Applied Surface Science 388 (2016) 49–56

Contents lists available at ScienceDirect

Applied Surface Science

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

Electrochemically enhanced surface plasticity of steels

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ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form 2 March 2016
Accepted 11 April 2016
Available online 13 April 2016

Keywords:
Hardness
Surface plasticity
Anodic polarization
Electrolyte

ABSTRACT

There are serious problems with the formability of alloys which are relatively hard and brittle below ambient temperatures, *e.g.*, in cold extrusion and drawing processes. It is known that electrochemical surface treatment can decrease residual stresses and hardness of the surface layer as a result of the chemomechanical effect (CME), and also improve the plastic deformation ability, *e.g.*, deep drawing of high-strength alloys. Plastic deformation ability of materials can be characterized by hardness measurements. The present study shows some possibilities to improve the surface ductility of carbon steels and FeSi6.5 steel under anodic polarization depending on the current density, composition and pH of acids and chloride electrolytes. The relative Vickers hardness (RVH) amounting to a squared ratio of the penetration depth of a cone indenter in air as compared to that in a solution $(h_{air}/h_{sol})^2$ was found as a function of the current density and the electrolyte composition. A decrease in hardness of the surface layer as a result of anodic electrochemical polarization was found for different steels.

1. Introduction

Due to the fact that high strength and ductility of materials are often mutually exclusive, cold drawing of high-strength and not enough ductile alloys using existing technologies meets serious problems (cracking, formation of dangerous defects, surface finish deterioration, *etc.*). Some high performance brittle alloys are hard to form by drawing. One of striking examples of such metals is FeSi6.5 steel, which has the highest permeability, lowest hysteresis loss, high electric resistivity and extremely low magnetostriction [1–3] among the iron-silicon electrical steels. However, relatively high silicon content dramatically reduces its workability, which makes it extremely hard to be deformed into thin ribbons or wires by cold rolling or drawing [3–5].

The problem of low workability can be, probably, overcome using a special high-performance electrolytic active medium and anodic polarization capable to plasticize a surface layer. Using thermodynamics of irreversible processes, Gutman has analyzed the simultaneous processes of plastic deformation and surface dissolution reactions between a solid and a solution [6]. He discovered that electrochemical or chemical reactions on the surface of a stressed solid cause additional dislocation flux, which changes mechanical properties and fine microstructure. This effect of increasing the plasticity of a solid under the influence of surface chemical reactions was named chemomechanical effect [6–8]. An additional dislocation flux is generated as a result of rapid surface layer saturation with dislocations to the maximum possible 'dynamic' density, followed by removal of this layer due to chemical dissolution. The dissolution mechanism of a crystalline solid (*e.g.*, anodic dissolution of metals) is based on the concept of initial monoatomic pit formation (bi-dimensional dissolution nucleus) and successive etching of atomic layers along the crystallographic plane by shifting the monoatomic step with successive repeating of layer dissolution process. Since monoatomic surface steps may serve as sources of new dislocations, we can come to the conclusion that the appearance of additional dislocation flux due to surface atom dissolution by anodic current is caused by heterogeneous nucleation and the action of new surface sources of dislocations resulting from heterogeneous surface dissolution with monoatomic step formation [9]. Saturation with dislocations of the dissolving layer is possible due to incomparable values of the velocities of dislocation multiplication and motion on the one hand and solid dissolution on the other hand.

Thus, the generation of surface dislocation sources in the process of CME realization leads to rapid surface layer saturation with dislocations. This fact creates favorable conditions for multiple slip (including dislocation cross slip) and, hence, for the destruction of planar piles-ups generated earlier, *i.e.* for microstress relaxation and hardness decreasing. Indeed, in the early 70s, experiments

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http://dx.doi.org/10.1016/j.apsusc.2016.04.071
0169-4332/

were carried out on single crystals of calcite and iron, as well as on polycrystalline steels, which for the first time confirmed the CME by direct observation of dislocation etch pits in microhardness tests and under macroscopic loading [8–10]. For example, for 18-10 type stainless steel in 3.5 M H_2SO_4 water solution, a linear dependence of hardness loss on the current density logarithm (as predicted by the theory [9,10]) has been established over all the ranges of active and passive state potentials. That points to the predominant role of CME despite the formation of passive film, which is transparent for dislocations [8–10]. The elongation of a high-strength alloy (25Cr-60Ni-15V) tested at the speed of 10^{-3} s^{-1} increased under anodic polarization in 0.5 M sulfuric acid by around 40% as compared to the results obtained in air [8–10]. Another example of a manifestation of the CME was a reduction in the drawing force by 20% while sinking from 8.0 to 5.5 mm in diameter of 0.65-mm-wall-thick tubes (made of 18–10 type stainless steel) under anodic polarization in the electrolyte containing 1.5 M H_2SO_4 and 2.2 M $C_3H_8O_3$ (glycerol) [9].

