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Particle-Stimulated Nucleation (PSN) in the Co–28Cr–5Mo–0.3C Alloy

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Received: 5 April 2020; Accepted: 19 May 2020; Published: 21 May 2020

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Abstract: The present work is aimed at refining the grain size in the Co–28Cr–5Mo–0.3C (wt%) cast alloy using particle-stimulated nucleation (PSN) of recrystallization. It is pointed out that PSN resulted in considerable grain refinement (≈80%) of the as-cast structure, leading to an increased yield and tensile strength (around 30%). Partial solutionizing is associated with the formation of γ_{fcc} and athermal martensite. During PSN, the intensity of the hexagonal close-packed (hcp) phase increases due to the formation of isothermal martensite. It appears that new dynamic recrystallized (DRX) grains are formed around coarse undissolved particles (≈10 μm in size), especially where these particles are present in large clusters. The high-resolution TEM image shows the formation of heavily faulted regions and subgrains, with maximum misorientation near the carbides providing the driving force for the nucleation of new grains.

Keywords: CoCrMoC alloy; particle-stimulated nucleation; grain size; martensite

1. Introduction

Co–Cr–Mo alloys (hereafter referred to as CCM alloys) have been widely used in biomedical applications, such as artificial hip and knee joints, due to their excellent corrosion and wear resistance [1]. CCM alloys are frequently used in the as-cast condition, but they show intrinsic defects such as coarse dendritic microstructures and microsegregation. The presence of hard precipitates, mainly located at interdendritic regions, can also affect strength and ductility in particular [2]. Alternatively, microstructural modification and grain refinement seem to be imperative to improve mechanical properties without deteriorating toughness. In CCM alloys, using severe plastic deformation (SPD) to reduce grain size has reached its limit due to work hardening effects and stress-induced martensitic transformation (face centered cubic (fcc) → hexagonal close-packed (hcp)) [3]. Recently, Yamanaka et al. [4,5] showed that dynamic recrystallization (DRX) in CCM alloys could refine grain size (from 40 to 1.6 μm after hot deformation) and improve mechanical properties. Deformation twinning and inhomogeneities in local strain distribution induced by planar dislocation slips were proposed as the mechanism contributing to grain refinement.

The current work is focused on particle-stimulated nucleation (PSN) as a unique recrystallization mechanism that usually occurs in alloys containing large second-phase particles. The nucleation sites in PSN are well-defined regions, and this gives the capability of controlling grain size and recrystallization texture by adjusting the amount of PSN. The presence of hard $M_{23}C_6$ carbides embedded in the ductile γ_{fcc} matrix in CCM cast alloys makes them ideal candidates for PSN. It should be noted that PSN requires predeformation below a critical temperature or above a critical strain rate in order to take place. Dislocations during deformation can bypass these particles, and the nature of the dislocation structure developed around nondeformable particles is almost independent of particle mechanical properties.

During strain deformation of materials containing coarse nondeformable particles, these particles can induce a high degree of local lattice curvature in their vicinities due to particle-matrix strain incompatibility, and, consequently, more complex dislocation structures are formed. These regions are referred to as deformation zones. During subsequent annealing, such particle-related deformation zones are favorable nucleation sites for primary recrystallization. This mechanism is, hence, referred to as PSN [6].

PSN has been observed and investigated in many alloys, including those of iron, aluminum, nickel, and copper [7–9], but it has not been reported in CCM implant alloys so far. Therefore, this might be the first time that PSN is investigated in CCM alloys. It was found that the undissolved carbides have great implications on deformation and PSN recrystallization. We believe that this finding can be employed for further microstructural control and material processing.

2. Material and Experimental Procedures

A 4-mm thick plate with a chemical composition of Co–26Cr–8Mo–0.3C (wt%) was prepared. The plate was subjected to solutionizing heat treatment in an argon atmosphere at 1230 °C for 60 min, followed by water quenching to attain a partially solutionized specimen. The annealing time was chosen based on our previous work [10], where holding at 1230 °C for 180 min resulted in complete dissolution of primary carbides. The volume fraction of undissolved carbides was estimated to be 2%. The partially solutionized specimen was subjected to cold rolling with a 5% thickness reduction, followed by isothermal aging at 850 ± 5 °C for 15 and 30 min to achieve a partially recrystallized microstructure appropriate to study PSN. Further microstructural examination was conducted on the polished samples using optical microscopy (OM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). Uniaxial tensile tests were carried out on specimens that were 11.5 mm in length and 1.8 mm in diameter. The tests were performed with a strain rate of 10^{-4} s^{-1} at room temperature.

