The Effect of Simple Shear Extrusion on the Corrosion Behavior of Copper

Morshed Behbahani, Khashayar; Najafisayar, Pooria; Abbasi, Zahra; Pakshir, Mahmoud*+; Ebrahimi, Ramin

Department of Materials Science and Engineering, Shiraz University, P.O. Box 7134851154 Shiraz, I.R. IRAN

ABSTRACT: *In this study, corrosion behavior of copper that was deformed by Simple Shear Extrusion (SSE) method was investigated in 3%wt NaCl solution. Modified Williamson-Hall method, applied on the X-ray diffraction patterns of the samples, showed that increase in the number of SSE passes led to increasing in the dislocation density in the copper samples. Moreover, such deformed samples exhibited fewer corrosion currents, in the potentiodynamic polarization test results, than that of annealed one. In addition, Electrochemical Impedance Spectroscopy (EIS) test was employed to assess the SSEed copper corrosion performance and the results revealed that the SSE technique has a beneficial effect on the corrosion behavior of copper in 3 wt% NaCl aquatic solution.*

KEYWORDS: *Simple shear extrusion; Corrosion behavior; Impedance spectroscopy; Potentiodynamic polarization; Modified Williamson-Hall method; Copper*.

INTRODUCTION

In the recent years, research activities in the field of Severe Plastic Deformation (SPD) technique have increased due to some interesting mechanical properties (such as high strength values in conjunction with reasonable amount of ductility) that may be found in metallic materials manufactured by this technique [1]. Simple Shear Extrusion (SSE) is one of the modern techniques utilizing SPD to improve mechanical strength of materials by increasing dislocation density and considerable grain size reduction down to sub-micron/nano scale [2, 3]. The corrosion behavior of severe plastically deformed metallic materials is the subject of many research studies since it may have significant effect on the performance of such materials under corrosive service conditions no matter how much they can sustain mechanical forces [4, 5]. Copper and its alloys have various industrial applications based on their accessibility and reasonable costs. The corrosion behavior of copper has been the subject of many studies in which the influence of various factors, such as mechanical processing techniques, heat treatments, material purity and also the type of corrosive environment, on its corrosion performance has been cited [6-9].

The anodic polarization behavior of ARBed copper in 3.5 % NaCl solution has been reported by the pioneering work of *Danaee et al.* [4]. They have shown that the anodic current of ARB-fabricated copper, up to 2 cycles, is higher than that of annealed one, in other words, the SPD process had an adverse effect of the corrosion performance of copper in such corrosive environment. In fact, the type of corrosive environment and also processing parameters may have a great effect

** To whom correspondence should be addressed.*
+ E-mail: pakshir@shirazu.ac.ir
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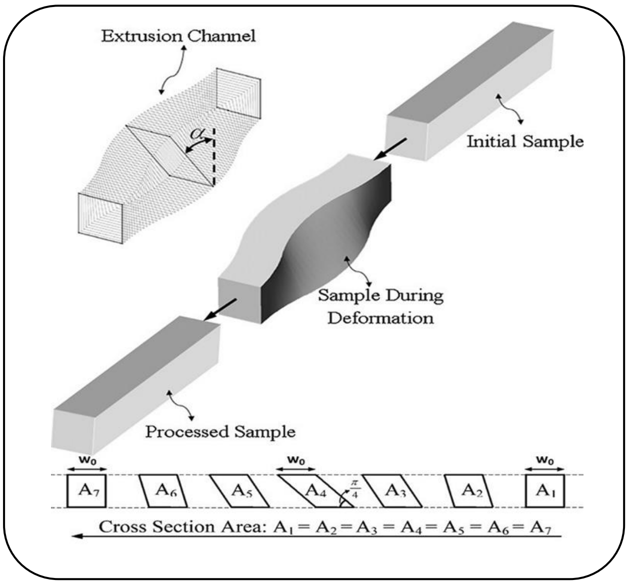

Fig.1. Schematic presentation of Simple Shear Extrusion process and the geometry of extrusion channel in the die [2].

