4版

様　式　C－19、F－19－1、Z－19　（共通）

科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

令和　６年　６月１７日現在

機関番号：１２７０１

研究種目：研究活動スタート支援

研究期間：2022～2023

課題番号：２２Ｋ２０４７８

研究課題名（和文）Enhancement of strength-ductility trade-off by microstructure control of C-doped FeNiCoCr HEA.

研究課題名（英文）Enhancement of strength-ductility trade-off by microstructure control of C-doped FeNiCoCr HEA.

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　2,100,000円

研究成果の概要（和文）：CoCrFeNi合金の強度と延性のトレードオフは1at%の炭素添加と焼鈍中の微細組織の作製により行われた。炭素添加による粒界強化と固溶強化の増加の組み合わせによって炭素析出強化が可能となった。析出物と微細組織の特性は異なる焼鈍条件と相互作用した。1000℃で60分焼鈍した合金（降伏強度391MPa）は、より均一な粒形と粗大な粒子が得られた。これらの特性により降伏強度の低下が補償された。対照的に、900℃で焼鈍されたサンプル（降伏強度514MPa）は不均一な粒界と微細な粒子配列が形成された。但し、これら2つのサンプルの伸びは35-40%で類似していた。強度は塑性変形中の転位蓄積と相関があった。

研究成果の学術的意義や社会的意義
In-situ neutron diffraction experiment was carried out to study microstructure evolution of CoCrFeNi + 1at%C alloy during annealing and tensile deformation. High strength and ductility are resulted by fine grain sizes, nanosized precipitates and deformation mechanism (shear-bands and twinning).

研究成果の概要（英文）：The strength-ductility trade-off in CoCrFeNi alloy has been dealt with 1at% carbon addition and microstructure fabrication during annealing. The carbon addition leads to being capable of carbon precipitation strengthening combined with increased grain boundary strengthening and solid solution strengthening. The precipitate and microstructure characteristics were interplayed with different annealing conditions. More uniform grain sizes and coarser particles in the samples annealed at 1000°C for 60 min (391 MPa of yield strength) compensated for a decrease in yield strength, in a comparison with the sample annealed at 900°C for 60 min (514 MPa of yield strength), where the inhomogeneous grain sizes and fine particle arrays were formed. However, the elongations of these two samples are similar between 35% - 40%. Their strengths were correlated to dislocation accumulation during plastic deformation.

研究分野：Metallurgy

キーワード：High entropy alloy　Microstructure　Mechanical Properties　Texture　Neutron scattering　Recrystallization

１．研究開始当初の背景

Multi-principal element alloys (MPEAs), which include both high-entropy alloys (HEAs) and medium-entropy alloys (MEAs), often show superior mechanical properties with good potential for the use as structural materials. The single-phase face-centered cubic (FCC) Cantor CoCrFeMnNi HEA (HEA) and its derived alloys exhibit superior deformability and plasticity; however, their low yield strength restricts practical industrial applications. Minor addition of interstitial carbon atoms is a favorable method to improve the strength due to more pronounced solid solution hardening. The carbon addition possibly leads to being capable of precipitation strengthening combined with increased grain boundary strengthening due to a reduced size of recrystallized grains. However, carbide precipitation can cause a detrimental effect on the ductility with excess content and grain boundaries precipitation.
Annealing of a heavily rolled CoCrFeMnNi and CoCrFeNi doped with minor carbon content led to precipitation of $M_{23}C_6$ particles along deformation-induced boundaries concurrently with recrystallization. It is reported that volume fractions and characteristics of carbide particles are caused by annealing conditions. Carbide precipitation has a great effect on grain size reduction and subsequently on mechanical properties. The microstructure characteristics including grain size and precipitation determine the dislocation activities during plastic deformation. Moreover, carbon addition alters deformation mechanism because stacking fault energy increases with C-addition [1]. The shear band-induced plasticity and twinning-induced plasticity in FCC HEAs are often claimed for increases in both strength and ductility [2]. Therefore, microstructure fabrication can be a favorable approach to improve strength-ductility trade-off in correlation with optimizing dislocation activities.

２．研究の目的

To deal with strength-ductility trade-off in CoCrFeNi alloy doped with 1 at%C, microstructure is designed for enhancing hardening effect and delaying fracture. In this study, microstructures of CoCrFeNi alloy doped with 1 at%C have been fabricated with cold-rolling and subsequent annealing. The microstructure formation and evolution are studied through in situ monitoring using neutron scattering by recording diffractograms during annealing of the deformed material at different temperatures. The different microstructure characteristics (e.g., recrystallized grain size, particle size and content) are expected to lead to different mechanical properties. The deformation behaviors of the controlled microstructures are further studied during in-situ tensile test by monitoring using neutron scattering. The development of dislocation characteristics is investigated in a correlation with tensile mechanical properties during in-situ tensile deformation. An ideal microstructure can be suggested to optimize dislocation characteristics and to achieve the target of strength-ductility.

