Corrosion Science 75 (2013) 434–442

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Sulphuric acid corrosion of ultrafine-grained mild steel processed by equal-channel angular pressing

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ARTICLE INFO

Article history:
Received 15 March 2013
Accepted 19 June 2013
Available online 28 June 2013

Keywords:
A. Mild steel
A. Iron
B. Polarization
B. TEM
C. Acid corrosion
C. Passivity

ABSTRACT

A bulk ultrafine-grained (UFG) mild steel with a ferrite grain size of approximately 200 nm and a dispersed distribution of iron carbide particles was fabricated by equal-channel angular pressing (ECAP) at 400 °C. The corrosion behaviour of the ECAP-processed mild steel and pure iron was investigated in a 0.5 mol/L H_2SO_4 solution. They exhibited a higher corrosion rate and better anodic passivity properties due to the presence of more crystalline defects. As a result of the refinement of the iron carbide particles, the forming ability of a continuous dense passive film was improved.

1. Introduction

Grain refinement is known to achieve both high strength and good plasticity for a metallic material. Severe plastic deformation (SPD) has been developed through a group of techniques to fabricate ultrafine-grained (UFG) metals, which have attracted significant scientific interest due to their unique mechanical characteristics [1–3]. Among these SPD techniques, equal-channel angular pressing (ECAP) is one of the effective methods to prepare UFG metals. The ECAP process consists of a metal billet being pressed through a die, which contains two channels intersecting at an angular φ with an identical cross section [4].

A number of studies on the relationship between the corrosion resistance and the grain size have been performed for many different materials. Ralston et al. produced and developed a summary definitive understanding of how the grain size affects the corrosion rate and passivity of various metals [5,6]. Additionally, Liu et al. summarised that if the corrosion products were dissoluble, the corrosion rate would increase because of nanocrystallization; however, if the corrosion products were insoluble, the corrosion rate would decrease [7].

In addition to the grain size, various other factors, including grain size distribution [8], texture [9–11], residual stresses [9] and composition [12–14], may have a significant influence on the corrosion behaviour of the metals. Several studies have focused on the influence of these factors on corrosion behaviour.

Gollapudi noted that a broader grain size distribution in a pure metal led to an increased corrosion resistance in a non-passivating environment and decreased corrosion resistance in a passivating environment [8]. Pu et al. found that, after severe plasticity burnishing (SPB), the remarkably improved corrosion resistance of an AZ31B Mg alloy in a 0.855 mol/L NaCl solution was primarily attributed to the dramatically reduced grain size and the strong basal-textured grain orientation. Furthermore, the residual stresses by SPB reportedly influenced the corrosion resistance as well [9]. Kumar et al. found that the corrosion behaviour was affected by textures in metals [10]. The presence of the close pack crystallographic planes parallel to the specimen surface improved the corrosion resistance of an austenitic AISI 304 stainless steel in a 0.6 mol/L NaCl solution. Aung et al. reported that the existence of twins in an AZ31B Mg alloy accelerated its corrosion rate in a 0.6 mol/L NaCl solution [11]. Ralston et al. revealed that the pitting resistance of an Al–1.1 Cu–1.7 Mg (at.%) alloy in a 0.01 mol/L NaCl solution was improved by reducing the critical width of the second phase to less than approximately 3 nm [12]. Son et al. found that the improved pitting resistance of the ECAP-processed AA1100 aluminium alloy in a 0.2 mol/L $AlCl_3$ solution was attributed to a decrease in the size of the impurity precipitates [13].

Mild steels have been widely used in industries as structural materials because of their good mechanical and welding properties and low cost. Compared with the traditional mild steels, UFG mild steels have higher strength and better ductility [14–20]. Shin et al.

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http://dx.doi.org/10.1016/j.corsci.2013.06.028

reported that the ferrite grain size of one kind of mild steel after 4 passes of ECAP was approximately 200 nm and relatively stable in the annealing temperature range of 420–510 °C [21–23]. However, mild steels are known to often suffer from severe corrosion when they are in an acidic or moist atmosphere [24–26]. The microstructure of the metal is one of the influencing factors on its corrosion behaviour [27]. Therefore, it is necessary to investigate the corrosion behaviour of the mild steel after severe plastic deformation.

The corrosion behaviour of pure iron and steels with microcrystalline or nanocrystalline (NC) surfaces has been described by many researchers [28–38]. According to present theory, corrosion of the UFG metals should be accelerated in active solutions [5–7]. Oguzie et al. reported that a bulk NC iron produced by severe rolling showed lower corrosion resistance than the conventional polycrystalline ingot iron in 0.1 and 0.5 mol/L H_2SO_4 solutions [28,29]. The corrosion susceptibility of one kind of mild steel in an aerated 0.5 mol/L H_2SO_4 solution was enhanced by surface nanocrystallization through magnetron sputtering [30]. Sherif reported that repeated quenching refined the microstructure of a BSK46 steel, but its corrosion rate increased in a 1 mol/L H_2SO_4 solution [31].