3. Results and Discussion

The microstructures of CCM alloys in the as-cast condition are the combination of dendritic matrixes and secondary phases, mainly identified as $M_{23}C_6$ carbides (M = Cr, Mo, and Co) located at interdendritic regions and grain boundaries. A detailed description of the CCM alloy microstructure used in this work can be found elsewhere [11]. Partial solution treatment at 1230 °C for 60 min resulted in an incomplete dissolution of interdendritic carbides, and subsequent quenching led to the development of a single-phase supersaturated solid solution with undissolved carbide particles, as shown in Figure 1a. Basically, the dissolution of $M_{23}C_6$ carbides in γ_{fcc}-austenite is a diffusion-controlled slow process, which means that after partial solution treatment, some round-like carbide particles still exist and remain embedded in the matrix. Figure 1b shows the morphology and distribution of the undissolved carbide particles at higher magnification, showing particle sizes larger than 1 μm. According to X-ray line scan analysis (see the inset in Figure 1b) and EDS point analysis (see Figure 1c), the carbide particle is enriched with Cr, Mo, and Co. The particles are precipitated both within the grains as well as along the grain boundaries. The measured volume fraction of particles in the alloy was around 2 ± 0.2%. The small particle-to-grain size ratio makes it reasonable to determine the effect of particles on recrystallization.

Typical microstructures after a 5% thickness reduction followed by isothermal aging at 850 °C for 15 and 30 min, respectively, are shown in Figure 2a–d. Figure 2a,b shows many fine grains formed in the microstructure upon isothermal aging at 850 °C for 15 min. Interestingly, unlike normal recrystallization phenomena taking place in other alloys, the nucleation sites are well restricted within the vicinity of carbide particles, and the γ matrix seems to be stable in regions far away from the particles, showing a typical feature in particle-stimulated nucleation (PSN). In addition, Figure 2c,d shows the microstructure after isothermal aging at 850 °C for 30 min at two different magnifications.

It seems that PSN was completed at 30 min and also grain coarsening started to occur at some grains. Isothermal martensite was also developed at the grain boundaries at this stage of aging.