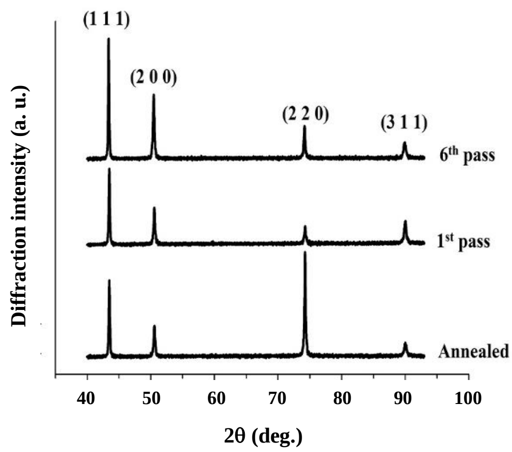

Fig. 2: XRD patterns of annealed and SSEed samples.

on the corrosion behavior of materials [10, 11] and such factors for SPDed copper have not been investigated appropriately through the literature. In this regard, the aim of the present work is to investigate the effect of SSE process (as a recent forming method to produce ultrafine grain metallic components) on the corrosion behavior of the copper. To do so, the effect of the number of extrusion passes during SSE process on the corrosion behavior of copper in 3 wt% NaCl solution were examined using polarization and EIS techniques. In addition, the effect of number of SEE passes on the resulting dislocation density in the extruded copper samples was investigated by modified Williamson-Hall method applied on the samples X-ray diffraction patterns and the results were related to their corrosion performance.

EXPERIMENTAL SECTION

Commercial pure copper billets (with dimensions of 10mm×10mm×30mm) were employed as the starting materials for SSE process. Before extrusion, the samples were first annealed at 625 ^{o}C for 2 hours and then cooled down to ambient temperature in the furnace. Then, they were mechanically polished with abrasive papers up to 1200 grit size. Finally, the samples were SSEed for different number of passes (one to six passes) at ambient temperature using a die with maximum distortion angle α of $\pi/4$ and 1.1 pass strain (ε) based on Mises criterion (Fig. 1)

A three electrode conventional cell, including a platinum rod as the counter electrode, Ag/AgCl reference electrode and differently treated SSEed samples as the working electrode, was used to investigate the corrosion performance of the samples in 3 wt% NaCl solution at room temperature. Polarization tests were carried out at a scan rate of 1 mV/s starting from -250 to +250mV with respect to Open Circuit Potential (OCP). Impedance spectroscopy measurements were performed at the OCP over a frequency range of 100 kHz – 0.1 Hz with amplitude of 10 mV. All the electrochemical tests (including potentiodynamic polarization and EIS) were conducted using microautolab 3 potentiostat/galvanostat and the results were analyzed using GPES and FRA 4.9 software. The X-ray diffraction patterns were obtained using Cu Kα radiation at a scan rate of 5^{o} min^{-1} in a Bruker D8 advance diffractometer.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The XRD spectra of copper samples at their annealed state, SSEed for one and six passes are presented in Fig. 2. The major diffraction peaks at 44^{o}, 51^{o}, 74^{o} and 90^{o} are related to (111), (200), (220) and (311) planes, respectively. Modified Williamson-Hall method [12] was used to investigate the effect of number of SSE passes on the dislocation density that presents in the samples. In this method, it is assumed that the strain peak broadening is caused by dislocations and may be calculated based on the following equation:

