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# Surface nanocrystallization by mechanical punching process for improving microstructure and properties of Cu−30Ni alloy

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**Abstract:** A punching process was employed to produce nanocrystalline on the surface of Cu−30Ni alloy. Compared with the original sample, corresponding changes of the grain size, mechanical properties and corrosion resistance of surface nanocrystalline induced by punching process were characterized by atomic force microscopy, nanoindentation, microhardness, electrochemical behavior and electron work function. It was observed that the grain size was about 40 nm in the topmost surface. The increasing mechanical properties were also demonstrated. Additionally, the dynamic polarization test showed that the surface nanocrystallization improved the resistance to electrochemical attacks. Such increasing corrosion resistance was identified with the higher EWF value. This study demonstrates that surface nanocrystallization can be generated by punching process, and thus mechanical properties and corrosion resistance of alloy can be improved.

**Key words:** Cu−30Ni alloy; mechanical punching; surface nanocrystallization; mechanical properties; corrosion resistance

## 1 Introduction

The nanostructured materials，with many interesting physical and chemical properties and behavior, fundamentally different from their traditional coarse-grained polycrystalline counterparts, exhibit high strength and hardness, excellent frictional behaviors and improved workability and so on [1−4]. Potentially, the nanostructured materials are very useful to develop new materials for engineering applications and industrial manufacturing processes. Therefore, various kinds of synthesis techniques have been developed in recent years for producing bulk nanocrystalline materials, such as the consolidation of ultrafine powders [2], crystallization of amorphous solids [4], ball-milling [5], severe plastic deformation (SPD) [6] and electrodepositing [7]. Among these ways, one of the promising ways to fabricate the bulk ultrafine grained materials is SPD. Many productions of SPD have been developed including equal-channel angular pressing (ECAP) [8], high pressure torsion strain [9] and the bulk ultrafine grain or nanocrystalline materials have been actually realized. However, the production of the ultra-refine or nano-scale grain by SPD has disadvantages of requiring large amount of plastic working energy, using special equipments or facilities.

In many cases, failures of a workpiece may initiate at the surface, such as fatigue fracture, fretting fatigue, wear and corrosion. Therefore, the modification of surface microstructure and properties of engineering materials can thus play an important role in failure control [10]. Compared with bulk nanocrystallization, surface nanocrystallization induced by SPD can be achieved much more easily. Besides its simple and low-cost operation, it combines the superior properties of nano-materials with conventional engineering materials. Therefore, surface nanocrystallization induced by SPD has attracted increasing significant scientific interests during the past few years [10−12]. It was reported that the techniques of surface nanocrystallization induced by SPD have surface mechanical attrition [11,12], ultrasonic shot peening [13,14], high-energy shot peening [15], sliding wear [16], surface rolling [17], wire-brushing [18], and sandblasting [19,20]. However, because of the complexity of interactions among process conditions

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and material properties, there has been no good industrial application in past few years. In addition, the depth of nanocrystalline layer produced by these processes is below 100 μm, which is limited to high load wear and aggressive corrosive environments.

Besides all processes mentioned above, hammer peening, called punching, is also an efficient mechanical surface treatment technique for introduction of nanocrystallization. In combination with punching, sandblasting and recovery treatments, the nanocrystalline of titanium alloy has been successfully produced on aluminum surface [21]. It is well known that the plastic deformation induced by the punching is very severe. And it is also very easy to punch the surface of materials using a hammer. The punching process seems to offer solutions to increase depth of surface nanocrystallization layer. In this study, cupronickel (Cu−30Ni) alloy, which is a single phase, face centered cubic alloy with medium stacking-fault energy, is chosen as the sample material. The objective of this work is to investigate the effect of punching on grain size and mechanical properties and corrosion resistance of the surface layer.

## 2 Experimental

### 2.1 Sample preparation

The commercial cupronickel (Cu−30Ni alloy) tube had the chemical composition (mass fraction): 30.57%Ni, 0.87%Mn, 0.98%Fe, 0.04%C, 0.10%Zn, 0.005%P and Cu balance. The samples cut from Cu−30Ni alloy tube were machined to 30 mm in diameter and 3 mm in thickness. These samples were ground with silicon carbide paper up to 600-grit, and then rinsed with acetone, ethanol and deionized water, finally dried using an air flow. These samples were punched for 30 min with a roto-hammer (Robert Bosch Tool Corporation, USA) at a frequency of 50 Hz in a stainless steel holder. Figure 1 gives a schematic illustration of the punching process. These samples punched for 30 min were annealed at 275, 350 and 425 °C, respectively, in argon atmosphere for 1 h. Subsequently, the samples punched for 60, 90, 120 min, respectively, were also prepared. These samples punched for different times were annealed at 350 °C in argon for 1 h. For the samples to facilitate electrochemical monitoring, an electrical connecting wire was attached to the back face of the sample prior to its encapsulation in insulating cement. The face of 5 mm×5 mm was finally exposed to 3.5% NaCl solution.