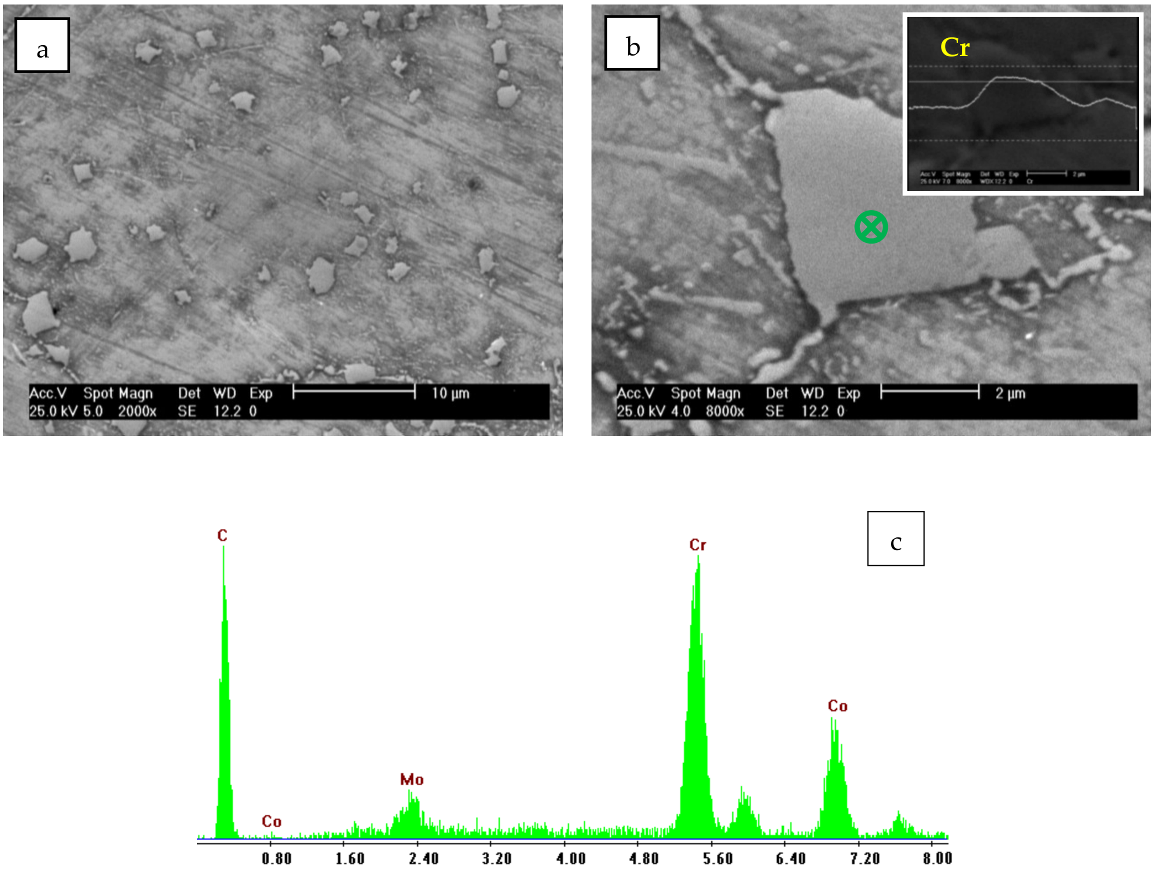

Figure 1. SEM micrographs of (**a**) the partial solution sample and (**b**) undissolved primary carbides. (**c**) EDS point analysis of the precipitated carbide.

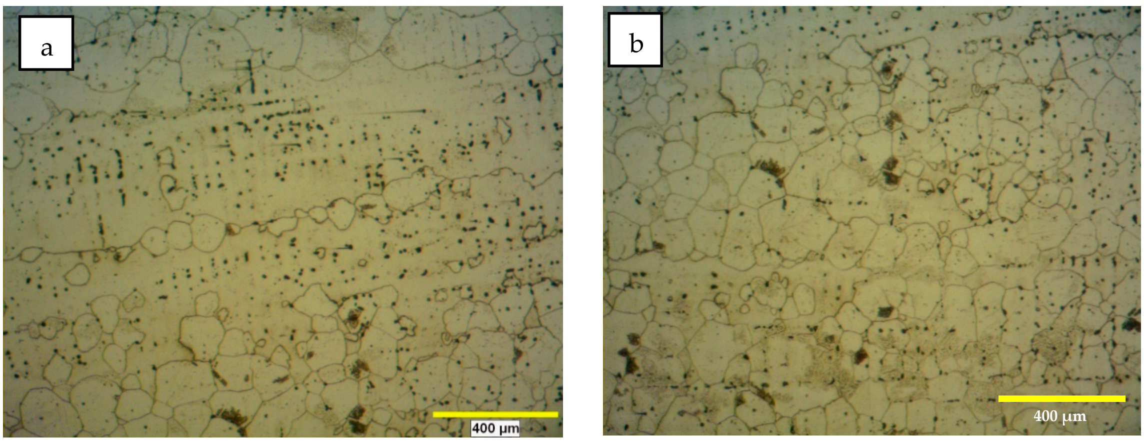

Figure 2. *Cont.*

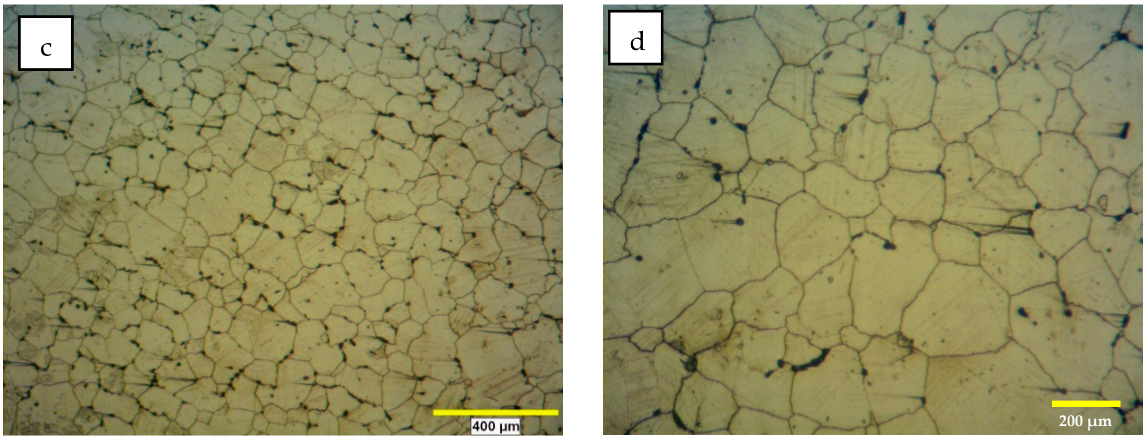

Figure 2. (**a**–**d**) Optical micrographs of the fine recrystallized grains nucleated in the vicinity of carbide particles for 15 and 30 min, respectively.