$$\Delta K = 0.9/D + \alpha(KC^{1/2})^2 + O(K^4C^2) \quad (1)$$

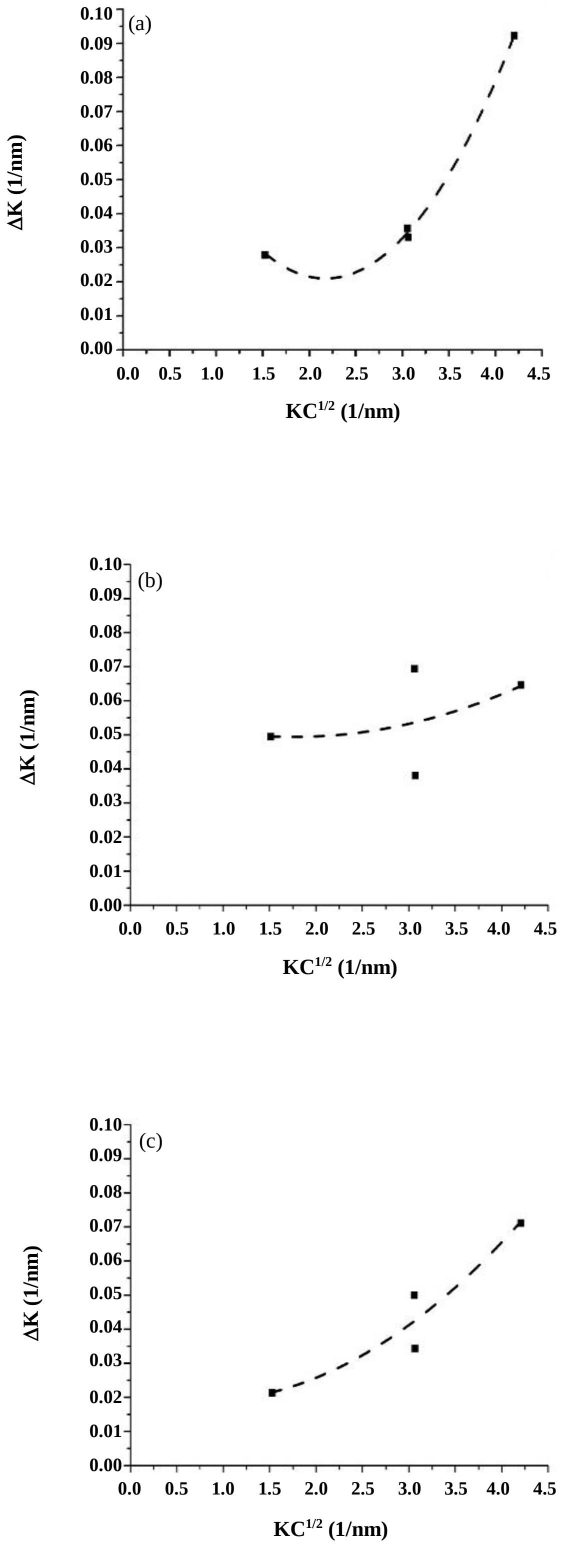

Fig. 3: Modified Williamson-Hall plot (ΔK versus $KC^{1/2}$) of annealed and SSEed specimens.

In which $K=2\sin\theta/\lambda$ and $\Delta K=[\cos\theta(FWHM)]/\lambda$ where θ is the diffraction angle, λ is the wavelength of the X-ray and FWHM is the full width at half maximum of diffraction peak after subtracting instrumental broadening, D is the average crystallite size, α is a constant that is related to dislocations density, C is the average dislocations contrast factor and O stands for higher order terms in K^2C parameter. The average dislocation contrast factor (C) is calculated for each set of (hkl) diffraction peak using the following equation:

$$C=C_{h00}(1-qH^2) \tag{2}$$

where C_{h00} is the average dislocation contrast factor for h00 reflections, q is a parameter depending on the character of dislocations and elastic constants and finally $H^2=(h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2$. The values of C_{h00} and q parameters have been reported as 0.3040 and 2.0100 for copper [13] that were used in calculation of C values for different diffraction peaks. The modified Williamson-Hall plot (ΔK versus $KC^{1/2}$) based on such calculations, using the experimental data shown in Fig. 2, are presented in Fig. 3. As seen, the fitted second order parabolic equation has higher values of α parameter as the number of SSE passes increases. In other words, an increase in the number of SSE passes leads to increase in the dislocation density in the microstructure of deformed samples.

The effect of SSE process on the corrosion behavior

The Nyquist diagrams of various specimens that prepared at different experimental conditions are illustrated in Fig. 4. As seen, the AC responses of all the samples includes a semicircle at high frequency range followed by a Warburg type behavior at low frequency region. The equivalent circuit that was used to fit such experimental data (Fig. 4) is shown in Fig. 5. In this circuit, R_s is the solution resistance, R_{ct} is the charge-transfer resistance, C_{dl} is a double-layer capacitance and W is a Warburg element. The fitting results to the experimental data using such equivalent circuit are presented in Table 1. As seen, as the number of extrusion passes in the SSE process increases, the charge transfer resistance (R_{ct}) of the samples increases too. It has been reported that the rate of anodic dissolution for copper in aqueous NaCl solutions is proportional to the rate of diffusion of stable $CuCl_2^-$ ions or CuCl complexes

Table 1: The fitting results to the experimental EIS data shown in Fig. 4.