However, several reported results are contrary to this view. Wang et al. reported that the corrosion resistance of a bulk NC iron produced by severe rolling was improved in a 1 mol/L HCl solution or 0.05 mol/L H_2SO_4 + 0.25 mol/L Na_2SO_4 solution compared with the conventional polycrystalline ingot iron [32,33]. Zheng reported that a ECAP-processed 304 stainless steel with NC grains exhibited a higher corrosion resistance in a 0.5 mol/L H_2SO_4 solution as compared to the as-received counterpart [34]. Ye et al. investigated the corrosion behaviour of a NC 309 stainless steel coating processed by magnetron sputtering and a bulk counterpart [35]. The results showed that their corrosion behaviour was less differential in a 0.25 mol/L Na_2SO_4 + 0.05 mol/L H_2SO_4 solution; however, the localised corrosion resistance of the NC coating was much better in a 0.5 mol/L NaCl + 0.05 mol/L H_2SO_4 solution. In addition, Wang et al. reported that a NC layer in a 304 stainless steel, produced by sandblasting and an annealing process, had a higher corrosion resistance, greater repassivation capability and higher chemistry stability in a 0.6 mol/L NaCl solution [36]. Hadzima reported that an interstitial-free ferrite steel processed by ECAP did not show significantly higher corrosion resistance in neutral 0.01–1 mol/L NaCl solutions, but it formed a more stable protective passive layer in a 0.9 mol/L NaOH solution than the coarse-grained counterpart [37]. Balusamy revealed that an excess micro strain and defect density introduced in a NC surface layer of a AISI 409 stainless steel by surface mechanical attrition treatment (SMAT) resulted in a decrease of the corrosion resistance in a 0.6 mol/L NaCl solution [38].

Conversely, heavy loss of steels in the corrosive surrounding can be reduced by using corrosion-inhibitors [39–41] or anodic protection [42,43], and these anti-corrosion methods for acid solutions are developed according to the electrochemical experimental results. In the present study, the corrosion behaviour of one kind of mild steel severely processed by ECAP was investigated by an electrochemical measurement in a dilute sulphuric acid solution. In addition, the effects of the microstructure change on the corrosion behaviour and mechanism were discussed in comparison with the ECAP-processed pure iron.

2. Experimental

The used mild steel was cut from a hot-rolled rod with a chemical composition (wt.%) of 0.10–0.13 C, 0.11–0.15 Si, 0.38–0.45 Mn, 0.027 S, 0.024–0.028 P, 0.01Cr, 0.01 Ni, 0.02 Cu and the remainder Fe. The pure iron used as the contrast material had a chemical composition (wt.%) of 0.002 C, 0.02 Si, 0.10 Mn, 0.008 S, 0.01 P and the remainder Fe. Before the ECAP processing, the steel samples (dimension: ∅30 mm × 50 mm) were annealed at 900 °C for 50 min. The dimension of the samples used for ECAP was 19.5 mm × 19.5 mm × 40 mm.

The samples were processed by ECAP for 4, 8, 12 and 16 passes. The processing route is shown in Fig. 1, which shows that the sample is rotated 180° around the *Y*-axis between any two pressing passes. The inner angle of the die is 90°. More details on the ECAP processing can be found in Ref. [44]. The ECAP processing temperature of the mild steel was 400 °C. The pure iron samples were processed by ECAP at room temperature and then annealed at 500 °C to remove residual stresses.

The specimens for microstructure observation and corrosion tests were cut from the central region of the ECAP-processed samples (as shown in Fig. 1) because this region had more uniform plastic deformation [45].

The microstructures were observed by an optical microscope and transmission electron microscopy (TEM, Tecnai G2). The samples for the TEM observation were prepared by a twin-jet polishing technique, which consisted of an electrolyte solution containing 20% perchloric acid and 80% methanol, and the potential and operating temperatures were 40 V and −40 °C, respectively.

The dimension of the specimen used for electrochemical tests was 10 mm × 10 mm × 3 mm. Then, they were molded in epoxy resin, with a 1.0 cm^2 window exposed to the solution. Before the electrochemical test, the exposed surface was ground on silicon carbide (SiC) papers ranged from 240 grit to 400, 800, 1000 and 1200 grits, mechanically polished, washed with distilled water and ethanol, and dried by cold flowing air.

The corrosion behaviour of all samples was measured by an open circuit potential (OCP), anodic polarization and linear polari-

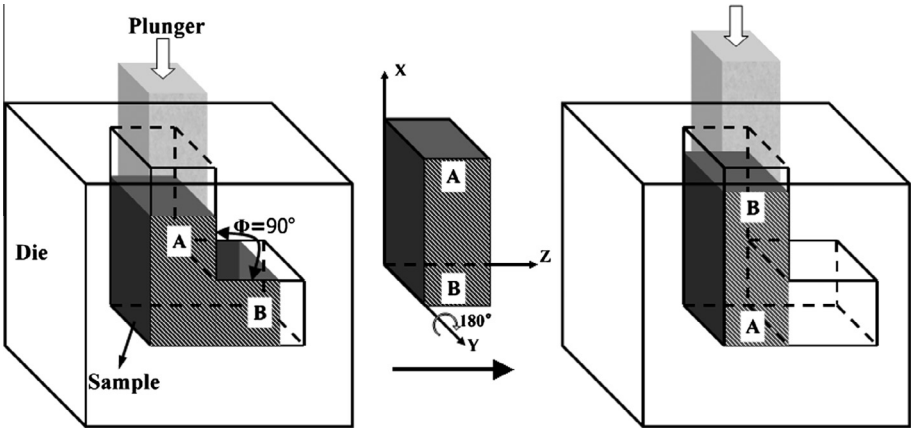

Fig. 1. Schematic illustration of the ECAP process.