A study on microstructural change of 1 %C-doped CoCrFeNi high entropy alloy during isochronal annealing

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The microstructure evolution of moderately deformed 1%C-doped CoCrFeNi high entropy alloy was investigated during an annealing at 973, 1073 and 1173 K for 1 hour. The microstructures in terms of phase formation, phase fraction and dislocation density were characterized by using the Time-of-Flight neutron diffraction experiment. The microstructure morphologies were additionally characterized by using electron backscatter diffraction (EBSD) and transmission electron microscope (TEM). After 60% thickness reduction of cold rolling, the highly deformed microstructure and deformation twinning were observed. The dislocation density was investigated as large as 2 x 10^{16} m^{-2}, which caused large stored strain energy of 370 J/mol. A large dislocation accumulation in moderately deformed microstructure emphasizes the dislocation activities promoted by carbon addition due to the larger solid solution hardening and carbide precipitations. An increase in stacking fault energy by carbon addition decreases deformation twin density and promotes the dislocation activities. The large stored energy associated with large dislocation density is related directly to microstructure evolution during the annealing. An increase in annealing temperature increased volume fraction of carbide precipitation. Chain-like carbide precipitations were formed during annealing at 1073 K and 1173 K. The solute drag effect and carbide precipitations were considered to inhibit boundary movement and, thus, delay the recrystallization process. The complete recrystallization with fine grains was observed at 1173 K of annealing for 1 hour. The fine recrystallized grains correspond to a large dislocation density of as-rolled sample. A reduction of hardness was resulted by the dislocation annihilation, content of carbide precipitation and grain morphology.

Keywords: *High entropy alloy, Neutron diffraction, Recrystallization, Dislocation density*

1. Introduction

High entropy alloys (HEAs) are designed based on high entropic stabilization of solid solution phase in relation to their high compositional complexity with a large number of constituent elements in near- or equiatomic ratios [1]. Due to their complex compositions, HEAs are expected to possess severe lattice distortion, which leads to an improvement of mechanical properties [2]. However, recent experimental evidence revealed that the existence of severe lattice distortion is not guaranteed in every HEAs. In CoCrFeMnNi and CoCrFeNi HEAs, the lattice distortion was not evident and the local lattice strains were anomalously large due to small atomic size misfit. This led to small solid solution hardening, similar to less component alloys [3].

It is well known for conventional alloys, e.g., carbon steels that an addition of interstitial atoms improves hardness and strength. The addition of C in HEAs might increase the level of lattice distortion, which corelates to localized strain fields and larger solid solution hardening. Besides an improvement of mechanical properties, the microstructure formation is expected to be changed due to interstitial solid solution and possible carbide precipitation. In this study, the effect of C addition on plastic deformation and recrystallization behavior of 1 %C-doped CoCrFeNi HEA was studied by using neutron diffraction and microstructure observation. This work revealed a correlation between a stored strain energy and microstructure evolution.

2. Experiment

An ingot of $Co_{24.72}Cr_{24.72}Fe_{24.72}Ni_{24.72}C_1$ (at. %) alloy was cast by using a vacuum induction furnace. A cut rectangular sticks (2.5 × 2.5 × 50 mm^3) of as-cast samples were cold rolled by 60% total thickness reduction for 1 mm thickness of the sheet. The cold rolled sheets were transferred to 1 hour isochronal annealing at 973 K, 1073 K and 1173 K under vacuum atmosphere, followed by water quenching.

To examine with the Time-of-Flight neutron diffraction experiment at BL20 iMATERIA, MLF, J-PARC, Ibaraki, Japan, the rolled and annealed samples with the length of 20 mm were inserted into vanadium cells for room temperature experiment. The dislocation density was evaluated by using Convolution Multiple Whole Profile (CMWP) method on the neutron diffractogram. The CMWP method is based on the convolution of three functions (size, strain and instrumental effects). The background is determined separately. The phase identification and crystallographic texture were analyzed by using Rietveld analysis with Materials Analysis Using Diffraction (MAUD) software on the neutron diffraction data. The microstructural observation and characterization were carried out by SEM, EBSD and TEM.

