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Communication

On the Effect of Annealing on Cryogenically Rolled Medium Entropy Alloy

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How To Cite: Misra, R.D.K. On the Effect of Annealing on Cryogenically Rolled Medium Entropy Alloy. *Journal of Innovations in Materials and Manufacturing Engineering* **2026**, *1*(1), 3.

Received: 22 November 2025
Revised: 15 December 2025
Accepted: 19 December 2025
Published: 23 December 2025

Abstract: The objective of the study is to understand the evolution of structure during annealing of a cryogenically rolled medium entropy alloy and compare the annealing behavior with a high entropy alloy. The understanding of annealing kinetics is important to optimize the mechanical properties. Cryogenically rolled medium entropy alloy (CoCrNi) was annealed in the temperature range of 600–850 °C. Recrystallization occurred at a temperature of 600 °C, which is about 200 °C lower than the temperature required to induce recrystallization in the CoCrFeMnNi high entropy alloy at identical cryogenically rolling reduction of ~30%. High fraction of annealing twins was observed with fraction in the range of ~53–59%. The geometrically necessary dislocation density for the annealed alloy was ~1×10^{14} m^{-2}. The study underscores that the annealing temperature depends on the number and nature of constituent elements in the alloy. A high annealing temperature is conducive to the formation of annealing twins when the unstable deformed microstructure transforms into a new equilibrium and recrystallized structure.

Keywords: medium entropy alloy; annealing; recyrstallization; microstructure

1. Introduction

High entropy alloys (HEAs) continue to be of interest to the scientific community because they are envisaged to provide immense opportunity for their use in diverse applications. Based on the concept of high entropy alloys [1,2], they primarily consist of at least 5 alloying elements in near-equiatomic ratio. The configurational entropy that influences solubility and phase formation is maximum when the alloying elements are present in the alloy in equiatomic ratio [3]. It is believed that maximizing the number of alloying elements enhances the mechanical properties of the alloy. This is, however, not considered to be true because of the microstructure-property relationship, where the microstructure depends on the content and nature of alloying elements [4–6].

In recent years, medium entropy alloys, a spin-off of high entropy alloys, have generated increasing interest because they are conceived to exhibit a high strength-high ductility combination [7]. An important example is CoCrNi alloy with equiatomic ratio. It is proposed that low stacking fault energy (SFE) and high critical stress necessary for twinning [8,9] is the underlying reason for high strength-high ductility combination, where the greater critical stress for twinning compared to the Cantor alloy (CoCrFeMnNi) leads to mechanical twinning at large strains and necking is inhibited, leading to high ductility [8,9].

Homogenization of high entropy alloys is an aspect of significant concern. In this regard, rolling at cryogenic temperatures introduces significant structural defects that provide diffusion paths during homogenization and/or annealing enabling chemical homogeneity of the alloy [10–12]. Keeping this in mind, the objective here is to study the annealing behavior of cryogenically rolled medium entropy alloy.

2. Experimental Procedure

The experimental CoCrNi medium entropy alloy (MEA) in equiatomic ratio was melted in a vacuum induction furnace using constituent elements of purity greater than ~99%. To eliminate elemental segregation and enhance chemical homogeneity after solidification, the alloy was subjected to a solution treatment at 1100 °C for 10 h.

The alloy was cooled in liquid nitrogen for 10 min before each pass of rolling and cryogenically rolled to ~30% reduction. The cryogenically rolled CoCrNi alloys (MEAs) were annealed at 600 °C, 700 °C, 800 °C, and 850 °C for 6 h, and the corresponding samples were designated as MEA600, MEA700, MEA800, and MEA850, respectively. The microstructure of the isothermally treated alloy samples was examined and studied via scanning electron microscope (SEM, Zeiss EVO18, Oberkochen, Germany) equipped with an electron backscatter diffraction (EBSD) system (EBSD, Oxford Nordlys Nano, Abingdon, UK). This analysis was aimed at studying the microstructural evolution and phase composition of the alloy. All samples for SEM and EBSD analysis were mechanically ground using SiC paper of different grits to reduce the thickness of specimens to ~0.2–0.3 mm and subsequently electropolished. The EBSD samples were electropolished in a solution 15% perchloric acid and 85% ethanol at a at a constant voltage of potential of 18 V for ~10–20 s, and the temperature of the electropolishing solution was maintained at −10 °C. The objective of conducting EBSD studies was to obtain pole figure maps, grain size distribution, band contrast and grain boundary maps and geometrically necessary dislocations (GNDs) maps. This objective facilitated the study of microstructural evolution during the annealing process in relation to the as-cast alloy.