### 2.2 Characterization

The morphology and grain size were evaluated with an atomic force microscope (Digital Instruments, CA, USA). Nanoindentation experiments were conducted using a Triboscope (Hysitron, Minneapolis,USA) with the AFM attachment. The forces of 50, 100 and 200 μN were used for the indentation tests, respectively. During the indentation test, the two mechanical properties of hardness, and the ratio of the elastic deformation energy ($W_e$) to the total deformation energy ($W_t$), $\eta$, were determined by the resulting indentation load—depth curves. Microhardness of the samples was measured using a micro-indenter probe (Fisher Technology Ltd., Winsor, CT) with a diamond tip under a load of 50 mN. The hardness was measured at least three times. The dynamic polarization measurement was carried out using a commercial electrochemical system (model Pc4-750, Gamry Instruments Inc., Warminster, PA) by sweeping

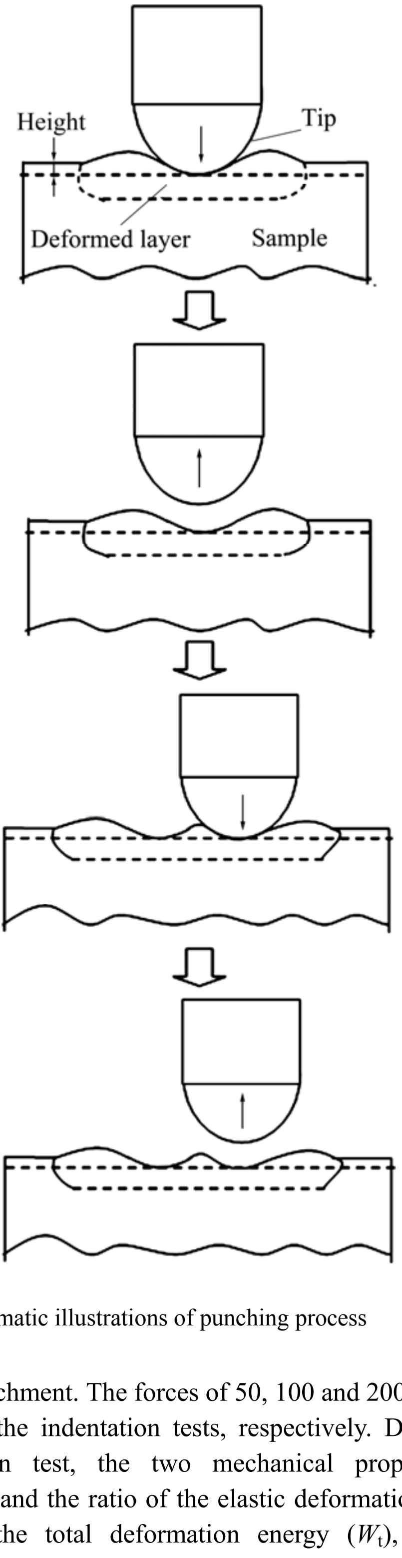

**Fig.1** Schematic illustrations of punching process

the potential at a scanning rate of 3 mV/s from −0.4 to 0.1 V vs open corrosion potential (OCP) in 3.5% NaCl solution. Prior to the electrochemical tests, the sample with electrical connecting wire was stabilized for 50 min in the solution. The exposed face of 5 mm×5 mm was the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate of 20 mm×20 mm was used as the counter electrode. In order to better understand the corrosion behavior, the electron stability of the original and punched samples was evaluated by employing a scanning Kelvin probe (SKP, provided by KP Technology Ltd., Wick, UK) by measuring the electron work function (EWF) in an ambient environment. A gold tip of 1 mm in diameter was used to scan the surface with an area of 2 mm×2 mm covering 10×10 measurement points. The principle of operation and experimental procedure of the SKP system to measure EWF had been described in detail in previous studies [22,23].

