Nanoscale Characterization of Oxide Dispersion Strengthened CoCrFeMnNi High-Entropy Alloy by Small Angle Neutron Scattering

SeungHyeok Chung, Ho Jin Ryu*
Nuclear and Quantum Engineering Department, Korea Advanced Institute of Science and Technology, 291 Daehakro, Yuseong, Daejeon, 34141, Republic of Korea
**Corresponding author: hojinryu@kaist.ac.kr*

1. Introduction

Oxide Dispersion Strengthened (ODS) alloy is a promising structural material due to its good mechanical properties at high temperatures and irradiation resistance [1, 2]. The presence of a nanosized dispersoids in ODS alloy matrix are providing irradiation defect sink sites and high creep strength at high operating temperature (>750°C) [3]. ODS alloys are characterized by high number density of nanosized oxide dispersoids within the alloy matrix. Dispersoids lead to grain refinement and strengthening by pinning the grain boundary and inhibiting the dislocation motions during the plastic deformation [4]. Transmission Electron Microscopy (TEM) analysis is a very powerful method to investigate the nanosized dispersoids. However, TEM can give us limited microstructural information due to its very small detection volume and it is intrinsically limited in resolution [5]. Small Angle Neutron Scattering (SANS) technique provides the statistically representative microstructural information from macroscopic detection volume i.e., dispersoids size distribution, volume fraction [6].

In this study, SANS and TEM analysis on ODS CoCrFeMnNi High-Entropy Alloy (HEA) was perfomed as an effort to investigate the in situ and ex situ dispersoid formation mechanism according to the alloy powder preparation methods.

2. Methods and Results

2.1 ODS-HEAs preparation

In order to fabricate the ODS-HEAs, the powder metallurgy method including alloy powder fabrication, mechanical alloying and consolidation was employed. CoCrFeMnNi HEA powder and 0.5wt%Y-CoCrFeMnNi HEA powder using metallic yttrium are prepared by gas atomization. To induce the in situ dispersoid formation, CoCrFeMnNi HEA powder and 0.5wt%Y CoCrFeMnNi HEA powder are mechanically alloyed, respectively, denoted as HEA and Y ODS-HEA. On the other hand, a mixture of CoCrFeMnNi HEA powder and 0.5wt% of Y_2O_3 powder are mechanically alloyed to induce ex situ dispersoids formation, denoted as Y_2O_3 ODS-HEA. Cryomilling was selected for mechanically alloying of the gas atomized powders, considering the high toughness of CoCrFeMnNi HEA at the cryogenic temperature. 6 mm-diameter stainless balls were used as the grinding media and 10:1 of a ball to powder ratio was employed. Mechanical alloying was conducted for 24 hours with 600 rpm at 97K. The mechanically alloyed powders are subsequently sintered by using spark plasma sintering at 1173K (Fig. 1). The sintering was performed with a constant uniaxial pressure of 50 MPa. A constant heating rate of 100K/min was employed to the desired sintering temperature and a holding period for 10 minutes used at the sintering temperature.

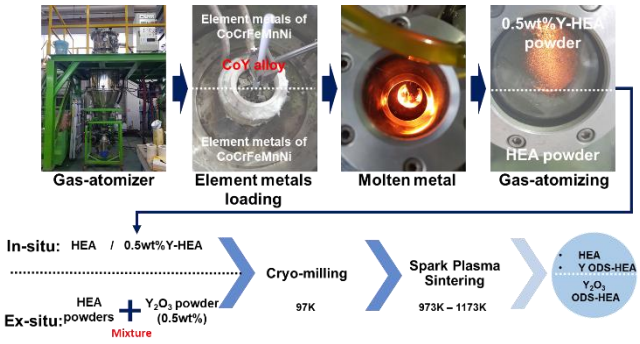

Fig. 1. In situ and ex situ ODS-HEAs fabrication process based on powder metallurgy method.