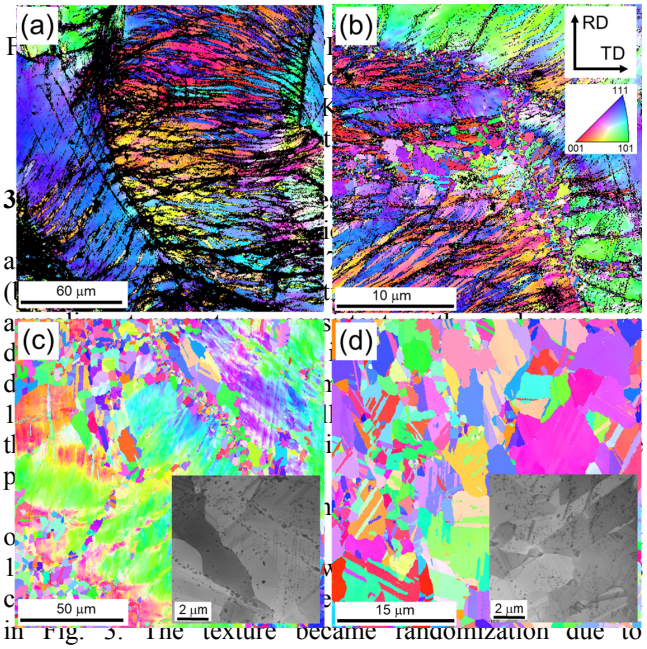
3. Result and discussion

3.1 Cold-rolled microstructure

After moderate degree of cold rolling with 60% thickness reduction, inhomogeneous microstructure with grain fragmentations and deformation bands was observed as shown in Fig. 1 (a). Twin boundaries were moderately detected in comparison with C-free CoCrFeNi HEA. It is reported that C addition increases the stacking fault energy (SFE) which promotes dislocation activities rather than deformation twinning during the plastic deformation [4]. Furthermore, C addition delays the transition of

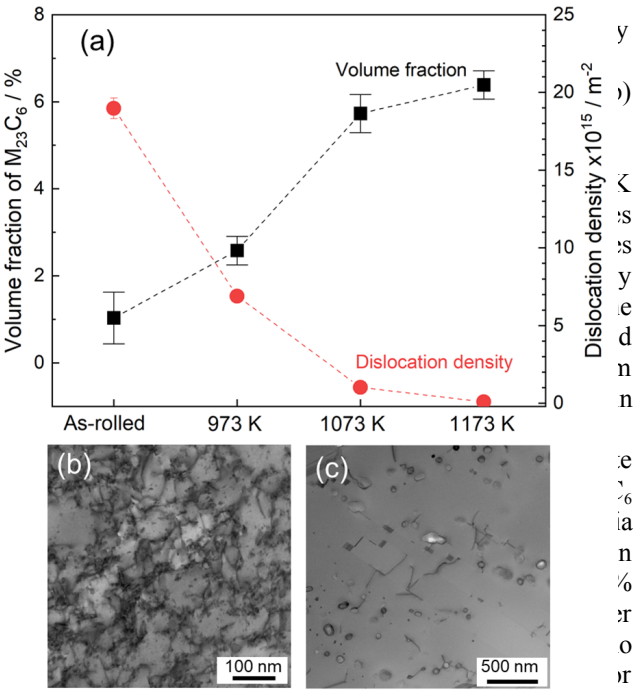
deformation mechanism form dislocation activities to deformation twinning at higher degree of deformation. The dislocation density was evaluated by CMWP method on neutron diffractograms, as 2 x 10^{16} m^{-2}, which was larger than C-free CoCrFeNi HEA under similar degree of deformation [5]. TEM image (in Fig. 2 (b)) shows nano-sized dislocation cells. The high dislocation density was not resulted only by interstitial C atoms in solid solution, but also $M_{23}C_6$ carbide precipitation, evident in neutron diffractograms and microstructure observation. The interstitial C atoms and carbide particles inhibited the dislocation motions, resulting in large dislocation density. The stored strain energy was calculated as 370 J/mol.