Additional experimental proofs of the influence of dissolution of metals on the hardness of near-surface regions and plastic flow were discussed in the Review [11]. Recently, Guo and coauthors obtained around two-fold decrease in the hardness of pure iron in decimolar sulfuric acid under anodic current density of 1 mA/cm^2 and loads up to 2.0 mN using an *in situ* nano-indentation technique [12]. The authors [12] concluded that the hardness degradation resulting from anodic dissolution could be attributed to the generation of vacancies in the metal surface layer. The highest hardness decay in different solutions, including sodium bicarbonate 1 M $NaHCO_3$, tap water and sodium sulfate Na_2SO_4, as compared to air, was found in 0.1 M Na_2SO_4, and the lowest one – in 0.001 M Na_2SO_4. Both hardness and elastic modulus of the surface layer reduced with anodic current density increase from 0.01 mA/cm^2 to 10 mA/cm^2 [13]. A good linear correlation between the current density logarithm and hardness was obtained for AISI 1020 and AISI 1070 carbon steels in sulfuric acid: with current density increase from 0.4 mA/cm^2 to 40.0 mA/cm^2, the hardness of 1070 type steel under the load of 2.9 N in 0.5 M H_2SO_4 solution in comparison to that in air reduced by 49% and 79%, respectively [14]. Using an *in situ* scanning electrochemical microscopy, Zhu with coworkers found a 30% decrease in nano-hardness of both as-received and cold worked Cr-Ni 800 alloy under anodic polarization in 0.1 M KCl with a small addition of ferrocene methanol (Fc), in which KCl was the supporting electrolyte and Fc was used as a redox addition [15].

The above-mentioned results demonstrate a decrease of hardness and enhancing plasticity of the surface layer using electrochemical anodic dissolution of metals. In the present work, we have studied the effect of anodic polarization on the plasticization of carbon steels, and electrical steel containing 6.5 wt% Si with unique magnetic properties, but limited ductility at room temperature.

2. Materials and methods

As materials for hardness tests assisted by anodic polarization, cold-rolled 2-mm-thick AISI sheet steels 1020 and 1070, as well as 4.36-mm in diameter 1055 wire steel were used. For hardness tests, the wire was grinded from two sides up to the thickness of 3 mm. Besides, "dog-bone" shaped tensile samples and the foil of FeSi6.5 steel with the thickness of 2 mm and 0.08 mm, respectively, were produced from a 22-kg ingot. This steel was prepared by melting iron (99%) and silicon (99.6%) in an induction vacuum furnace. The as-cast ingot was homogenized at the temperature of 1050 °C for 1 h and then forged into a Plate 20 mm thick. Then samples for the tension test were cut out from the plate by an electric discharge machining. Half of the samples were heat treated at 850 °C for 2.5 h and then quenched in salt water. Chemical composition

Table 1
Chemical composition (wt.%) and hardness of steels.

Material	C	Mn	Si	Cr	S	P	VH (GPa)
AISI 1055 wire	0.56	0.72	1.45	0.21	0.045	0.035	3.12
AISI 1020, 2-mm-thick sheet	0.20	0.51	0.27	0.081	0.038	0.021	1.32
AISI 1070, 2-mm-thick sheet	0.72	0.78	0.24	–	0.042	0.032	1.72
FeSi6.5[a]	0.004	<0.1	6.5	–	0.003	0.004	4.43
HT FeSi6.5[b]							4.12
FeSi6.5 foil[c]							5.38

[a] 2 mm-thick as-machined sample, no heat treatment.
[b] 2 mm-thick as-machined heat-treated sample.
[c] 80 μm-thick as-rolled foil.

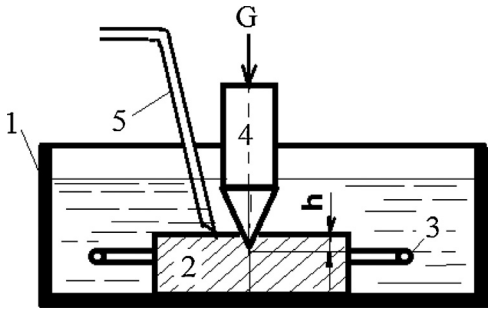

Fig. 1. Scheme of electrochemical cell for in situ hardness measurements under anodic polarization.
1—cell body made of PMMA, 2—sample (anode), 3—platinum ring (cathode), 4—indenter, 5—electrochemical bridge connected to the reference electrode.

of materials and their microhardness are presented in Table 1. The Vickers microhardness (VH) of AISI carbon sheet (1020 and 1070) and wire (1055) steels under a load of 2.9 N amounted to 1.32, 1.72 and 3.12 GPa, respectively. The hardness of FeSi6.5 steel without heat treatment, heat-treated samples and foil amounted to 4.43, 4.12 and 5.38 GPa, respectively (Table 1).

Hardness measurements were performed in air as a reference and in acids, sodium and potassium chloride aqueous solutions. The experiments were carried out on a Vickers micro-hardness tester (Zwick Co., Germany) equipped with a potentiostat or AC/DC ZUP36-24 power supply and an electrochemical cell allowing to realize local plastic deformation of metal with simultaneous anodic polarization of the sample. The transparent cell included the sample as anode, platinum ring (anode), electrochemical bridge connected to the reference electrode and a special indenter (Fig. 1). Before the hardness measurements, the samples were cleaned in alcohol and dried in acetone.

The three-electrode cell comprises platinum as a counter electrode (cathode), the sample (anode) as a working electrode and a calomel reference electrode filled with a saturated potassium chloride solution. In this cell, the hardness measurements in air and in solutions with anodic polarization were performed using a 90° cone-shaped indenter made of tungsten carbide-cobalt alloy under a load varied from 2.9 N to 49.0 N at the dissolution area of 0.5 cm^2. The depth h of its indentation was registered by a digital indicator with the accuracy of ±0.5 μm [14].

Hardness is inversely proportional to the imprint area or to the squared indentation depth. Therefore, a squared ratio of the penetration depth $(h_{air}/h_{sol})^2$, *i.e.*, RVH = $(h_{air}/h_{sol})^2$ was used as a parameter of the relative Vickers hardness (RVH) in solution as compared to that in air. The contact of the indenter with the polished surface of the sample was controlled using measurements of the electric resistance. Each set of hardness measurements included