As shown by the arrow in Figure 3a, DRX did not occur around some isolated particles in the original grains, even for those with sizes as large as 10 µm in diameter. According to the OM and SEM images, it appears that clusters of particles are more favorable sites for PSN than single particles. This can be seen in the SEM micrograph in Figure 3c, showing the occurrence of particle-stimulated nucleation originating from the region located close to the interface (shown by the yellow arrow). Hence, it is suggested that in CCM alloys, the formation of new DRX grains around coarse particles only occurs where these particles are present in large clusters.

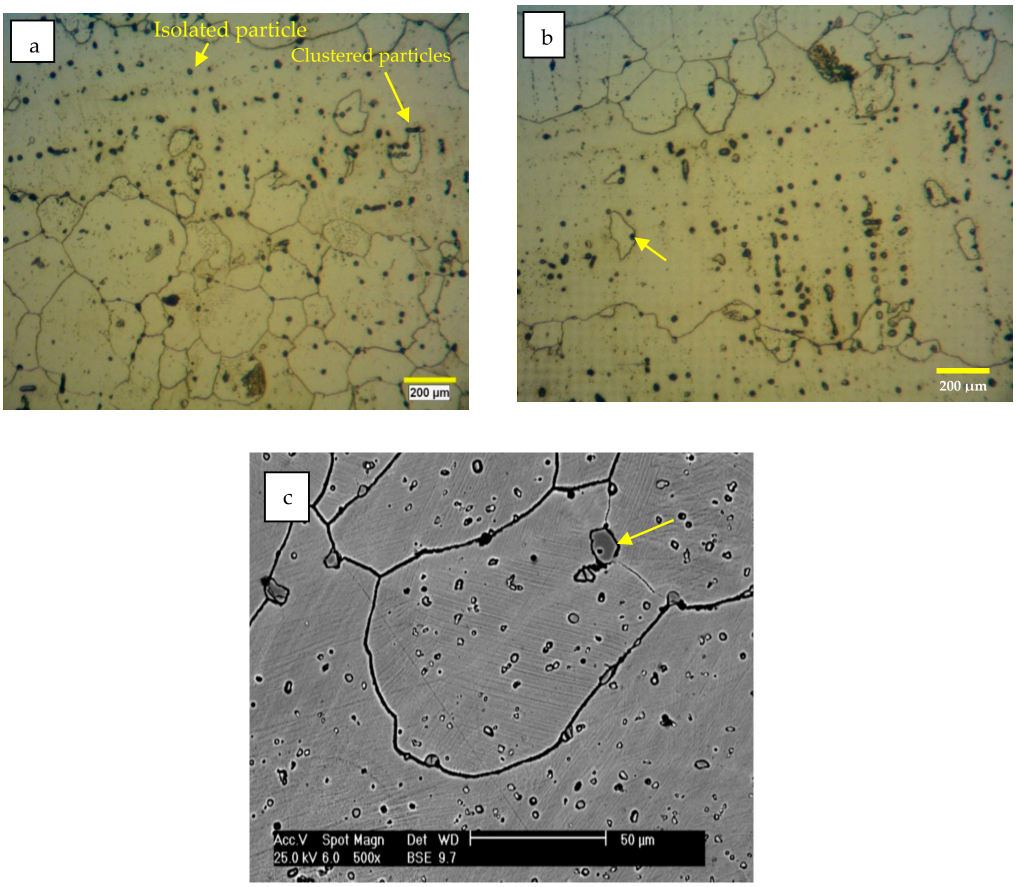

Figure 3. *Cont.*

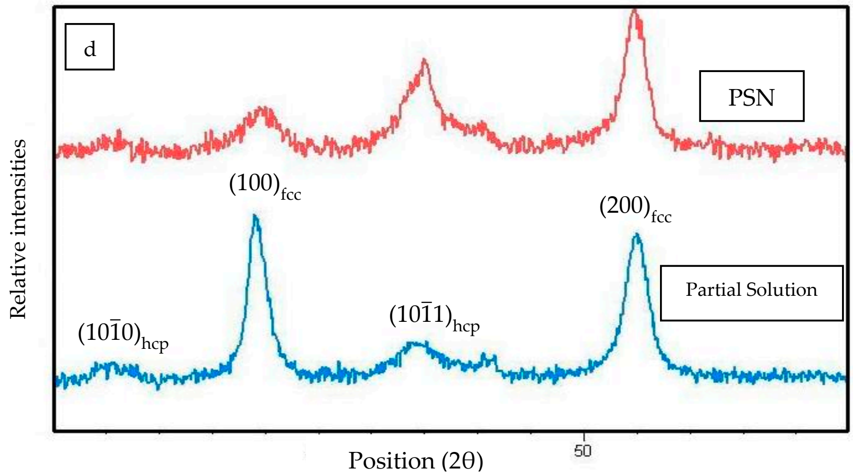

Figure 3. (**a**,**b**) Particle-stimulated nucleation of recrystallization at carbides. (**c**) Recrystallization originates from the deformation zone near the carbides. (**d**) XRD graphs of the partial solution and particle-stimulated nucleation (PSN) specimens.

The small subgrains and the maximum misorientation gradient that forms a high-angle grain boundary at the particle/matrix interface and/or within the deformation zone in the matrix are two key features determining the manifestation of particle-stimulated nucleation [6]. In other words, the onset of nucleation depends on particle size and strain introduced in the matrix.

The heavily faulted region at the interface of the carbide/matrix is observed in the high-resolution TEM image after 5% plastic deformation in Figure 4. The development of stress-induced hcp martensite and generation of dislocations could stimulate the nucleation of new grains at the particle/matrix interface or somewhere in the deformation zone but very close to the particle surface.

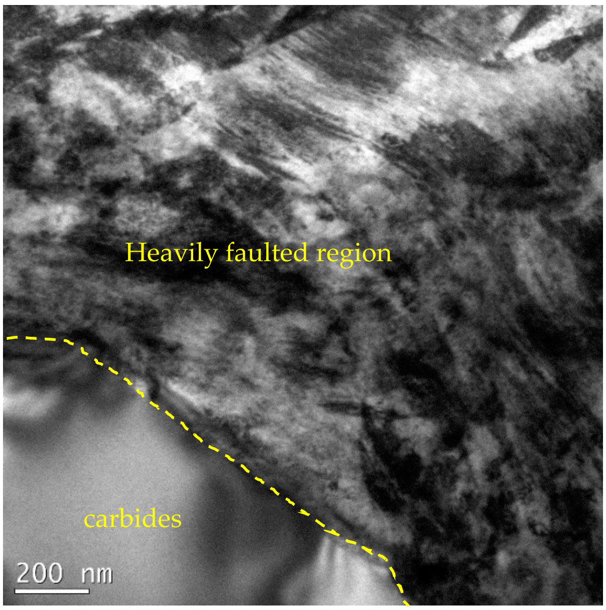