Furthermore, the crystallographic texture was analyzed from the neutron diffraction data. The $\varphi_2 = 0°$ section of the ODF in Fig. 3 indicates α-fiber with high intensity of Goss ({011}<100>) texture at Euler angle ($\phi_1 = 0°$, $\Phi = 45°$, $\phi_2 = 0°$). It is consistent with rolling texture of C-free CoCrFeNi HEA under 60% thickness reduction. The presence of strong Goss texture has been reported in solid solution Ni-60Co alloy [6].



in Fig. 3. The texture became randomization due to recrystallization.

In this C-doped CoCrFeNi HEA, the recrystallization was complete at 1173 K for 1 hour. Despite the large dislocation density of pre-annealed microstructure, the annealing temperature for achieving full recrystallization in C-doped CoCrFeNi HEA is higher than the reported temperature of C-free CoCrFeNi and CoCrFeMnNi HEAs. It is reported that recrystallizations of the C-free HEAs were completed at ≥ 973 K [7]. The C addition affects the recrystallization kinetic [8]. The fraction of $M_{23}C_6$ precipitations increased with the annealing temperature, as presented in Fig. 2 (a). The increase in the carbide fraction increasingly retards the grain boundary mobility via Zener pinning effect. The resistances of recrystallization and grain growth can be correlated with the effect of the fine carbide precipitations on immobilizing the dislocations, the low-angle and the high-angle grain boundaries. This phenomenon was similarly found in austenitic stainless steel [9].



0.5 h was as large as approximately 30 μm. It can be noted that the $M_{23}C_6$ particles impact the resistance of recrystallization and grain growth.

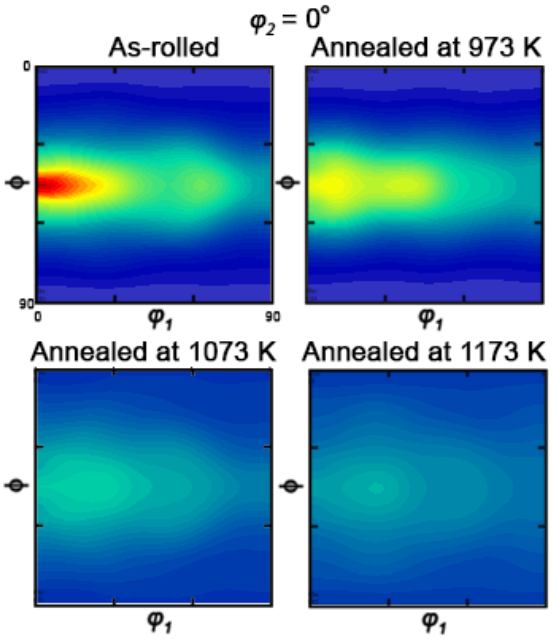


Fig. 3 The $\varphi_2 = 0$ sections of the ODFs of as-rolled and as-annealed samples.

4. Summary

In this study, the microstructure evolution of as-rolled 1%C-doped CoCrFeNi HEA was investigated during annealing at 973, 1073 and 1173 K for 1 h. The main results can be summarized as follows:

1) In as-rolled sample (60% thickness reduction), the dislocation density was as large as 2 x 10^{16} m^{-2} due to C atoms in solid solution and $M_{23}C_6$ carbide particles. The large dislocation density supplied stored strain energy as

370 J/mol.
2) During the annealing between 973 - 1173 K, the dislocation density exponentially decreased due to recovery and recrystallization. The microstructure was partially recrystallized at 973 and 1073 K and the recrystallization was completed at 1173 K.
3) The $M_{23}C_7$ particles were increasingly precipitated with an increase in annealing temperature. It indicated that the $M_{23}C_7$ precipitation affected the resistance of recrystallization and grain growth.

Acknowledgments

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