Specimen	R_s (ohm)	C_{dl} (μF)	R_{ct} (ohm)	W	chi square
Annealed	4.82	25.21	6.52	2.92E-03	3.65E-02
SSEed of 1st pass	4.89	16.06	6.79	1.90E-03	3.56E-02
SSEed of 2nd pass	5.36	7.65	39.8	4.66E-04	8.07E-01
SSEed of 6th pass	6.59	1.62	44.7	2.72E-04	5.19E-01

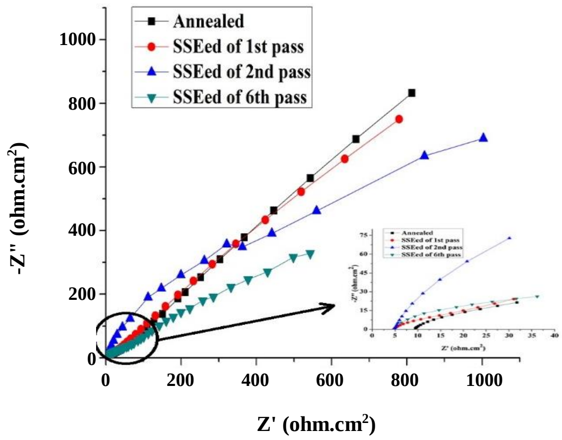

Fig. 4: Nyquist plots of annealed and SSEed samples.

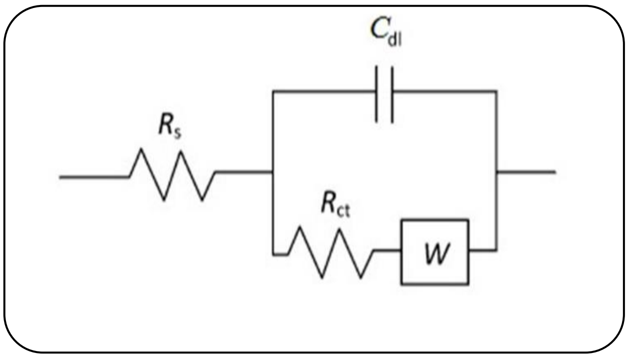

Fig. 5: The equivalent circuit used for fitting the experimental EIS data.

into the solution bulk. If the rate of diffusion is so small that we have a built up of such corrosion products at the electrode surface, so the corrosion rate would be ceased [8]. In this regard, the increase in the charge transfer resistance, as a result of increase in the number of extrusion passes, would be related to the formation of such insoluble corrosion products ($CuCl_2^-$ and CuCl) at the surface. In addition, lower Warburg element values are fitted to the low frequency AC response of the samples that experienced more number of extrusion passes. In other words, the diffusion length of electroactive species (in this case oxygen molecules) through the protective layer is increased as the number of extrusion passes increases (formation of thicker layer of $CuCl_2^-$ ions or CuCl complexes at the electrode surface). Such behavior would be related to the increase in dissolution affinity, as a result of increase in dislocation density, as the number of SSE passes increases. Such high dissolutions would cause built up of insoluble corrosion products at the surface which may retard corrosion reactions to proceed at the surface.

The polarization curves, contributed to the samples prepared at different experimental conditions, are shown in Fig. 6 and the related data are presented in Fig. 7. As seen, the corrosion current density decreases and corrosion potential becomes more positive as the number of extrusion passes increases. In other words, the SSEed specimens showed better corrosion performance despite the fact that they contain higher density of dislocations. Such condition may promote the formation of a uniform $CuCl^-_2$ layer (corrosion products) at the surface which in turn would enhance the corrosion performance by keeping the electrode surface away from the corrosive environment. This is in accordance with the results of the EIS tests that are presented above.

