Annealing-induced hardening of laminated structured nickel fabricated by electrodeposition

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Abstract
Annealing of deformed metals is considered as a process which necessarily leads to softening, due to the annihilation of lattice defects. However, in laminated materials, annealing at moderate temperatures may induce hardening. In this study, a laminated structure at two sides of the sample is produced by ultrasonic introduced intermittently for 15 min, during the electrodeposition process. For comparison, a sandwich structure is prepared under ultrasonic without interruption at two sides of the sample. All the samples are annealed for 30 min at 373 K, 473 K and 573 K. The common softening after annealing is observed for the sample without laminated structure in the two sides. However, for the other sample that possesses laminated structure in the same area at the two sides, the strength and ductility increase rather than decrease after annealing. The sample that possesses laminated structure in the same area at the two sides annealed at 373 K shows an evident change, which increases in $\sigma_{0.2}$ from 299 to 353 MPa, in $\sigma_{\text{UTS}}$ from 477 to 533 MPa, and in $\varepsilon_{\text{ue}}$ from 7.6% to 9.5%. According to the XRD results, annealing-induced hardening is not attributable to occurring phase transformation. Detailed microstructural TEM results demonstrate that the annealing-induced hardening is attributed to the surface laminated interfaces and high-density growth twins in interfacial transition zones. In addition, the detwinning occurred during subsequent tensile deformation, also plays a crucial role.

1. Introduction

In general, it is accepted that plastic deformation leads to hardening of metallic materials, while annealing after deformation results in softening. In recent years, heat treatment is used to improve the physical and mechanical characteristics of materials in industrial processes and studies [1]. The material achieves strength-ductility synergy by annealing [2, 3], or cold rolling followed by annealing [4–6]. The strength of metals or alloys is commonly decreased after annealing, except for the precipitation-induced hardening during annealing [7]. The hardening phenomena in nanocrystalline metal after annealing, which is produced by accumulative roll bonding, has been recently studied [3, 8–10]. However, the annealing-induced hardening (AIH) is highly affected by the annealing temperature and time [8, 11, 12]. The segregation of element and formation of second phase are the main causes of this phenomenon [13–16]. It is also caused by reduced dislocation density, grain boundaries relaxation, and grain coarsening [8, 17–19]. It is known that these hardening phenomena are recognized since several years. However, the mechanisms behind them are still a debate subject in several studies. A large part of these studies is summarized as explanations in the sequel.

In pure nanomaterials, the mainly cause of hardening is the reduction of dislocation density within the grain and relaxation of the boundary structure during the heat treatment [20], which results in a strength increase and ductility decrease. However, in a cryo-rolled CoCrFeNi high-entropy alloy, it is a result of the fact that the stress accumulated in cryo-rolled is not enough to activate the reaction between dislocations and stacking faults, and additional thermal activation (by annealing) is required to provide the energy requirements for twinning [17].
However, for the cold rolled CrMnFeCoNi alloy, hardening phenomenon caused by the formation of long-range ordered structures [7]. In Cu/Fe multilayer composite, the AIH mechanisms mainly closely linked to the evolution of defects and interaction of interface-dislocation in multilayers with different layer thickness [18]. For pure laminated metals, the AIH mechanisms are not completely understood. Therefore, the experiments mainly focus on the analysis of the annealing hardening mechanism and its role during tensile deformation.

In this study, a powerful evidence for AIH of laminated Ni is presented. In addition, this study explains the underlying hardening mechanisms responsible for such behavior through an in-depth postmortem and microstructural analysis. The microstructural characterizations demonstrate that AIH mechanisms in laminated structured nickel fabricated by electrodeposition, are not only simply caused by detwinning, but also closely related to high density growth twins in interfacial transition zones and introduced interfaces.

This paper aims at exploring the possibility for improving the mechanical properties of bulk FCC materials by annealing, in order to improve the understanding of the changes in properties and structure when metal is annealed, and therefore inspire the development of new optimization processes. In addition, the experiments are carried out by intermittent introduction of ultrasonic waves during electrodeposition, and the cavitation effect of ultrasonic waves is used to refine the grains so that two different grain sizes can be deposited without interfacial combination problems. This also provides a method for the manufacturing of new laminated materials.

