# **Electrochemically Enhanced Plasticity of Steels**

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### **Abstract**

It is known that electrochemical surface treatment can decrease the residual stresses and the hardness of the surface layer as a result of the chemomechanical effect (CME), and also to improve the ability to plastic deformation, e.g., deep drawing for high strength alloys. The present research is aimed at using CME in order to improve such technological processes as rolling, deep drawing and other processes requiring an increase in the ductility of the metal surface layer using the hardness test assisted by electrochemical polarization.

The hardness measurements were carried out using a microhardness tester equipped with a special three-electrode electrochemical cell on AISI 1020, 1055 and 1070 steels. The measurements were made in air and in an electrolyte, mainly, sulfuric acid solutions. It was found that the relative hardness of the steel under polarization in sulfuric acid with molarity varied from 0.5 to 2 comparing to air amounted to 20-80% with anodic current density ranged from around 0.1 mA/cm² to 50 mA/cm².

The method of hardness control permits to optimize the parameters and regimes of surface treatment for different materials, where additional surface plasticity is desirable.

**Key words:** steel hardness, anodic dissolution, surface plasticity

## Introduction

Decreasing residual stresses and the hardness of the surface layers, as a result of the chemomechanical effect, to improve the deep drawing ability for high alloys by anodic electrochemical polarization was shown earlier. (1) In this paper we intent to show such ability for carbon steels to facilitate cold-rolling processes. The improving workability may be realized using an application of special lubricants or/and by some methods, that are able to decrease resistance to deformation and to increase the extent of plastic deformation before fracture, respectively. One of such methods we proposed is based on using a special high-performance electrolytic active medium (with or without anodic polarization) capable to plasticize the thin surface layer. The reason for such a surface plasticization is the chemomechanical effect that consists in increasing the ductility of the surface layer of a solid surface due to exposure of the surface to chemical or electrochemical reactions. (2)

In accordance to the theory, the effect is proportional to the chemical reaction affinity, i. e. to the logarithm of the anodic current density, if the reaction proceeds in the non-linear region of chemical kinetics. For example, such a state arises at the Vickers hardness VH and tension tests of chromium-nickel

steel, if the surface participates simultaneously in chemical reactions. It was shown that the VH value is proportional to the logarithm of anodic dissolution current density over the entire range of anodic potentiostatic polarization in the states of active dissolution, passivity and transpassivity. (2)

Recently, these results were confirmed on pure iron using very small loads (0.2-0.8 mN). It was showed that the anodic currents reduced both hardness and elastic modulus of the material surface layer, and the degradation effect declined with increasing distance from the surface. (3)

In the present work, the effect of anodic dissolution of common carbon steels in acid solutions on Vickers micro-hardness was investigated.

## **Materials and Experimental Procedures**

The two-mm-thick carbon steel samples (AISI 1020, 1070) were used for the tests under polarization in acids. In addition, carbon wire AISI 1055 steel wire produced by cold-drawing from the rod with diameter of 5.5 mm without any heat treatment was investigated. A wire sample of 4.36-mm in diameter was grinded from two sides up to thickness of 3 mm and used in hardness tests.

The samples were tested both in air and un acid solutions. The chemical composition of steels is given in Table 1.

**Table 1.** Chemical composition of steels, wt.%

Material	С	Mn	Si	Cr	S	P
AISI 1055 wire	0.56	0.72	1.45	0.21	0.045	0.035
AISI 1020	0.20	0.51	0.27	0.081	0.038	0.021
AISI 1070	0.72	0.78	0.24	-	0.042	0.032

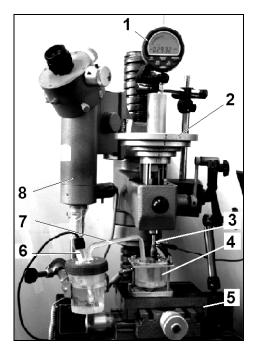
The experiments were carried out as measurements of the indenter penetration on a Vickers micro-hardness tester (Zwick Co., Germany) equipped with additional devices (three-electrode electrochemical cell, potentiostat/ galvanostat or AC/DC ZUP36-24 power supply allowing realize local plastic deformation of metal with simultaneous polarization (Figure 1).

Indentation was accomplished with a diamond pyramid or a hard needle made of tungsten carbidecobalt (WC-Co) hard alloy (Figure 2a) under load varied from 2.9 N to 49.0 N with indenting time of 10 s. Indenter penetration depth h was registered by a digital indicator with the accuracy of  $\pm 1$  micron. The diameter of the contact area between the sample and the solution amounted to 8.0 mm. The surface layer hardness was determined with the help of a calibration curve obtained by simultaneous measurements of the Vickers hardness (VH) and the depth h of the needle penetration into samples of different hardness (Figure 2b). For example, the fitting equation for VH ranged from 1.3 GPa to 4.5 GPa under weight of 49 N is the following: VH = -0.049h + 6.76 with the square correlation coefficient of 0.95.