３．研究の方法

(1) Sample preparation
An ingot of the CoCrFeNi alloy doped with 1 at% C was cast in a vacuum induction furnace. As-cast samples were homogenized at 1200°C for 5 h, followed by water quenching. The homogenized samples were machined into rectangular strips with a thickness of 25 mm, and these strips were cold rolled to a thickness reduction of 74%. After rolling, the samples were in-situ and ex-situ annealed at 700°C -1000°C for 60 min.

(2) In situ neutron scattering experiment
Neutron diffraction experiments were performed using the time-of-flight BL20 iMATERIA diffractometer at the Materials and Life Science Experimental Facility of the Japan Proton Accelerator Research Complex (J-PARC). For in-situ neutron scattering experiment during annealing, as-rolled specimens with a size of $52 \times 6 \times 2$ mm^3 were mounted with the rolling plane oriented perpendicular to the neutron beam. The in-situ measurements during annealing were conducted at 700°C-1000°C for 60 min. For in-situ neutron scattering experiment during tensile test, dog-bone shaped tensile test pieces of annealed samples with 25 mm of gauge length were vertically set with the rolling plane oriented perpendicular to the neutron beam. The tensile test pieces were deformed under uniaxial tensile load with the initial true strain rate of 4×10^{-5} s^{-1} at room temperature. The Convolutional Multiple Whole Profile (CMWP) fitting approach was carried out to analyze the dislocation density and dislocation arrangement parameter. The quantitative analysis of phases was conducted using the Rietveld refinement technique implemented in the Maud software. Orientation distribution functions (ODFs) were calculated using the extended Williams–Imhof–Matthies–Vinel (E-WIMV) method.

(3) Microstructure observation and characterization

Another set of the as-rolled or annealed specimens was prepared for SEM/EBSD and TEM characterizations. These specimens were annealed in a preheated furnace at temperatures identical to those used in the in-situ neutron diffraction experiments.

４．研究成果

(1) As-rolled microstructure

Minor volume fraction of $M_{23}C_6$ precipitations (<1%) was observed both before and after cold rolling. After rolling by 74% thickness reduction, the dislocation density was evaluated as large as 1.6×10^{16} m^{-2} (Fig. 1). In a comparison with carbon-free CoCrFeNi alloy (0.84×10^{16} m^{-2}) deformed by rotary swaging [3], the carbon addition is considered to be a key role in an increased rate of dislocation storage. It is due to the solute pinning effect and more pronounced lattice distortion as well as carbide precipitations in a correlation with inhibition of dislocation motions.

As-rolled microstructure presented significant heterogeneity in deformation structures with different crystallographic orientations. The typical brass-type rolling texture with a spread of orientations between the G and Bs components (all belonging to <110>//ND fiber) was observed after the rolling, which is similarly observed in carbon-free CoCrFeNi alloy [4]. However, carbon addition is expected to cause a weaker rolling texture due to increased stacking fault energy. In addition, the strong <111>//ND fiber was observed and dominated in the region containing shear bands and deformation twins. The large deformability of this alloy is consistent with a high frequency of deformation twins and shear bands.

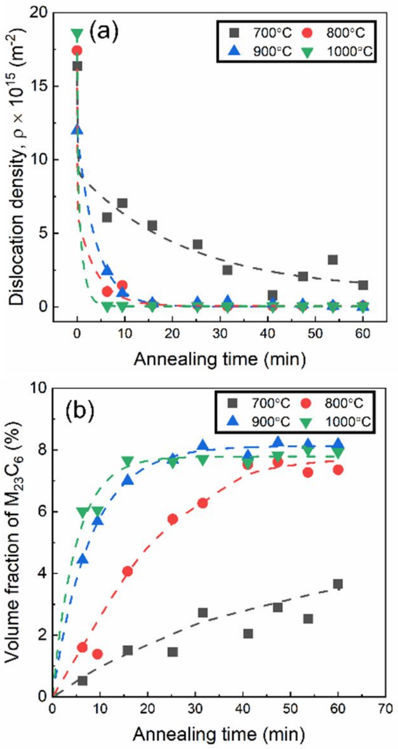

Fig. 1 Changes in (a) dislocation density and (b) $M_{23}C_6$ volume fraction during annealing.