3. Results and Discussion

3.1. Microstructure

Figure 1 presents a summary of microstructural characteristics of CoCrNi medium entropy alloy (MEA) after isothermal treatment at 1100 °C for 10 h comprising of SEM micrographs, EBSD analysis results, and energy-dispersive X-ray spectroscopy (EDS) results. SEM observations (Figure 1a) reveal that the alloy is primarily composed of coarse columnar grains formed during solidification, which remain largely unchanged after subsequent isothermal treatment. It is pertinent to mention that some dark spots observed within the microstructure of Figure 1a are artifacts from sample preparation. They do not influence the alloy's properties or microstructural evolution.

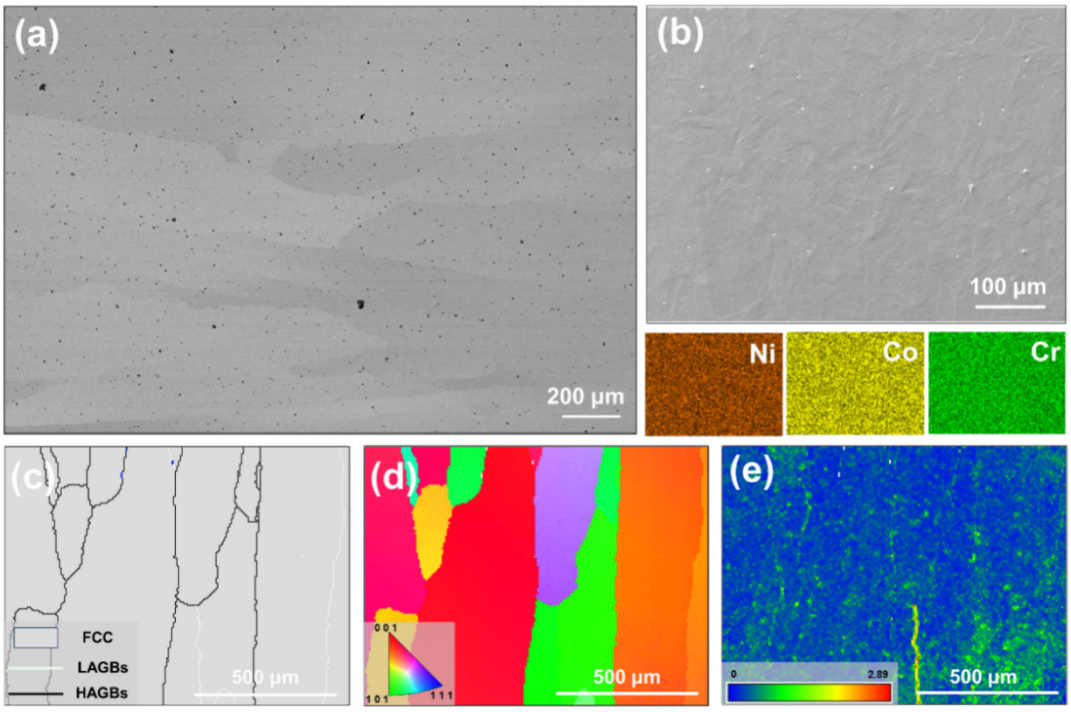

Figure 1. The microstructural characteristics of isothermally heat-treated medium entropy alloy (MEA) at 1100 °C for 10 h. (**a**) Back-scattered image; (**b**) EDS analysis; and (**c**–**e**) EBSD analysis results.

The EDS results (Figure 1b) indicate a uniform distribution of alloying elements, Co, Cr, and Ni, throughout the microstructure, with no significant elemental segregation at the micro-level. This suggests that the elemental

diffusion under high-temperature conditions is sufficient to promote chemical homogeneity, thereby enhancing the overall performance and microstructural stability of the alloy.