## 3 Results and discussion

### 3.1 Grain size

Figure 2 shows the AFM images of the original sample (Fig. 2(a)) and punched samples (Figs. 2(b) and (c)). It is found that there is a remarkable difference of grain size between the original sample and the punched sample. Compared with the grain size of original sample (about 250 nm), the grain size of sample punched for 30 min is approximately 60 nm, as shown in Figs. 2(a) and (b). This is in agreement with the previous results of surface nanocrystallization induced by single sandblasting process [20], and combination sandblasting by punching process [21]. The grain size of sample punched for 120 min is indicated in Fig. 2(c). It is obvious that the grain size decreases to average value of 40 nm by increasing the punching time. Therefore, from the grain size, the punching process is nearly identical to other surface nanocrystallization process, such as shot peening, surface mechanical attrition and sandblasting, all of which can effectively generate a nano-crystallized surface while maintaining a coarse-grained matrix. Cu−30Ni alloy has similar crystal structure to pure Cu metal. The exact stacking fault energy of Cu−30Ni alloy has not been determined but it is known that it is in the medium range [24]. Therefore, the grain refinement mechanism of Cu−30Ni alloy induced by punching process may be similar to that of pure Cu induced by surface mechanical attrition process, which is supported by the formation of deformation twinning and sub-boundaries with small misorientations over the dislocation activity under the high strain rates experienced in the surface SPD process [24].

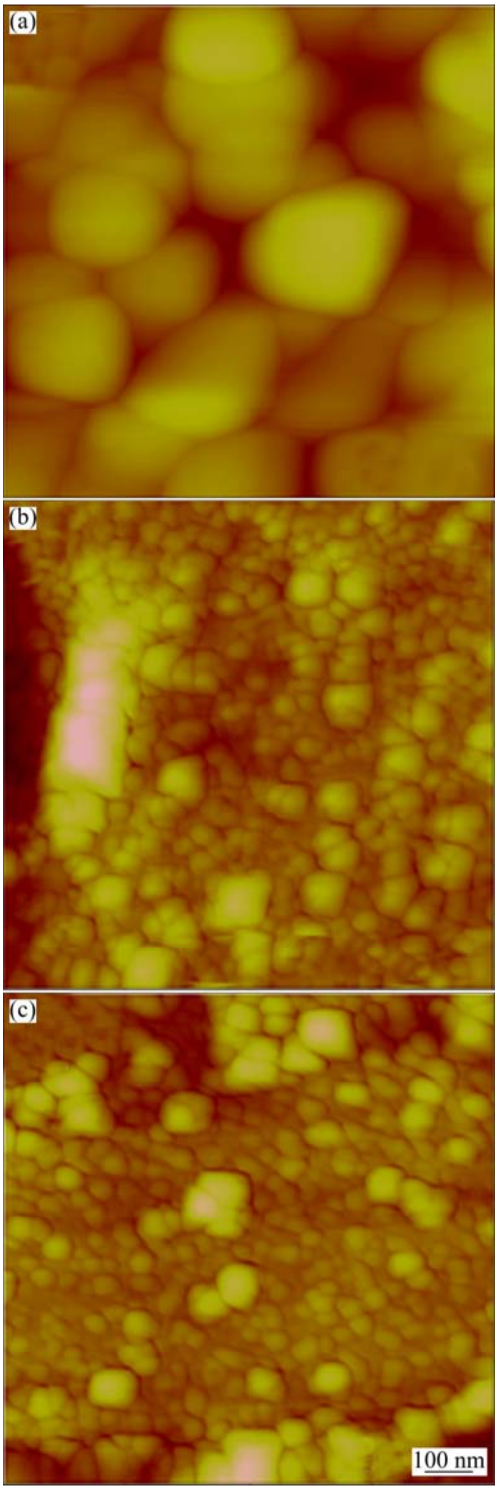

**Fig. 2** AFM images of original sample (a), sample punched for 30 min (b) and punched for 120 min (c)

### 3.2 Mechanical properties of surface nano-crystalline

Figure 3 illustrates the load—depth curves of the original sample and punched samples measured under loads of 50, 100 and 200 μN, respectively. In general, under a fixed load, the smaller the indentation depth is, the harder the sample is. It can be seen from Fig. 3 that the original sample and punched sample exhibit significantly different depth under equivalent loads. At 50 μN, the depth for the original sample is about 9 nm while for the punched sample the depth is about 5 nm. At 100 μN, the depths are about 16 nm and 9 nm, respectively. Under load of 200 μN, the depths are about 28 nm and 15 nm, respectively. Surface nano-crystallization induced by punching process obviously enhances the resistance to penetration, which results in the increasing hardness of surface.