As seen, the corrosion resistance of SSEed specimens is improved monotonically as the number of passes increases; however, it has been reported that the improvement in the corrosion behavior of ARBed copper will occur by increasing the number of roiling passes more than two [4]. Such a difference would be attributed to the higher amount of deformation experienced by a SSEed sample compared to that of ARBed one that makes the former with more active surface than the latter [2, 14].

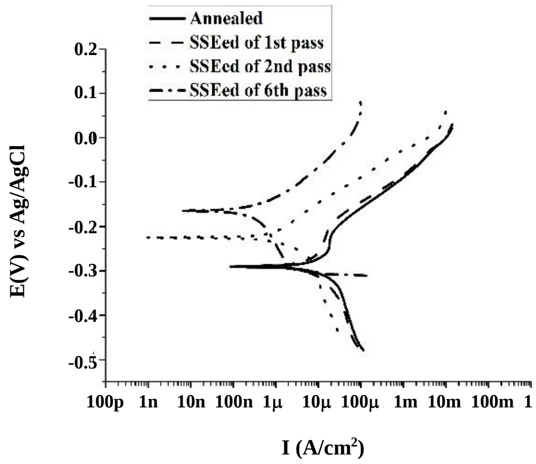

Fig. 6: Tafel plots of annealed and SSEed samples.

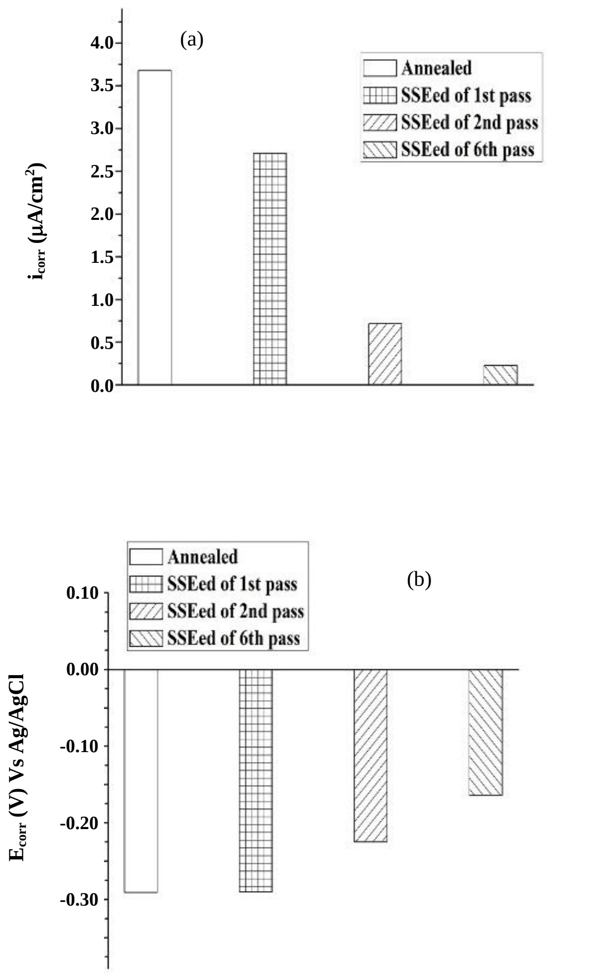

Fig. 7: Corrosion currents (a) and corrosion potentials (b) of annealed and SSEed samples.

CONCLUSIONS

Simple shear extrusion process has beneficial effect on the corrosion performance of pure copper in 3 wt% NaCl solution. Such behavior would be related to the formation of thick and stable layer of corrosion products at the surface as a result of increased dislocation density in the microstructure of the SSEed samples (examined by modified Willianson-Hall method). The results of the polarization and EIS tests showed that as the number of SSE passes increases the corrosion resistance of the samples increases too. In other words, the microstructure of those samples that were extruded for higher number of passes contains more dislocation density that leads to have promoted dissolution occurring at the surface; this in turn results in the built up of corrosion products at the surface and formation of protective layers of $CuCl_2^-$ and CuCl complexes that retards the corrosion phenomenon.

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