FCC}} // [001]_{\text{oxide}}$, $(200)_{\text{FCC}} // (400)_{\text{oxide}}$). The Moiré fringes with spacings of $\sim 0.9 \text{ nm}$ were formed by the superposition of the $(200)_{\text{FCC}}$ ($\sim 0.18 \text{ nm}$) and $(400)_{\text{oxide}}$ ($\sim 0.22 \text{ nm}$) planes.

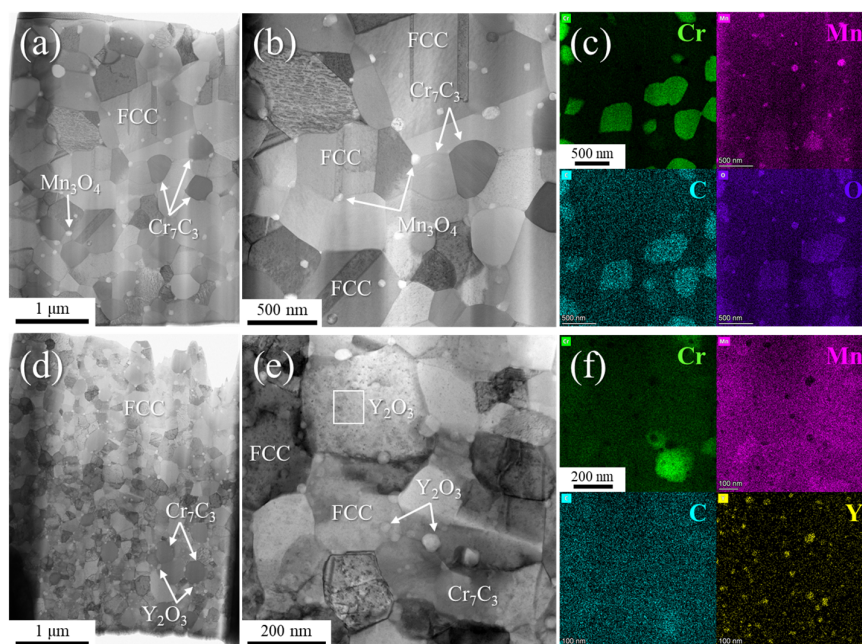


Figure 7. BFSTEM image and EDS element mapping of (a–c) PG and (d–f) YG alloys.

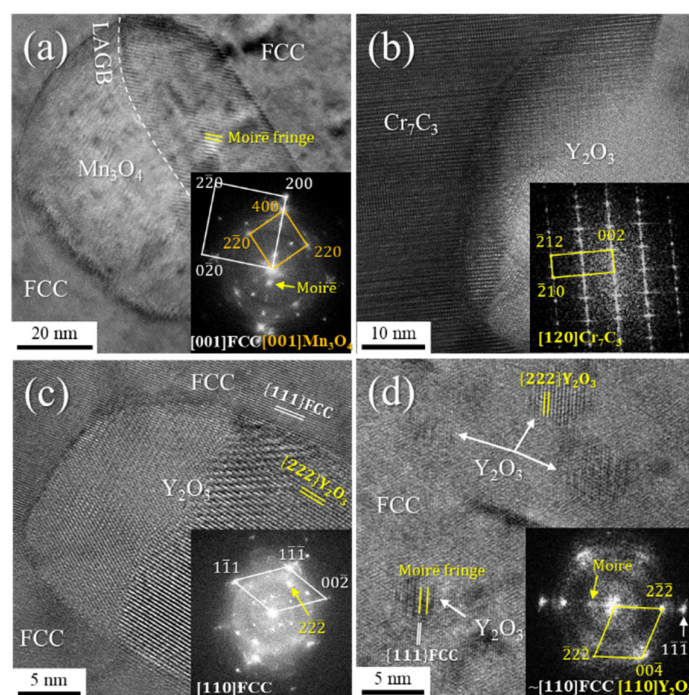


Figure 8. HRTEM and FFT results of (a) Mn_3O_4 particle in the PG alloy and (b) Cr_7C_3 and (c,d) Y_2O_3 particles in the YG alloy.