Phase analysis confirms that the alloy predominantly consists of a face-centered cubic (FCC) structure (Figure 1c), which remains stable during high temperature isothermal treatment. The IPF map clearly shows that the microstructure continues to be dominated by coarse columnar grains (Figure 1d), with no evidence of grain refinement. Based on statistical analysis of grain size, the average grain size was ~365 μm, reflecting excellent thermal stability of as-cast grains under high-temperature conditions. Additionally, grain boundary analysis in Figure 1c reveals no apparent recrystallization during the 1100 °C treatment. This behavior may be attributed to the alloy's compositional characteristics and initial microstructural state: the coarse as-cast grains exhibit high thermal stability, and the material has not undergone sufficient plastic deformation to reach the critical conditions (e.g., strain or stored energy) required for recrystallization. The unrecrystallized microstructural features may significantly influence the alloy's high-temperature mechanical properties and stability, warranting further investigation.

To further study the microstructural evolution of medium entropy alloy (MEA) after cryogenic rolling and subsequent annealing, EBSD analyses were conducted on MEA annealed at 600–850 °C, as shown in Figures 2–4.

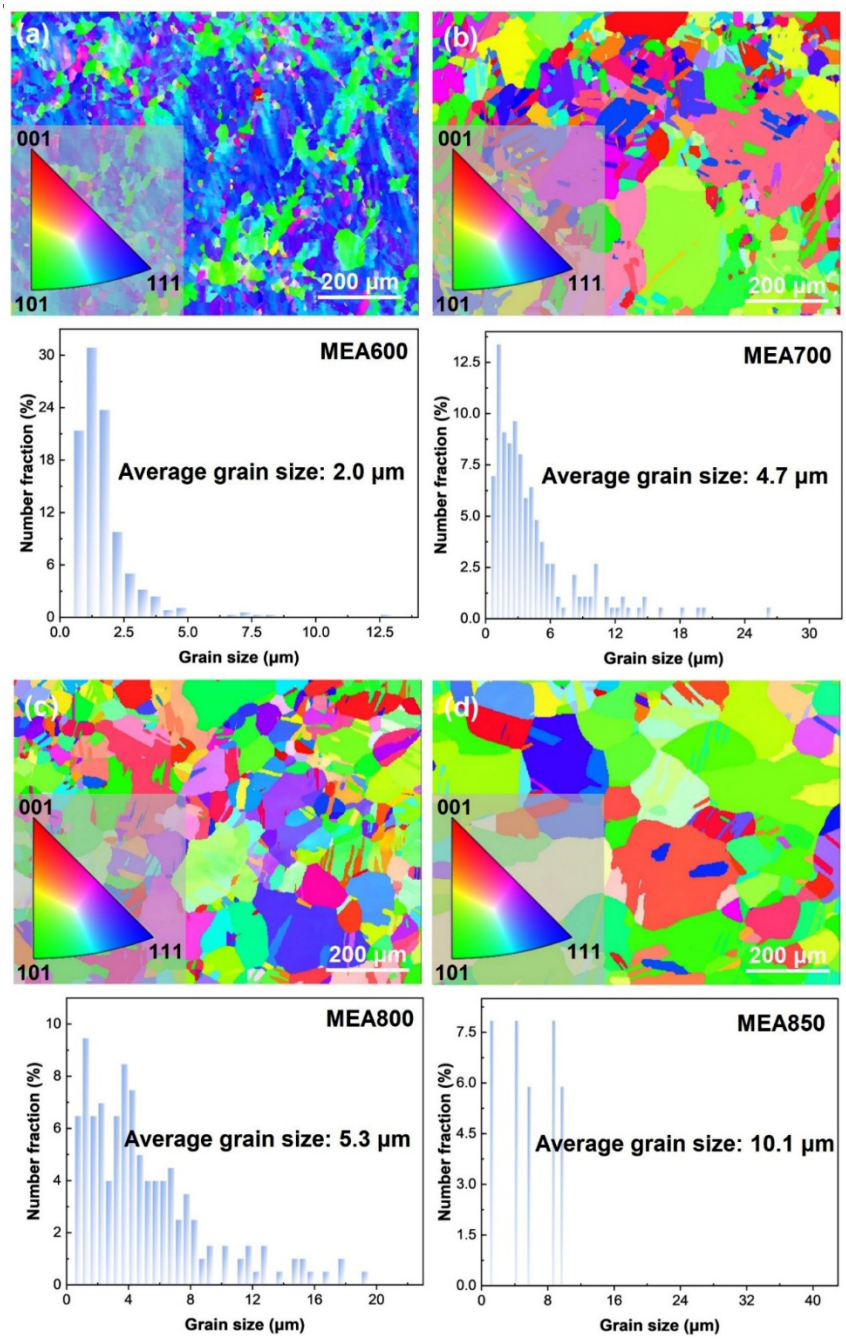

Figure 2. EBSD inverse pole figure (IPF) maps and grain size distribution of medium entropy alloy (MEA) annealed at (**a**) 600 °C; (**b**) 700 °C; (**c**) 800 °C; and (**d**) 850 °C.