(2) Microstructure evolution during annealing

The recrystallization behaviors and microstructure evolution were studied during annealing at between 700°C-1000°C for 60 min. Annealing at 700°C led to the slowest evolution with gradual increase in recrystallization fraction and slow dislocation annihilation. During annealing at 700°C, the recrystallized grains were observed to nucleate preferentially along shear bands and within regions of mixed orientations. Additionally, the arrays of fine $M_{23}C_6$ particles were preferentially precipitated at shear bands and non-twin HABs, concurrent with recrystallization. After 60 min of annealing at 700°C, the recrystallization was not complete with a presence of deformed microstructure. In a recrystallized region, the various recrystallized grain sizes were observed in this sample (Fig. 2).

Annealing at 800°C-1000°C resulted in a higher rate of dislocation annihilation (Fig.1(a)) and of recrystallization. The samples annealed at ≥800°C for >20 min were fully recrystallized and, in addition, the full recrystallization was observed in the sample annealed at 1000°C for at least 10 min. The $M_{23}C_6$ precipitation rates in the samples annealed at 800°C-1000°C were higher than those annealed at 700°C. Annealing at 700°C-900°C led to a formation of fine particle arrays. In contrast to annealing at lower temperatures, the particles in the samples annealed at 1000°C were coarser and formed shorter arrays containing fewer particles (Fig. 3). In this sample, the coarse particles were also observed along grain boundaries and at triple junctions of grains. The microstructure annealed at 1000°C demonstrated more uniform than the microstructure in the samples recrystallized at lower temperatures, where clusters of fine grains are combined with coarser grains. The average grain sizes in fully recrystallized samples were below 5 μm. as a result, 1 at% C in CoCrFeNi can effectively suppress grain growth even at very high temperatures. The annealing weakens the rolling texture. The rolling texture was retained in partially recrystallized sample. In fully recrystallized samples,

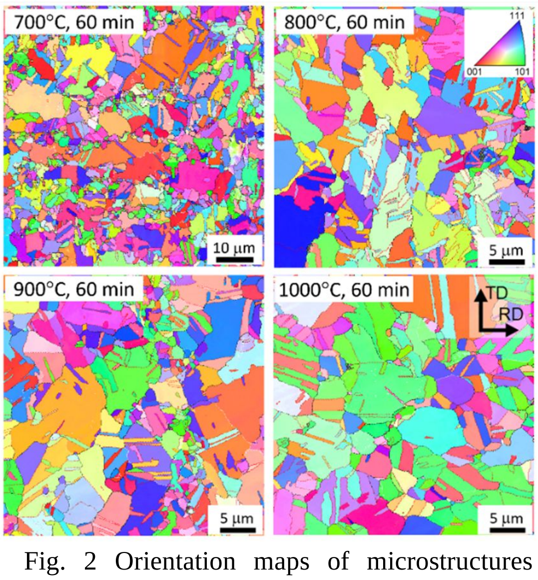

Fig. 2 Orientation maps of microstructures annealed at different temperature for 60 min.

new annealing textures with several new components were developed, as shown in Fig. 4. The development of texture during the annealing is also determined by initial rolling texture. However, carbon addition led to the fact that the rolling texture varies from specimen to specimen.