Hardness is inversely proportional to the imprint area S under the Vickers pyramid or to squared pinhole depth. Thus, ratio of the imprint areas measured in acid solution and in air  $S_{sol}/S_{ref}$  or squared ratio of the penetration depth of the needle into sample  $(h_{sol}/h_{ref})^2$  in solution comparing to that in air was used as a parameter of the hardness change.

Hardness measurements were performed in air as a reference and in acid solutions, mainly in sulfuric acid. Hardness in electrolytes measured using diamond pyramid was performed with an addition of two – three drops of an electrolyte one minute ago before sinking of an indenter without current application (open circuit condition). Hardness

in electrolytes measured using a WC-Co indenter was carried out in a special electrochemical cell (Figure 1b). The samples were polished by P#500, P#800 and P#1200 papers, washed by ethanol and dried by acetone. The calomel reference electrode filled by saturated potassium chloride was used in acid solutions within a three-electrode cell with platinum as a counter (cathode) electrode and the sample was an anode work electrode. The contact of the hard needle with the polish surface of the sample was controlled using measurements of the electric resistance both in "dry" conditions and in electrolyte.

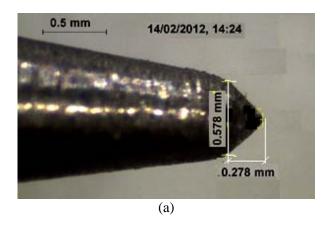


(a)



(b)

**Figure 1.** The Vickers micro-hardness tester (a) equipped with an electrochemical cell (b) 1 – digital displacement indicator, 2 –weights; 3 – needle's holder; 4 – three-electrode cell, 5 - the table; 6 - reference electrode, 7 - reference electrode bridge; 8 - the microscope.



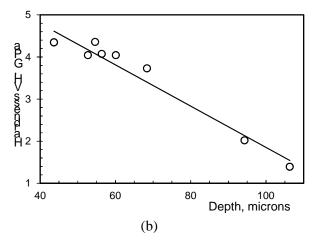


Figure 2. WC-Co indenter (a) and a calibration curve (b).

effect was demonstrated in sulfuric acid. An average decrease in hardness in solution in comparison to the reference one amounted to 8% for sulfuric acid and 4% for perchloric acid (Table 2).

It was found a significant decrease in hardness of AISI 1020 and 1070 steels in sulfuric acid solution under polarization into an electrochemical cell, The strongest effect was obtained for the smallest weight of 2.9 N with regards to the weight of 49 N: the hardness decreased by 36% and 25%, respectively, at current density of 2 mA/cm² (Table 2). With increasing current density i from 0.4 mA/cm² to 40 mA/cm², the relative hardness VH<sub>sol</sub>/VH<sub>ref</sub> of AISI 1070 steel under load of 2.9N decreased from 0.51 to 0.21 (Table 2). Fitting equation shows good linear correlation between log(i) and relative hardness: VH<sub>sol</sub>/VH<sub>ref</sub> = -0.147 log(i) + 0.433 with square correlation coefficient of  $R^2 = 0.96$ .

### **Conclusions**

- 1. The direct hardness measurement in solutions showed that the strongest effect was found for the smallest weight applied to an indenter.
- 2. The squared depth ratio  $(h_{ref}/h_{sol})^2$  and, respectively, the relative hardness  $VH_{sol}/VH_{ref}$  decreased with increasing current density with a

**Table 2.** Vickers hardness of AISI carbon steels tested using diamond pyramid (1, 2) and WC-Co indenter (3 - 7) in acid solutions compared with tests in air

No.	Material	Weight, N	i, mA/cm²	VH <sub>sol</sub> /VH <sub>ref</sub>	Hardness decrease,%	Solution	
1	1055	2.9	OC	0.92	8	3.5M H <sub>2</sub> SO <sub>4</sub>	
2	1055	2.9	OC	0.96	4	3.5M HClO <sub>4</sub>	
3	1020	2.9	2.0	0.64	36	2M H <sub>2</sub> SO <sub>4</sub> + +0.6M NaCl	
4	1020	49.0	2.0	0.75	25	$\frac{1}{2}$ ZIVI $\frac{1}{2}$ SO <sub>4</sub> + +0.0IVI NaCI	
5	1070	2.9	0.4	0.51	49		
6	1070	2.9	3.0	0.33	67	$0.5M H_2SO_4$	
7	1070	2.9	40.0	0.21	79		

## **Results and discussion**

The of about 20 measurements of Vickers hardness in open circuit (OC) conditions were performed on a 20-mm-long wire sample at the load of 2.9 N using diamond indenter in air and in an electrolyte. As active electrolytic media, a few drops of sulfuric acid (3.5M H<sub>2</sub>SO<sub>4</sub>) and perchloric acid (3.5M HClO<sub>4</sub>) were used. We observed some decrease in hardness measured in the solution in comparison to that in air. The strongest chemomechanical

good linear correlation between log(i) and hardness. With increasing current density from  $0.4~\text{mA/cm}^2$  to  $40.0~\text{mA/cm}^2$  the hardness in  $0.5M~\text{H}_2\text{SO}_4$  solution diminishes by 49% and 79%, respectively, in comparison to that in air.

#### References

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