Figure 4. High-resolution TEM image showing the heavily faulted region at the carbide/matrix interface.

It is interesting to note that the resulting grain size in the specimens after PSN is considerably finer than the initial grain size after partial solution treatment. In general, in PSN the nucleation sites are well distinct (unlike most other recrystallization mechanisms); therefore, it is possible to tailor the microstructure and increase the number of potential nuclei via alloying or processing to reduce the final grain size and subsequently enhance the mechanical properties. In the current work, the mean grain size of 83 ± 5 μm is achieved after PSN, as compared to the initial grain size of 500 ± 12 μm. X-ray diffraction peaks of the partial solution and PSN specimens are shown in Figure 3d. As expected, the microstructure of the partially solutionized sample is a combination of γ_{fcc} and athermal martensite. Upon PSN, the intensity of the hcp phase increases, showing the formation of isothermal martensite. In addition to grain refinement, there are indeed some other factors contributing to the strengthening of CCM alloy. Solid-solution elements such as Mo and Cr, and the role of carbon in promoting the precipitation of $M_{23}C_6$ and M_7C_3 carbides (M = Cr, Mo, Nb, Co, etc.), isothermal martensite, and stress-induced martensite are some important strengthening mechanisms in CCM alloys. In addition, partial dissolution of carbides would change the stacking fault energy, and this would affect the difficulty of cross slip and glide of dislocations. For example, Cr and Mo elements are both hcp stabilizers and they tend to decrease the stacking fault energy, while carbon is an fcc stabilizer element, and it tends to increase the stacking fault energy. The decrease of stacking fault energy would increase the spacing between partial dislocations, making the movement of dislocations more difficult.