Figure 7d–f show STEM and EDS mapping results of the fine-grained region for the sintered YG alloy. The sizes of the FCC matrix and Cr_7C_3 phase for the fine-grained region were measured to be 151 ± 69 nm and 210 ± 68 nm, which is in good agreement with EBSD data (Figure 6g–j). Y-rich oxide particles measuring 17 ± 9 nm in diameter were present along the grain boundaries of the FCC matrix and Cr_7C_3 phases. Additionally, numerous fine (~ 5 nm) Y-rich oxide particles were observed within the FCC matrix. The GNF phase was not observed in both PG and YG alloys, which means that all GNF phases react with solute Cr to form the Cr_7C_3 phase during the sintering process. The absence of GNF-related features in the sintered compacts is attributed to the aggressive milling and sintering conditions employed in this study. Under high-energy ball milling (250 rpm, 30:1, 24 h), carbon reinforcements are expected to undergo severe fragmentation and structural degradation, and subsequent high-temperature sintering further promotes carbon consumption via interfacial reactions. In contrast, CNT-reinforced metal matrix composites processed under milder milling and lower sintering temperatures reported the preservation of CNT morphology [19,31,32], suggesting that the present conditions are unfavorable for maintaining the structural integrity of carbon-based reinforcements.

The carbide and oxide phases in the YG alloy were further characterized by HRTEM analysis. Figure 8b shows HRTEM and FFT results revealing the orthorhombic-structured Cr_7C_3 phase in the YG alloy. The Y-rich oxide particles were present along the grain boundaries of the Cr_7C_3 phase (Figure 8b) and the FCC matrix (Figure 8c), and also within the FCC matrix (Figure 8d). The fine (~ 5 nm) Y-rich oxide particles within the FCC matrix were identified as a cubic Y_2O_3 phase (mp-2652, $Ia\bar{3}$, space group No. 206; $a = 1.061$ nm [33]) with a cube-on-cube OR with respect to the FCC matrix. This cube-on-cube OR between the Y_2O_3 and FCC matrix arises from the lattice match between the cubic-structured phases (e.g., similar $2d\{222\}_{\text{oxide}}$ (~ 0.613 nm) and $3d\{111\}_{\text{FCC}}$ (~ 0.624 nm) values). The Moiré fringes with spacings of ~ 0.6 nm (extra diffraction spot at the $1/3\{111\}_{\text{FCC}}$ positions) arising from $\{222\}_{\text{oxide}}$ and $\{111\}_{\text{FCC}}$ planes are also visible. This indicates that fine coherent Y_2O_3 phases were formed within the FCC matrix of the YG alloy during the sintering process of mechanically alloyed powders. The coarse Y_2O_3 phases along the grain boundaries

appear to be less coherent to the FCC matrix, exhibiting a lattice deviation of $\sim 10^\circ$ from the cube-on-cube OR (Figure 8c), implying that the growth of the Y_2O_3 phase resulted in a loss of coherency to the FCC matrix.

Both the Mn_3O_4 and Y_2O_3 oxide phases in the PG and YG alloys act as obstacles that impede the movement of grain boundaries, thus achieving an ultrafine-grained microstructure. The Y_2O_3 phase of the YG alloy is smaller and denser than the Mn_3O_4 phase of the PG alloy. Additionally, the YG alloy contains fine (~ 5 nm) Y_2O_3 particles within the FCC matrix. This means a greater pinning effect of the Y_2O_3 phase, which contributes to the formation of a finer FCC matrix and Cr_7C_3 carbide in the YG alloy. However, this enhanced grain boundary pinning effect of Y_2O_3 particles was limited to the fine-grained region with a larger amount of oxide particles.

3.3. Mechanical Properties

Figure 9 shows the compressive stress–strain curves of the sintered PG and YG alloys, along with their compressive yield strength (CYS), ultimate compressive strength (UCS), fracture strain (ϵ_f), and Vickers hardness data. The Vickers hardness of the sintered PG and YG alloys was 417 ± 1 and 489 ± 3 HV, respectively. Similarly, the CYS of the YG alloy (1373 ± 72 MPa) was higher than that of the PG alloy (1184 ± 31 MPa).

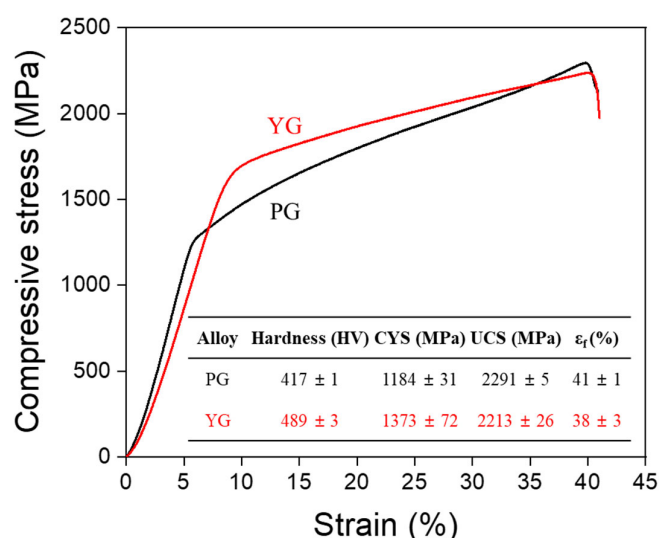


Figure 9. Compressive stress–strain curve of sintered PG and YG alloys.