2. Materials and methods

A commercial purity nickel(Ni,99.96 wt%) with plane dimensions of 150 mm × 90 mm and a thickness of approximately 10 mm, is used as the anode. The plating bath is a novel amino sulfonate electrolyte composed of Ni(NH2SO3)2·4H2O (300–400) g l−1, NiCl6H2O (10–15) g l−1 H3BO3 (30–40) g l−1 and CH3(CH2)11OSO3Na (0–0.01) g l−1. The PH is maintained at 3.5 to 4.0, and the temperature is maintained at 323 ± 2 K. A pure copper sheet with dimensions of 90 mm × 90 mm × 300 μm is used as the cathode. The initial current density is between 5 and 10 mA cm−2. Laminated structure at two sides of the sample I is produced by ultrasonic introduced intermittently for 15 min, which is repeated for 12 h at two sides of sample I, during the electrodeposition process (cf. figure 1(a)), and then the ultrasonic is discontinued without turning off the power. For comparison, a sandwich structure is prepared under ultrasonic without interruption for 12 h, at two sides of sample II, as shown in figure 1(b). Furthermore, the core of both samples I and II is prepared by direct current electrodeposition for 132 h under the same conditions. Therefore, the grain size of the core is similar, and the thickness of the surface layers is comparable. The dog-bone shaped tensile samples with a gauge length of 13 mm and a width of 3 mm, are machined from the as-deposited Ni plates using the wire electrical discharge machining, and then annealed for 30 min at 373 K, 473 K and 573 K. Note that the dimensions of the tensile specimens are coherent with the GB-T228–2002 national standard. Before the tensile tests, all the tensile samples are mechanically polished in order to minimize the surface roughness. Uniaxial quasi-static tensile tests are performed in a tensile testing machine (SHIMADZU universal Tester) at a strain rate of 1 × 10−3 s−1 at room temperature (RT). Three parallel samples are used for each mechanical experiment. The cross-sectional morphology of the samples is characterized using the metallurgical. The detailed microstructural characterization of the samples is carried out by transmission electron microscopy (TEM, FEI Talos F200X, 200 kV). TEM specimens are prepared from the laminated nickel, using the ion thinning after grinding and polishing. The orientation and boundary disorientation of the samples, before and after deformation, are observed using a field emission scanning electron microscopy (FE-SEM, NOVA Nano SEM 450) equipped with an electron backscattered diffraction (EBSD). Samples are prepared for EBSD analysis, by mechanically polishing and subsequently electro-polishing. EBSD maps are collected with a step size of 100 nm, and an indexing of over 85% is achieved. The microstructures of the fractures are analyzed by SEM.

3. Results

Figure 1(c) presents the cross-sectional image of the laminated nickel reference sample I. It can be seen that the evident laminated structure characteristic shown by the black line is consistent with the structure model in figure 1(a). The black lines represent the interfaces. The columnar grains along the grain growth direction produced by electrodeposition, are observed from the band contrast map of EBSD data in figure 1(d). The laminated structure with both the refined grain structure and the long columnar grain structure is demonstrated.

Figures 2(a) and (b) show the engineering stress-strain curves of sample I and sample II, under uniaxial tension, respectively. Three replications are performed for each sample. It is deduced that the tensile behavior of each sample is very repeatable. In addition, the two samples with different architectures represent the opposite mechanical behavior after annealing, at different temperatures for 30 min. As the annealing temperature
Figure 1. (a) Model microstructure of sample I; (b) Model microstructure of sample II; (c) Cross-sectional image of sample I in laminated areas; (d) EBSD band contrast map of sample I.

Figure 2. The typical engineering stress-strain curves of (a) sample I and (b) sample II. The strain-hardening rate and true stress curves, function of the true strain of sample I ($a_1$) and sample II ($b_1$).
increases, both the yield strength (0.2% offset, $\sigma_{0.2}$) and ultimate tensile strength ($\sigma_{\text{UTS}}$) of sample II respectively decrease from 387 to 304 MPa and 621 to 506 MPa, and the uniform elongation ($\varepsilon_{\text{ue}}$) increases from 8.72% to 10.37%. Moreover, as the annealing temperature increases, both the yield strength (0.2% offset, $\sigma_{0.2}$) and ultimate tensile strength ($\sigma_{\text{UTS}}$) of sample I are increased. Compared with the existing methods, sample I annealed at 373 K shows an evident change that there increases are observed in $\sigma_{0.2}$ from 299 to 353 MPa, in $\sigma_{\text{UTS}}$ from 477 to 533 MPa, and in $\varepsilon_{\text{ue}}$ from 7.6% to 9.5%. In general, all the samples I enhance the strength without sacrificing the ductility, compared with the as-deposited Ni. Roy et al [20].

Compared with the conventional multilayer composites [18], the proposed laminated structure is not a layer-to-

Figure 3. EBSD maps of the (a) as-deposited and (b) annealed (at 373 K) sample I, (a) and (b) are inverse pole figure (IPF) maps, (a) and (b) are twins distribution maps, (a) and (b) are geometrically necessary dislocations (GND) distribution maps.