2.2 Transmission Electron Microscopy Analysis

Prior to performing the SANS, TEM measurement was performed to investigate the microstructure of ODS-HEAs. TEM specimens are prepared by focused ion beam micromachining. Figure 2 shows the STEM EDS mapping of HEA, Y ODS-HEA and Y_2O_3 ODS-HEA. Different types of dispersoids are expressed depending on powder preparation methods. Dispersoid formation without adding Y_2O_3 particle, in situ dispersoid formation occurred in HEA and Y ODS-HEA. Homogeneously distributed Cr and Mn rich oxide dispersoids are observed in the case of HEA. However, Y ODS-HEA has Y rich (Yellow arrow in Fig. 2. (d)) and Y and Cr rich (White double arrow in Fig. 2. (d)) oxide particles as the dispersoid. In Y_2O_3 ODS-HEA, nanosized dispersoids are observed in the matrix, however, very coarsened oxide particles are also formed (~300 nm) on the grain boundary. This result might be attributed to the inhomogeneous milling energy transfer to a mixture of the Y_2O_3 particle and HEA powder during the mechanical alloying.

In order to quantify the diameter and the number density of dispersoids of HEA, Y ODS-HEA and Y_2O_3 ODS-HEA, TEM micrograph analysis was carried out. The several TEM micrographs were taken at the various

magnifications and the dispersoids are counted to obtain the statistically proper dispersoids information as shown in figure 3. Nano dispersoids, formed by in situ dispersoid formation, smaller than 25 nm in diameter are observed. Meanwhile, coarsening of dispersoids is observed in Y_2O_3 ODS-HEA, which was fabricated by the ex situ dispersoid formation method.

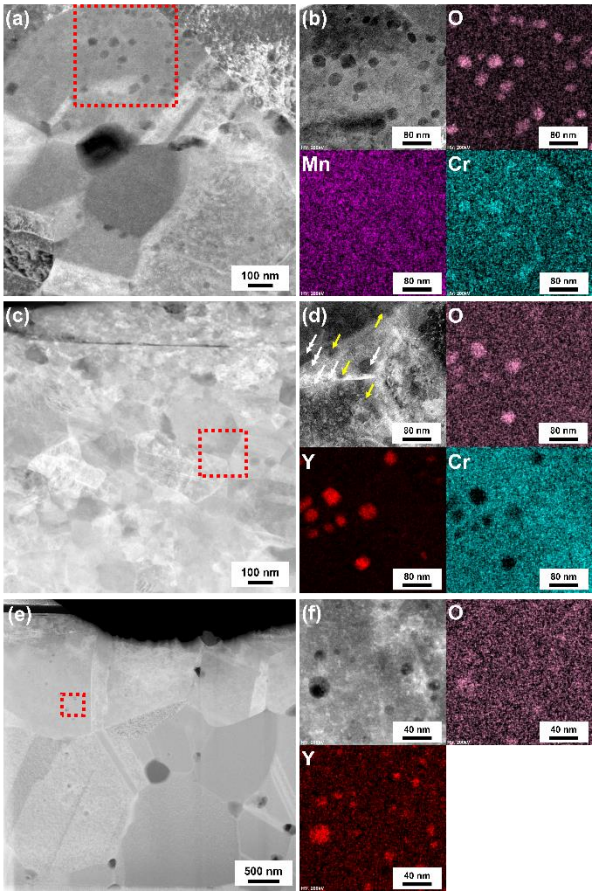

Fig. 2. STEM images of (a), (b) HEA, (c), (d) Y ODS-HEA and (e), (f) Y_2O_3 ODS-HEA.