The total yield strength (σ_{Total}) of the alloy can be estimated by the sum of strengthening components, including grain boundary strengthening (σ_{GB}), dislocation strengthening ($\sigma_{disl.}$), and oxide dispersion strengthening (σ_{Oxide}) as follows [34]:

$$\sigma_{Total} = \sigma_0 + \sigma_{GB} + \sigma_{disl.} + \sigma_{Oxide} \quad (2)$$

where σ_0 is the lattice friction stress of CrMnFeCoNi alloy (125 MPa [35]), inherently accounting for the solid-solution strengthening contribution [36]. The σ_{GB} can be described using the Hall-Petch relationship [37,38]:

$$\sigma_{GB} = kd^{-1/2} \quad (3)$$

where d is the measured FCC grain size and k is the slope ($494 \text{ MPa}/\mu\text{m}^{1/2}$ [35]) for Cantor alloy. Based on the average FCC matrix grain size of PG ($0.57 \mu\text{m}$) and YG ($0.71 \mu\text{m}$) alloys measured by EBSD data, the grain boundary strengthening of the PG and YG alloys was

calculated to be 654 MPa and 586 MPa, respectively. The $\sigma_{disl.}$ can be calculated using the Bailey-Hirsch equation [39]:

$$\sigma_{disl.} = M\alpha Gb\rho^{1/2} \quad (4)$$

where M is the mean orientation factor (3.06 for FCC metals), α is a constant (0.2 for FCC metals), G is the shear modulus (81 GPa [40]), b is the Burgers vector (0.254 nm), and ρ is the dislocation density. Based on the dislocation density of PG ($6.69 \times 10^{14} \text{ m}^{-2}$) and YG ($6.82 \times 10^{14} \text{ m}^{-2}$) alloys measured by EBSD, the dislocation strengthening of the PG and YG alloys was calculated to be 325 MPa and 328 MPa, respectively. The contribution of the Cr_7C_3 carbide phase with an area fraction of $\sim 10\%$ was excluded from the strength calculations because its strengthening effect was limited by its very large size ($\sim 400 \text{ nm}$).

Oxide dispersion strengthening (σ_{Oxide}) can be estimated using the Orowan equation [40]:

$$\sigma_{Orowan} = M \times \frac{0.4 \times G \times b}{\pi \times \sqrt{(1-\nu)}} \times \frac{\ln\left(\frac{2\bar{r}}{b}\right)}{\lambda} \quad (5)$$

$$\lambda = 2\bar{r} \times \left(\sqrt{\left(\frac{\pi}{4f}\right)} - 1 \right) \quad (6)$$

$$\bar{r} = r \times \sqrt{\frac{2}{3}} \quad (7)$$

where ν is Poisson's ratio (0.265 [40]), λ is the average interprecipitate distance, and f and r are the volume fraction and radius of the oxide particles. The sintered PG alloy contained Mn_3O_4 particles with a radius of 31 nm (Figure 7b). Previous study [15] has shown that Cantor powder milled with 1 wt.% PCA contains 0.12 wt.%O, which results in the formation of 2.16 vol.% of spinel oxide particles. Using the measured radius (31 nm) and expected volume fraction (2.16%) of Mn_3O_4 oxide particles, the σ_{Oxide} of the PG alloy can be estimated as 194 MPa. Meanwhile, sintered YG alloy contains both Mn_3O_4 and Y_2O_3 oxide particles. Mn_3O_4 oxide particles exhibit similar sizes in the PG and YG alloys; however, due to the absence of 1 wt.% PCA with a theoretical O content of 0.12 wt.%, the YG alloy is expected to contain fewer Mn_3O_4 particles ($\sim 1.57\%$), thus resulting in the σ_{Oxide} of 161 MPa. The sintered YG alloy contained coarse ($\sim 8.5 \text{ nm}$ in radius) Y_2O_3 particles along the grain boundaries and fine ($\sim 2.5 \text{ nm}$ in radius) Y_2O_3 particles within the FCC matrix. From the addition amount (1 wt.%), the total volume fraction of Y_2O_3 particles can be calculated as 1.59%. Assuming that 90% of the Y_2O_3 particles were formed along the grain boundaries, the σ_{Oxide} of the Y_2O_3 (GB) and Y_2O_3 (matrix) can be calculated to be 420 MPa and 300 MPa, respectively. Using the Pythagorean sum, the σ_{Oxide} of the three components is obtained as 541 MPa.