In order to elucidate the AIH mechanism of sample I, the microstructures of the as-deposited and annealed samples at 373 K are assessed using EBSD. Figure 3(a) and 3(b) present an EBSD analysis of the as-deposited and annealed samples at 373 K. It can be seen that the microstructure exhibits columnar grains with some fined grains. It is important to mention that, due to discontinuities in the columnar grains, the sharp transitions between colors indicate different texture transitions. It can be clearly observed from figure 3(a) that the green color exhibits a strong texture in [101] directions, and the red color exhibits a strong texture in [001] directions. Compared with the conventional multilayer composites [18], the proposed laminated structure is not a layer-to-
layer structure since there is an obvious interface of layers. There are few columnar grains that are continuously growing through the fined grain layer, and fined grains do not appear in a continuous layer, but gather randomly in some parts. The same phenomenon can also be seen from figure (b1). In the twin distribution maps in figures (a2) and (b2), the red lines represent the sigma 3 grain boundaries. Compared with the as-deposited sample, the twin density increases with a higher extent in the annealed samples (cf figure (b2)). It can also be seen from figure (a3) that some geometrically necessary dislocations (GNDs) exist in some fined grains, while few GNDs exist in large columnar grains. As a comparison, when the sample is annealed at 373 K, a large number of GNDs increases (cf figure (b3)). Similarly, an analogous phenomenon in which the dislocation density increases after annealing, is also observed [21].

It can be seen from Figure 4(a1) that the columnar grains undergo a significant deformation, especially in the right area near the surface where the deformation of the columnar grains are very serious. In addition, many sub crystalline structures appear in figures (a1) and (b1). In general, the dislocation density and twin density of the material increase after tensile deformation. Compared with the samples in figures (b2) and (b2), after plastic deformation, the twin density is highly decreased and only few twins exist in some ultra-fined areas. It is clear that the detwinning occurs during the deformation process. However, compared with the GND density in figures (a3) and (b3) before deformation, the GND density of the as-deposited sample and the annealed samples are highly increased in figures (b3) and (b3). In particular, due to the larger deformation, more GNDs are shown in the annealed sample in figure 4(b3).

Figure 4. EBSD maps of the (a) as-deposited and (b) annealed (at 373 K) sample I after tensile tests, (a1) and (b1) are inverse pole figure (IPF) maps, (a2) and (b2) are twins distribution maps, (a3) and (b3) are geometrically necessary dislocations (GND) distribution maps.
In order to highlight the AIH mechanism, a microstructural analysis is performed at different locations of the samples. It can be seen from figures 5 and 6 that three characteristic locations are selected to illustrate the microstructure segmentation of the samples. As shown in figure 5(a), these three locations in the sample are: near the surface (denoted by A), interface between two different layers (denoted by B), and the core of the sample (denoted by C). Figures 5(a)–(c) presents typical bright field TEM micrographs of sample I at the different locations. It can be observed from figures 5(a) and (a1) that the grains are equiaxed, with an average transversal grain size of 100 nm. Furthermore, the columnar grains with an average grain size of 3 μm can be seen in figures 5(c) and (c1), and high-density growth twins appear in interfacial transition zones with an average grain size of 1.1 μm (cf figures 5(b) and (b1)). Finally, no growth twins are observed in the center and surface of the sample.

It can be seen from figure 6 that the same three typical regions are chosen to compare with sample I. The location near the surface is denoted by A, the ultrasonic layer is denoted B, and the core of the sample is denoted by C, as shown in figure 6(a). The columnar grains are observed in the three regions A, B and C in figures 5(a)–(c). However, few growth twins are observed in figures 6, (b) and (c).

In order to reveal the fracture mechanism and its effect on the strength and ductility, a fractographic analysis is performed by SEM. It can be seen that severe necking after deformation is observed in sample I (cf figures 7(a) and (e)). In addition, the fractures-river patterns and dimples are presented in figures 7(b) and (f). The dimples are quite shallow with an average size of 3 μm. Compared with the dimples in the as-deposited sample in figure 7(d), the dimples on the fracture surface of the annealed sample at 373 K in figure 7(g) are much more homogeneous and regularization. However, the river patterns are observed in the laminated areas, and they are more obvious for annealing at 373 K in figure 7(h). Furthermore, it can be deduced that the fracture modes change between ductile and brittle during tensile deformation. Previous studies have demonstrated that the ductile to brittle transition behavior can be interpreted based on a competition between the effective yield stress and brittle fracture stress [21–25].
As the tensile fracture surface becomes smooth with the increase of the annealing temperature in sample II, as shown in figures 8(a)–(d). The holes and dimples that reflect the typical ductile fracture, are observed in figure 8(e) and The tensile fracture surface becomes smooth with the increase of the annealing temperature in sample II, as shown in figures 8(a)–(d). The holes and dimples that reflect the typical ductile fracture, are observed in figures 8(e) and (f).