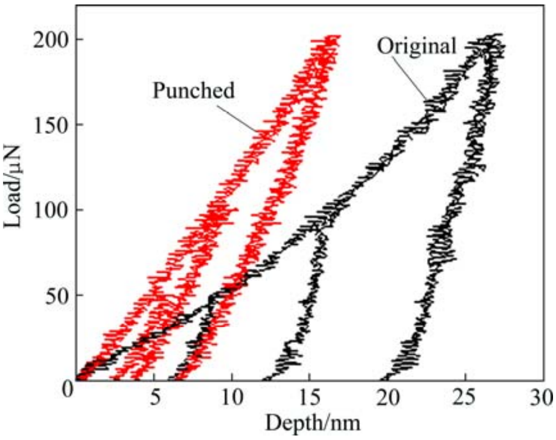

**Fig. 3** Load—depth curves of original sample and punched sample under various loads

In addition to the depth representing the hardness, the ratio ($\eta$) of the elastic deformation energy to the total deformation energy is also significant information obtained from the load—depth curves. From Fig. 3, it is obvious that the unloading curves for the original sample are almost vertical, which means that the elastic deformation is very small under load. However, the punched sample shows the smaller slope of unloading curve, and thus has a larger $\eta$ value. For instance, under a load of 200 μN, the $\eta$ values of the original sample and punched sample are approximately 15% and 60%, respectively. $\eta$ of the punched sample is four times as large as that of the original sample. The larger $\eta$ benefits the surface nanocrystallization, which provides a greater capability to reduce the damage by impact during indention test.

However, it is noted that $\eta$ values of the original sample and punched sample change with respect to the different load, as illustrated in Fig. 4. An interesting difference may be observed that for the punched sample the $\eta$ value decreases with the increasing load, while the $\eta$ value of the original sample has no change. But the former is always higher than the latter. The decreasing $\eta$ value may be due to the gradient surface with nano-crystallized layer, which was achieved by punching process with average grain sizes varying from about 40 nm in the topmost surface to more than 250 nm in the subsurface.

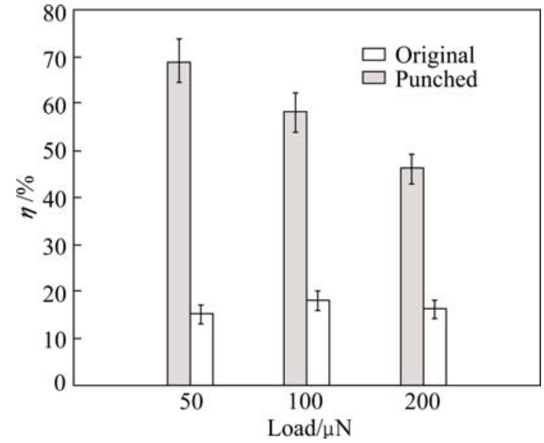

**Fig. 4** $\eta$ values of original sample and punched sample under various loads

The thickness of the deformed layer induced by punching process is determined by the cross-sectional hardness from topmost surface to matrix. The cross-sectional hardness of the punched sample was measured from topmost surface to unaffected zone using a micromechanical probe under a maximum load of 50 mN. Figure 5 shows that the variation in hardness of the samples punched for different times with the increase of depth from the topmost surface. It can be seen that for the samples punched for 30 min, the hardness reaches HV 360 at the topmost surface layer, decreases to HV 90 with the increase of depth to 70 μm, and then becomes stable with respect to the distance. The maximum hardness in the topmost surface of the sample punched for 30 min is about four times higher than that in the matrix. The deformed layer induced by punching for 30 min is estimated to have a depth of 70 μm in which the microstructure evolves gradually from a nano-scale to a micro-scale. As the punching time increases from 30 min to 120 min, the hardness in the topmost surface and the thickness of the deformed layer gradually increase, whereas the increasing interval gradually decreases. For instance, the hardness values of the sample punched for 30 min and 60 min are HV 360 and HV 450, respectively, and their thicknesses of deformed layer are 70 μm and 130 μm, respectively. For the samples punched for 90 min and 120 min, the hardness values are HV 490 and HV 510, respectively, and their thicknesses of deformed layer are 160 μm and 180 μm, respectively. During the punching process, with the increase of punching time the strain increases, which results in the increasing hardness and thickness of deformed layer. However, it is very difficult to further refine the nano-scale grain to smaller ones by only increasing punching time. In the conventional machining process produced surface nanocrystallization, including shot peening [13−15], sliding wear [16] and sandblasting [19,20], the thickness of the deformed layer is normally about 100 μm. Apparently, the thickness of the deformed layer is smaller than that in the present Cu−30Ni alloy sample induced by punching process (about 180 μm). In the punching process, a large compressive strain on the surface can be generated, and thus the primary deformation can spread over a much broader area and a greater depth.