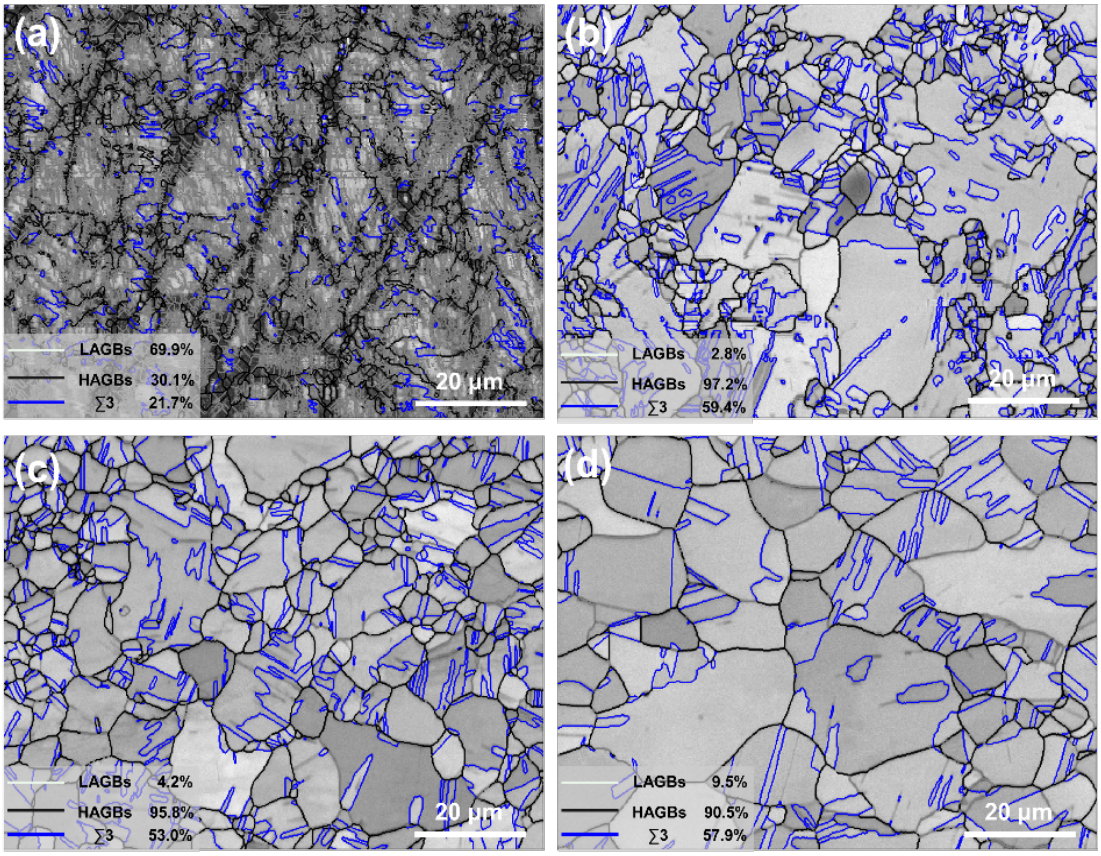

Figure 3. Band contrast (BC) and grain boundary (GB) maps of the experimental medium entropy alloy (MEA) annealed at (**a**) 600 °C; (**b**) 700 °C; (**c**) 800 °C; and (**d**) 850 °C.