4. Discussion

The similar AIH in pure Ni is previously observed. Wang et al [24] had studied the effect of annealing on the tensile behaviors of electrodeposited Ni and firstly found that the yield stress increased without obvious
reduction in ductility at the annealing temperatures below 423 K. However, they didn’t give the specific reason for this hardening phenomenon. Moreover, there is a transition from ductile to brittle behavior caused by S segregation to grain boundaries when the annealing temperatures higher than 523 K. However, this transition didn’t appear in our studies. We also investigated the impurity segregation and didn’t find S segregation by TEM, as displayed in figure 9(a). Zhang et al [10] deduce that, after the deformation and subsequent annealing treatment at 423 K, the hardness of electrodeposited Ni is increased, which is mainly attributed to a recovery transformation from $\alpha$ to $\gamma$ phase. The XRD results show that no phase transformation occurs in the samples in figure 9(b).

During tensile deformation of heterostructure materials, the mechanical incompatibility in the elastic-plastic deformation stage creates a strain gradient near the interfaces. This strain gradient should be accommodated by geometrical dislocations, which results in a synergetic strengthening [24]. Zhu et al [25] describe the back stress as hetero-deformation induced (HDI) stress. They believed that it is responsible for the strengthening and extra strain hardening. However, no strain hardening up-turn is observed in figure 2(a1), which indicates that the contribution of HDI stress may not be significant. The same results are also obtained in [26]. Therefore, compared with sample II, the interface and interfacial transition zones of sample I play an important role in stress transmission. After a low temperature annealing, dislocation emission and activation at

Figure 8. SEM micrographs of fracture for sample II: (a) as-deposited, (b) annealed at 373 K, (c) annealed at 473 K, (d) annealed at 573 K, (e) and (f) are local magnification graphs of (b).

Figure 9. (a) The typical cross-sectional TEM element line scanning map after annealing at 573 K. (b) The XRD patterns of sample I.
the interface are limited by the interface and high-density twin boundaries in the interfacial transition zones. The detwinning process is also observed in face-centered cubic materials. In addition, different detwinning modes are proposed in previous studies [27–29]. Moreover, other studies also demonstrate that the twinning can lead to the local incompatible strains in the grain boundary area, and the occurrence of detwinning is required for the twinned grain in order to accommodate the surrounding strain [29]. In this study, the high-density twins of sample I are formed in the interfacial transition area, and disappear in the subsequent deformation, which indicates that the detwinning process may be responsible for the intragranular rotation or dislocations pile-up in the interior grain. During the plastic deformation, the twin boundaries can hinder the initial dislocations slip, making the dislocations constantly change the slip direction, which increases the difficulty of dislocation motion. When a dislocation crosses a twin boundary, a twinning dislocation is released, which results in the growth or decay of the twin. Furthermore, the twin boundaries are easily transformed to low angle grain boundaries or moved to grain boundaries with the final annihilation, which leads to a strength and ductility increase.

5. Conclusions

In this paper, two types of samples are prepared by electrodeposition and a subsequent annealing procedure is proposed. Critical microstructures and defects in the samples, and their effects on the mechanical properties, are systematically investigated. This study provides a novel strategy for synthesizing laminated structure materials, as well as an additional insight into the excellent ductility in laminated structure materials. Based on the detailed experimental work and calculations, the following conclusions can be obtained.

1) Sample I with laminated structure contains a fined grain layer, columnar grain layer and interfacial transition zones with high-density growth twins, showing significant annealing hardening phenomenon. Sample II with columnar grains shows a typical annealing softening phenomenon.
2) The abnormal annealing hardening phenomenon of sample I is attributed to the surface laminated interfaces and high-density growth twins in interfacial transition zones. In addition, the detwinning occurred during subsequent tensile deformation also plays an important role in combining the strength and ductility.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

CrediT authorship contribution statement

Jian Zhang: Writing - original draft, Data curation, Software. Yun Lei: Resources, Project administration, Methodology. Ning Wang: Investigation, Methodology, Data curation. Ping Yang: Methodology, Data curation. Xinkun Zhu: Supervision, Visualization. Baipo Shu: Writing-review & editing, Funding acquisition, Data curation.

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