Figure 5 shows the engineering stress–strain curves of the specimens after partial solution treatment at 1230 °C for 60 min and particle-stimulated nucleation of recrystallization (PSN) at 850 °C for 30 min. As can be seen in this plot, the PSN sample shows a superior yielding point and tensile strength as compared to the partially solutionized sample, which can mainly be attributed to the role of PSN in grain refinement. In fact, for a given plastic strain, the amount of stress-induced martensite (fcc → hcp) increases as the initial grain size of the fcc phase decreases. The stress-induced martensitic phase transformation (fcc → hcp) plays two roles during plastic deformation. On the one hand, the fcc-to-hcp phase transformation contributes to relieve the rapid build-up of internal stresses caused by the relative inability of the fcc phase to accommodate plastic deformation via the dislocation glide mechanism. On the other hand, the volume change associated with the phase transformation provides the material with an additional strain-producing mechanism that inhibits the formation of internal cracks. Therefore, the smaller austenitic grain size formed after PSN increases the area fraction of stress-induced hcp, giving the microstructure more ability to accommodate plastic deformation and preventing premature failure.

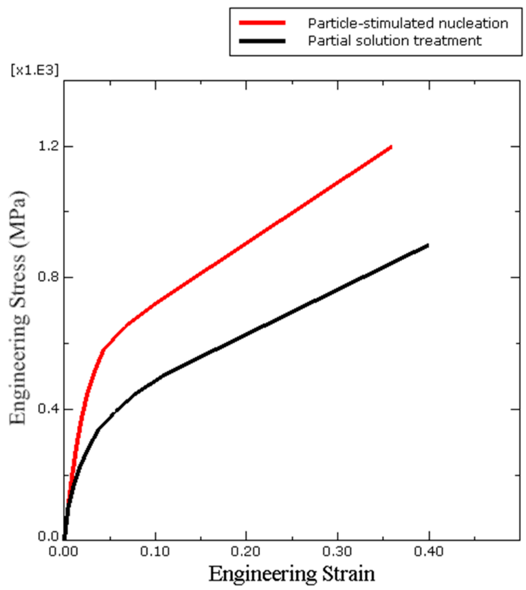

Figure 5. Engineering stress–strain curves of specimens after partial solution treatment (black curve) and particle-stimulated nucleation of recrystallization (red curve) at 850 °C for 30 min.

The results of the present study show that PSN is an effective method that can be employed to refine grain size and enhance mechanical properties, without the need to perform a severe plastic deformation process that would increase the risk of cracking and failure.

4. Conclusions

In this study and for the first time, the effect of particle-stimulated nucleation (PSN) on the grain refinement and tensile properties of a CCM alloy was investigated. It was pointed out that the volume fraction of ≈2% round-shape carbides provided nucleation sites for the new grains and contributed to considerable grain refinement (up to 80% reduction in grain size), leading to enhanced tensile properties (up to 30%). The heavily faulted regions at the carbide/matrix interface and small subgrains could effectively act as nucleation sites for PSN.

Author Contributions: Conceptualization, H.R.L. and S.Z.; methodology, H.R.L. and S.Z.; software, H.R.L. and S.Z.; validation, H.R.L. and S.Z.; formal analysis, H.R.L.; investigation, H.R.L. and S.Z.; resources, H.R.L. and S.Z.; data curation, H.R.L. and S.Z.; writing—original draft preparation, H.R.L. and S.Z.; writing—review and editing, H.R.L.; visualization, H.R.L. and S.Z.; supervision, H.R.L. and S.Z.; project administration, H.R.L. and S.Z.; funding acquisition, H.R.L. and S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Acknowledgments: The authors would like to thank Charlie Kong (Mark Wainwright Analytical Centre, UNSW, Sydney) for providing the opportunity to use HRTEM.

Conflicts of Interest: The authors declare no conflict of interest.

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