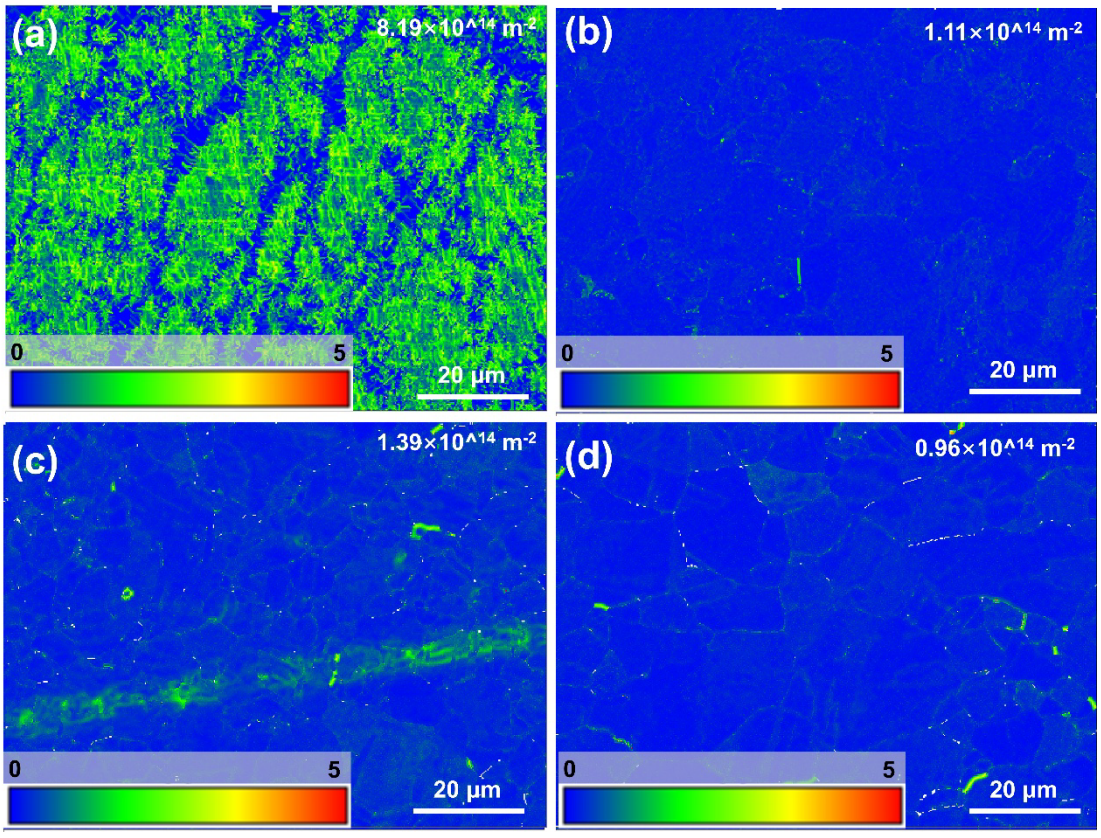

Figure 4. GND distribution maps of medium alloy (MEA) annealed at (**a**) 600 °C; (**b**) 700 °C; (**c**) 800 °C; and (**d**) 850 °C.

Figure 2 presents the inverse pole figure (IPF) maps and corresponding grain size statistics. It can be observed that the microstructure of MEA600 sample is primarily composed of heavily deformed grains because of cryogenic rolling, whereas the MEA700, MEA800, and MEA850 samples mainly consist of recrystallized grains, indicating significant differences among them. According to the literature, the melting point of the CoCrNi HEA is ~1690 °C, and its recrystallization temperature is around 0.4 Tm, i.e., ~676 °C. Therefore, the HEA700, HEA800, and HEA850 samples exhibit characteristic features of recrystallized microstructures. With increasing annealing temperature, the recrystallized grains grow larger and tend to form a more uniform, equiaxed morphology. As shown in Figure 3, the average grain size of MEA600, MEA700, MEA800, and MEA850 samples are ~ 2.0 μm, 4.7 μm, 5.3 μm, and 10.1 μm, respectively. The corresponding standard deviations for MEA600, MEA700, MEA800, and MEA850 samples are: 4.5 μm, 5.2 μm, 4.3 μm, and 8.9 μm, respectively.

Unlike the recently studied cryogenically rolled high entropy alloys, which were also cryogenically rolled to a similar 30% reduction, indicated that cryogenic rolling introduces twin bundles [12] that resembled slip bands at low magnifications [11,12] and are retained in the unrecrystallized grains at low annealing temperatures [12]. However, at high annealing temperature, the thermal energy was adequate for the structure to recrystallize and the atoms to reorganize such that the twin bundles were not observed in the recrystallized grains [11,12]. This type of microstructure was not evident in the MEA presented here. Furthermore, MEA appears to recrystallize at lower temperature (600–700 °C: present study) compared to the HEA that tends to completely recrystallize at temperatures greater than 800 °C [12].