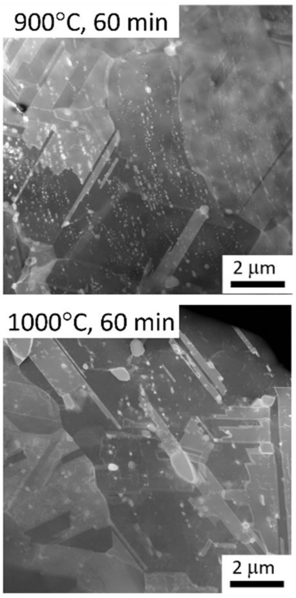

Fig. 3 MAADF STEM images for the samples annealed for 60 min at 900°C and 1000°C

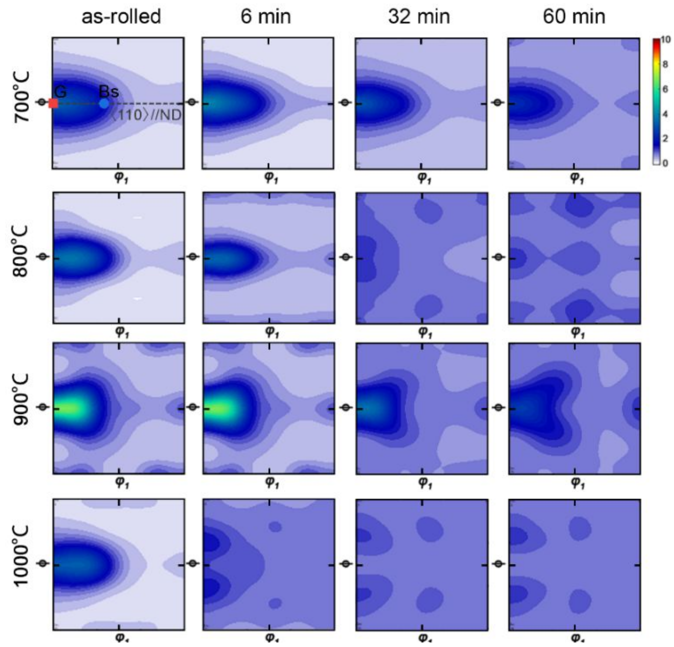

Fig. 4 φ_2 = 0° sections of ODFs calculated from the data collected during in situ neutron diffraction experiments at different temperatures.

(3) Microstructure evolution during tensile deformation

The samples annealed at 900°C and 1000°C for 60 min, which demonstrated distinct microstructure characteristics, were conducted for studying the dislocation activities during tensile deformation. The yield strength of the sample annealed at 900°C is about 514 MPa, higher than that of the sample annealed at 1000°C. The higher flow stress in the sample annealed at 900°C is consistent with the higher rate of dislocation accumulation. This is due to microstructure and carbide precipitate characteristics. In the sample annealed at 900°C, the grain sizes are in wider range and the arrays of fine carbide particles are formed. In contrast, the sample annealed at 1000°C demonstrates more uniform grains, intergranular precipitations and the arrays containing fewer particles. Furthermore, changes in dislocation arrangement parameters or M parameters ($M = R_e\sqrt{\rho}$, where R_e is the radius of the strain field of dislocations) in these two samples are also different, as shown in Fig. 5. The M parameters in these two samples at different strain were less than 1, indicating dislocation cell wall formation and strong dislocation arrangement. At low strain, the M parameter in the sample annealed at 900°C shows higher value due to the reason that finer particles lead to wider spacing between partial dislocations. A significant decrease in M parameter in this sample during plastic deformation is resulted by strong dislocation rearrangement.

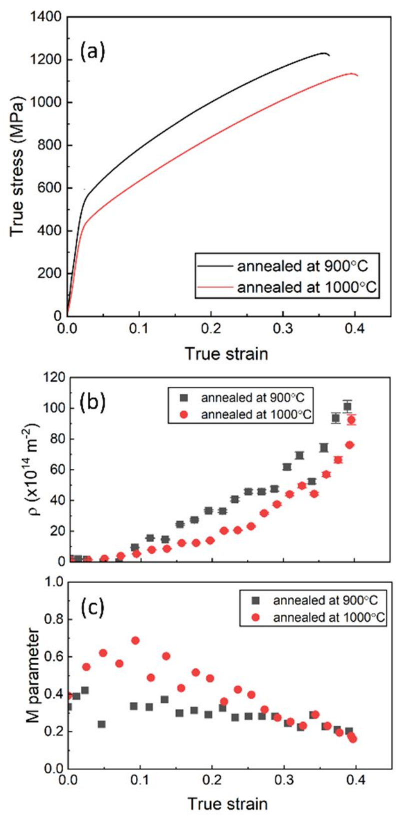

Fig. 5 (a) true stress- true strain curves, changes in (b) dislocation density and (c) M parameter.

引用文献

[1] Y. Ikeda, et al., Phys. Rev. Mater. 3.11 (2019) 113603.
[2] Y. Wang, et al., Acta Mater. 154 (2018) 79-89.
[3] P. Thirathipviwat, et al., J. Alloys Compd. 930 (2023) 167504.
[4] Y.W. Xiao, et al., J. Alloys Compd. 968 (2023) 172153.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　0件）