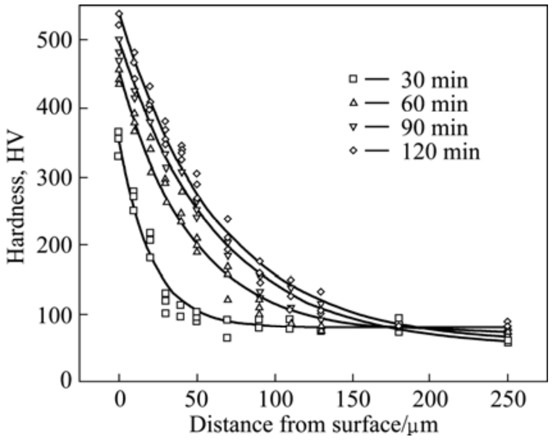

**Fig. 5** Hardness measured as function of depth from topmost surface for samples punched for 30, 60, 90, 120 min, respectively

The increases in hardness and thickness of the deformed layer benefit from the gradient nano-micro-structured surface layer induced by punching process. Generally, the increase of hardness comes from two factors. One is the actual increase by grain size reduction, and the other is the introduction of compressive residual stress into the material. During the punching process, the hammer provides repeated impacts on its surface and consequently high-density dislocation or dislocation network generates in the surface layer. And then the punched sample is subjected to an recovery treatment at 350 °C for 1 h. In this recovery case, the dislocations are rearranged and driven to subgrain boundaries, the strain is annihilated and the new fine nanocrystalline is formed. When these nanocrystallines exist on the surface layer, the movement of these dislocations is arrested by these nanocrystallines, so that these arrested dislocations are piled to cause the material to harden [25]. As a result, the increasing hardness is achieved due to the formation of nanocrystallines. In the meantime, the increasing $\eta$ value can also be obtained due to the increase of the yield strength resulting from the formation of nanocrystalline.

### 3.3 Corrosion resistance of surface nano-crystalline

The potentiodynamic polarization curves of the original sample and the punched samples annealed at 275, 350, 425 °C for 1 h in 3.5% NaCl solution are plotted in Fig. 6. It can be clear that the passive current density of the punched sample has an apparent low shift, and the corrosion potential increases to more positive value compared with that of the original sample. From Fig. 6, it is also demonstrated that the sample annealed at 350 °C obviously has the decreasing passive current density, and also has the tendency of shifting the corrosion potential to higher value. It has been well demonstrated that the material with a high density of grain boundaries corrodes more easily than that with few of grain boundaries. However, the situation is reversed when the material is passive [26]. From Fig. 6, it is found that Cu−30Ni alloy can be passivated in NaCl solution. Therefore, the increasing corrosion resistance benefits from the surface nanocrystallization.

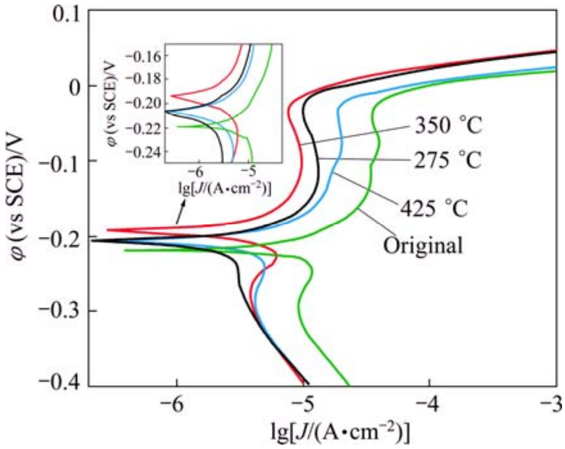

**Fig. 6** Potentiodynamic polarization curves (insert illustrating corrosion potentials for original sample and punched samples annealed at 275, 350 and 425 °C for 1 h)

During the corrosion, material loss occurs through electrochemical reaction on the surface. From the viewpoint of thermodynamics, the exchange of electrons between a metal and environment constitutes an electric current on the metal surface. It is, therefore, essential to investigate the electronic behavior to understand corrosion resistance of surface nanocrystalline. Recent studies [27,28] have demonstrated that the Kelvin probe is a promising tool for the investigation of relation between corrosion behavior and electronic behavior due to its high sensitivity of change in the electron work function (EWF) and high spatial resolution (down to a few tens of nm). EWF value is thus related to the chemical stability of a surface.