Figure 3a–d show the grain boundary distribution maps, where gray, black, and blue lines represent low-angle grain boundaries (LAGBs, 2–15°), high-angle grain boundaries (HAGBs, >15°), and annealing twin boundaries (Σ3 boundaries), respectively. At an annealing temperature of 600 °C, the fraction of HAGBs and twin boundaries is relatively low, while LAGBs are predominant, accounting for approximately 69.9%. These LAGBs are mainly formed by the accumulation and entanglement of dislocations generated during plastic deformation. In contrast, at higher annealing temperatures of 700 °C, 800 °C, and 850 °C, the proportion of HAGBs exceeds 90%, whereas the fraction of LAGBs is significantly reduced. During annealing at elevated temperatures, dislocations become more mobile and tend to rearrange through mechanisms such as slip and climb. As a result, many sub-grain boundaries either disappear or transform into HAGBs through recovery and recrystallization processes, leading to an increased fraction of HAGBs and a decreased fraction of LAGBs. Additionally, a higher fraction of annealing twin boundaries is observed in samples annealed at elevated temperatures. Specifically, the fractions of Σ3 twin boundaries in the MEA700, MEA800, and MEA850 samples are 59.4%, 53.0%, and 57.9%, respectively. It is widely known that low stacking fault energy alloys readily form annealing twins because it easier to create planar fault needed for twinning instead of extensive degree of dislocation slip. This leads to a fine-grained structure with high strength. Moreover, when the twin density increases, the twins act as growth accidents or nucleate twins at the twin boundaries, promoting the recrystallization process. In summary, a low stacking fault energy means that twins are preferred, low energy path for microstructural evolution than complex dislocation motion, enhancing twin formation during the recovery and recrystallization process.

Figure 4 presents the geometrically necessary dislocation (GND) density maps for the MEA600, MEA700, MEA800, and MEA850 samples. It is evident that the MEA600 sample retains a high density of dislocations introduced during cold rolling, with a GND value of 8.19×10^{14} m^{-2}. In contrast, the MEA700, MEA800, and MEA850 samples undergo recovery and recrystallization during annealing. During this process, dislocations and other defects generated during cold rolling serve as preferential nucleation sites for recrystallized grains. The substructures within the deformed grains rearrange through mechanisms such as rotation and dissociation to form sub-grains, which subsequently grow into new grains. As a result, the GND densities of the MEA700, MEA800, and MEA850 samples are significantly reduced, with values of 1.11×10^{14} m^{-2}, 1.39×10^{14} m^{-2}, and 0.96×10^{14} m^{-2}, respectively.

4. Conclusions

The primary conclusions of the study on the microstructural evolution during annealing of cryogenically rolled medium entropy alloys are the following:

(a) Cryogenically rolled medium entropy alloy (CoCrNi) was characterized by near-complete recrystallization at a lower temperature compared to the high entropy alloy (CoCrFeMnNi) subjected to similar cryo-reduction of ~30%
(b) High fraction of annealing twins was observed at higher annealing temperatures of 700 °C and greater
(c) FCC crystal structure was retained after cryogenic rolling and annealing and no new phase was observed
(d) The geometrically necessary dislocation density in the annealed samples was ~1×10^{14} m^{-2}.

The conclusions suggest that the annealing temperature required for near-complete recrystallization of medium entropy alloys is significantly lower than the high entropy alloy, a behavior that is related to stacking fault energy. However, the crystal structure is retained during the annealing process implying that the alloy is thermodynamically stable such that no new phase is nucleated. The study of kinetics of annealing and the microstructure is practically relevant to optimize mechanical properties.

Funding

This research received no external funding.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

The study presented here is part of the ongoing work and cannot be shared at this time.

Acknowledgments

RDKM sincerely thanks J.R. Yang, former colleague at the University of Cambridge and his student (T.F. Chung) for the medium entropy alloy and stimulating discussion. The author also sincerely thanks X. Jia for help with the experimentation.

Conflicts of Interest

The author declares no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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