１．著者名 Thirathipviwat Pramote、Hasegawa Makoto、Onuki Yusuke、Sato Shigeo、Mishin Oleg V.	４．巻 212
２．論文標題 In situ neutron diffraction study and electron microscopy analysis of microstructure and texture evolution during annealing of rolled CoCrFeNi alloy doped with 1 at.%C	５．発行年 2024年
３．雑誌名 Materials Characterization	６．最初と最後の頁 113980～113980
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.matchar.2024.113980	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Thirathipviwat Pramote、Onuki Yusuke、Umemura Kazuki、Sato Shigeo	４．巻 930
２．論文標題 Microstructure, dislocation density and microhardness of 1 %C-doped CoCrFeNi complex concentrated alloys during isochronal annealing	５．発行年 2023年
３．雑誌名 Journal of Alloys and Compounds	６．最初と最後の頁 167504～167504
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jallcom.2022.167504	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Thirathipviwat Pramote、Onuki Yusuke、Vishnu Jithin、Kesavan Praveenkumar、Raheem Ansheed、Manivasagam Geetha、V Shankar Karthik、Hasegawa Makoto、Sato Shigeo	４．巻 339
２．論文標題 Superior fretting wear resistance of 30Nb5Ta30Ti15V20Zr refractory high entropy alloy in a comparison with Ti6Al4V	５．発行年 2023年
３．雑誌名 Materials Letters	６．最初と最後の頁 134105～134105
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.matlet.2023.134105	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計10件（うち招待講演　3件／うち国際学会　6件）

１．発表者名 Thirathipviwat Pramote, Onuki Yusuke, Hasegawa Makoto, Sato Shigeo
２．発表標題 In-situ heating neutron diffraction study on changes of microstructure, dislocation density and crystallographic texture in 1 %C-doped CoCrFeNi high entropy alloy
３．学会等名 Thermec ' 2023（招待講演）（国際学会）
４．発表年 2023年

1．発表者名
Thirathipviwat Pramote, Hasegawa Makoto, Onuki Yusuke, Sato Shigeo

2．発表標題
Precipitation and recrystallization behavior of 1 %C-doped CoCrFeNi high entropy alloy during isochronal annealing

3．学会等名
2023 JIM Autumn Meeting

4．発表年
2023年

1．発表者名
Thirathipviwat Pramote, Hasegawa Makoto, Onuki Yusuke, Sato Shigeo

2．発表標題
In-situ neutron diffraction study on microstructure and texture evolution of 1%C-doped CoCrFeNi during annealing

3．学会等名
日本金属学会 第2回 結晶性材料の結晶配向評価および結晶方位解析技術研究会

4．発表年
2023年

1．発表者名
Thirathipviwat Pramote, Onuki Yusuke, Sato Shigeo, Hasegawa Makoto

2．発表標題
A study on microstructural change of 1 %C-doped CoCrFeNi high entropy alloy during isochronal annealing

3．学会等名
28th IFHTSE2023（国際学会）

4．発表年
2023年

1．発表者名
Pramote Thirathipviwat, Yusuke Onuki, Makoto Hasegawa, Shigeo Sato

2．発表標題
In-situ heating neutron diffraction study on changes of microstructure, dislocation density and crystallographic texture in 1 %C-doped CoCrFeNi high entropy alloy

3．学会等名
Thermec’2023（招待講演）（国際学会）

4．発表年
2023年

１．発表者名 Pramote Thirathipviwat, Makoto Hasegawa, Yusuke Onuki, Shigeo Sato
２．発表標題 Precipitation and recrystallization behavior of 1 %C-doped CoCrFeNi high entropy alloy during isochronal annealing
３．学会等名 2023 JIM Autumn Meeting
４．発表年 2023年

１．発表者名 Pramote Thirathipviwat, Makoto Hasegawa, Yusuke Onuki, Shigeo Sato
２．発表標題 In-situ neutron diffraction study on microstructure and texture evolution of 1%C-doped CoCrFeNi during annealing
３．学会等名 第2回 結晶性材料の結晶配向評価および結晶方位解析技術研究会
４．発表年 2023年

１．発表者名 Pramote Thirathipviwat, Yusuke Onuki, Shigeo Sato, Makoto Hasegawa
２．発表標題 A study on microstructural change of 1 %C-doped CoCrFeNi high entropy alloy during isochronal annealing
３．学会等名 28th IFHTSE2023（国際学会）
４．発表年 2023年

１．発表者名 Thirathipviwat Pramote, Sega Nozawa , Moe Furusawa, Onuki Yusuke, Hasegawa Makoto, Matsumoto Katsushi, Sato Shigeo
２．発表標題 In-situ neutron diffraction study of dislocation density evolution during tensile deformation in Al-Mg Alloys
３．学会等名 The 18th International Conference on Aluminium Alloys (ICAA18)（国際学会）
４．発表年 2022年

1．発表者名 Thirathipviwat Pramote, Onuki Yusuke, Hasegawa Makoto, Sato Shigeo
2．発表標題 A Contribution of Large Dislocation Accumulation to Large Work Strengthening in FeNiCoCrMn High Entropy Alloy
3．学会等名 International Conference and Exhibition on Science, Technology and Engineering of Materials (ISTEM2022)（招待講演）（国際学会）
4．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
デンマーク	Technical University of Denmark			