Figure 7 illustrates typical EWF value distributions of the original sample and punched samples annealed at 275, 350 and 425 °C, respectively for 1 h. The punched sample annealed at 350 °C has the highest EWF value and that of the original sample is the lowest. Clearly, the surface with nanocrystalline has a higher EWF value, which also has the more resistant to corrosion, namely, the higher the EWF value is, the better the corrosion resistance is. Such relationship can be explained that higher EWF value reflects lower activity or reactivity of electron that makes the material more difficult to be attacked. In this study, the punched sample suffered recovery can release the majority of strain and dislocation. The effects of strain and dislocation on the EWF are thus diminished in a certain degree. Therefore, the EWF value and corresponding corrosion resistance are determined by the grain size. It is well know that the formation of passive film is controlled by local atomic migration or diffusion, and higher density of grain boundaries may considerably enhance atomic diffusion owing to faster mass transport along grain boundaries [29]. Therefore, such a positive effect of surface nanocrystallization on corrosion behavior should be attributed to the formation of protective passive film that can be enhanced by nanocrystallization induced by punching process.

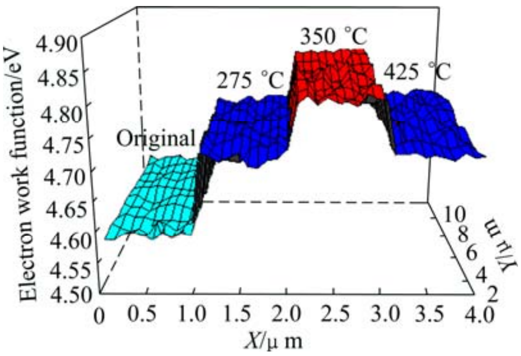

**Fig. 7** EWF of original sample and punched samples annealed at 275, 350 and 425 °C, respectively, for 1 h

## 4 Conclusions

A simple technique of surface severe plastic deformation treatment, punching with a hamper, is developed to achieve a surface nanocrystallization layer on Cu−30Ni alloy sample. This investigation suggests that punching process is a new surface nanocrystallization technique to improve the mechanical properties and corrosion resistance. Through punching process, the nanocrystalline (about 40 nm) can be generated in the topmost surface layer. The thickness of deformed layer (from unaffected zone to topmost surface) is about 180 μm in terms of the punching time. The mechanical properties are considerably improved by the surface nanocrystallization. The hardness of deformed layer apparently has a gradient increasing change from HV 90 in the matrix to HV 510 in the topmost surface. The $\eta$ value of punched sample is four times higher than that of original sample. In relation to the corrosion resistance, surface nanocrystallization may produce a decreasing passive current density and a more positive corrosion potential. A close correlation between the EWF value and the corrosion resistance is observed that higher EWF value corresponds to increasing corrosion resistance.

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# Cu−30Ni 合金机械冲击表面纳米化组织和性能

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**摘 要**：采用大应力塑性变形(机械冲击)技术对 Cu−30Ni 合金表面进行纳米化处理。利用原子力显微镜技术、纳米压痕试样、显微硬度测量、电化学分析和电子功函数等手段分别测试原始样品、大应力塑性变形纳米化处理样品的晶粒尺寸、力学性能、腐蚀性能。结果表明，与原始样品相比，大应力塑性变形纳米化处理样品的表面晶粒尺寸达到 40 nm；力学性能显著改善。电化学测试表明，表面纳米化提高了合金的耐腐蚀性能，耐腐蚀性能变化与电子功函数变化一致。机械冲击工艺技术能够使 Cu−30Ni 合金表面纳米化，从而提高了表面力学性能和耐腐蚀性能。

**关键词**：Cu−30Ni 合金；机械冲击；表面纳米化；力学性能；耐腐蚀性能

**(Edited by Hua YANG)**