According to theoretical strength calculations, the σ_{Total} values of the sintered PG and YG alloys were calculated to be 1298 MPa and 1580 MPa, respectively, which are similar to the measured CYS values of the PG (1184 MPa) and YG (1373 MPa) alloys within a $\sim 15\%$ error range. The main strengthening factor in PG and YG alloys is grain boundary strengthening, which accounts for 50% (645 MPa) and 45% (586 MPa) of the calculated yield strength, respectively. Dislocation strengthening (25%, 325 MPa) and oxide dispersion strengthening (15%, 194 MPa) are the secondary strengthening factors of PG alloy. The YG alloy exhibits a similar dislocation strengthening effect (25%, 328 MPa). However, the YG alloy exhibits a significantly greater oxide dispersion strengthening effect (42%, 541 MPa) due to the added Y_2O_3 nanoparticles. Therefore, the finely dispersed Y_2O_3 particles distributed along grain boundaries and within the FCC matrix are the main cause of the increase in CYS ($\sim 200 \text{ MPa}$). The UCS and fracture strain of sintered YG alloy were measured to be $2213 \pm 5 \text{ MPa}$ and $38 \pm 1\%$, which are similar to the values ($2291 \pm 26 \text{ MPa}$,

$41 \pm 3\%$) of the PG alloy when considering the standard deviation. This indicates that adding Y_2O_3 nanoparticles is a beneficial strategy for increasing yield strength while maintaining compressive strength and ductility. It is well known that coarse-grained regions preferentially accommodate plastic strain during deformation, while ultrafine-grained regions contribute to strain hardening, thereby suppressing strain localization and enhancing deformation compatibility. Thus, maintenance of the compressive strength and ductility of the YG alloy can also be attributed to their bimodal grain structure [41].

4. Conclusions

In this study, the microstructure and mechanical properties of ultrafine-grained CrMn-FeCoNi alloys fabricated via MA of PCA + GNF or Y_2O_3 + GNF and subsequent SPS were investigated using thermodynamic calculations, XRD, SEM, EBSD, TEM, hardness, and compression tests. The main conclusions are summarized as follows.

- (1) After MA of additives, the PG and YG powders showed irregular and agglomerated morphologies, with average powder sizes of $14.8 \mu m$ and $27.9 \mu m$, respectively. The PG and YG powders exhibited a single FCC phase with crystallite sizes of 10.2 and 6.8 nm, respectively.
- (2) The PG and YG sintered alloys consisted of an FCC matrix, Cr_7C_3 carbide, and oxide phases. The PG alloy exhibited uniformly distributed FCC grains with an average grain size of $0.57 \mu m$, whereas the YG alloy showed a bimodal distribution of fine and coarse grains, with an average grain size of $0.71 \mu m$. The PG alloy, with its higher C content, contained a more abundant coarse Cr_7C_3 phase (376 nm, 10.5%) than the YG alloy (210 nm, 8.0%).
- (3) The PG and YG sintered alloys contained coarse (~ 62 nm) Mn_3O_4 oxide particles mainly along grain boundaries. The spinel Mn_3O_4 particles exhibited cube-on-cube ORs with respect to the FCC matrix. The YG alloy contained additional Y_2O_3 particles distributed along grain boundaries as well as within the FCC matrix. The fine Y_2O_3 particles (~ 5 nm) formed in the FCC matrix had cube-on-cube ORs to the FCC matrix. A slightly deviated ($\sim 10^\circ$) cube-on-cube ORs were observed in the coarse (~ 17 nm) Y_2O_3 particles formed along the grain boundaries.
- (4) The YG alloy exhibited higher hardness (489 HV) and CYS (1373 MPa) compared to the PG alloy (417 HV and 1184 MPa). Yield strength modeling revealed that grain boundary strengthening is the dominant strengthening mechanism in both PG and YG alloys. Dislocation strengthening and oxide dispersion strengthening are the secondary strengthening factors of the PG and YG alloys. The YG alloy had greater oxide dispersion strengthening arising from finely dispersed Y_2O_3 particles along the grain boundaries and within the FCC matrix, which led to an increase in CYS of ~ 200 MPa. The UCS and fracture elongation were similar in the PG (2291 MPa and 41%) and YG (2213 MPa and 38%) alloys.

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