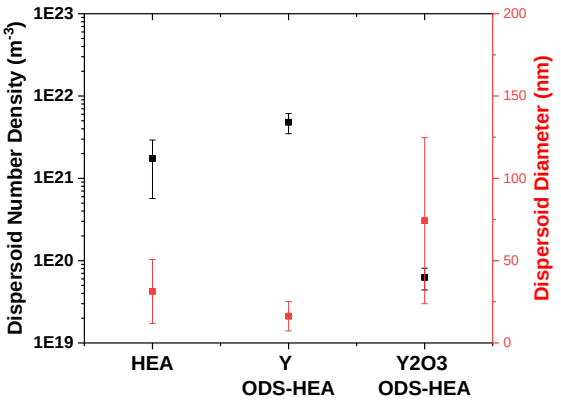

Fig. 3. Dispersoid number density and diameter of ODS-HEAs estimated by TEM micrographs analysis

2.3 SANS measurement

A SANS measurement performed using EQ-SANS instrument at ORNL. Figure 4 shows SANS intensities from the HEA, Y ODS-HEA and Y_2O_3 ODS-HEA sintered at 1173K. The SANS profiles from ODS-HEAs have different forms due to different dispersoid size distribution and dispersoid types. The SANS profiles are fitted by IRENA software package, Unified fit, developed by Argonne National Laboratory [7]. The unified fit is an appropriate tool to deal with data for which a specific scattering model does not exist [7, 8]. The intensity is given by:

$$I(q) = Gexp\left(-\frac{q^2R_g^2}{3}\right) + \exp\left(-\frac{q^2R_g^2}{3}\right) B\left\{\frac{\mathrm{erf}\left(\frac{qR_g}{\sqrt{6}}\right)}{1}\right\}^P \quad (1)$$

where G is the Guinier prefactor and B is the Porod constant. q is defined as $4\pi\sin\theta/\lambda$, θ is the scattering angle and λ is the wavelength of the neutron.

Figure 5 shows the dispersoid size distribution obtained from the data of ODS-HEAs. A bimodal size distribution and much higher density of the smaller dispersoid size distribution are confirmed at entire ODS-HEAs. The smallest dispersoid size distributions are detected in the Y ODS-HEA, followed by HEA and Y_2O_3 ODS-HEA, which has good agreement with TEM results.

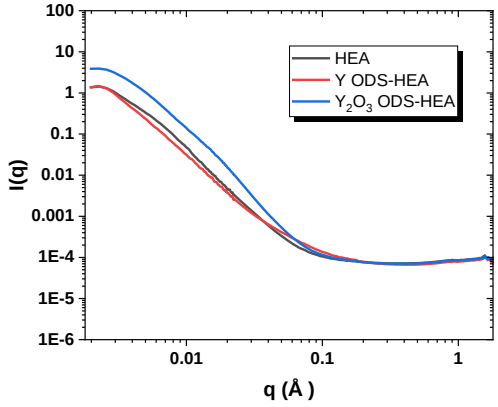

Fig. 4. SANS intensities of HEA, Y ODS-HEA and Y_2O_3 ODS-HEA sintered at 1173K.

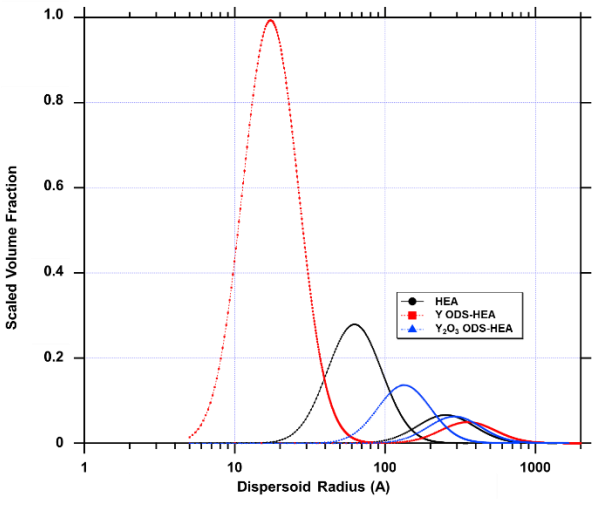

Fig. 5. Comparison of dispersoid sizes distribution

3. Conclusions

ODS HEAs are successfully prepared by the powder metallurgy method including gas atomization, cryomilling and spark plasma sintering. The influence of powder preparation on microstructure of ODS-HEAs was investigated. SANS and TEM analysis identified that in situ dispersoid formation can refine the dispersoid size with high number density. However, ex situ dispersoid formation causes coarsening of dispersoids.

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