Variation in Mechanical Properties Due to The Effect of Electric Potential

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Abstract: Metal microhardness as a function of electric potential was investigated experimentally for the test samples of aluminum, zirconium and siliceous iron. The effects of electric potential proper and of contact potential difference, which are due to metals having different electron densities, are compared in terms of variation in metal microhardness. Two sets of microhardness data obtained for the test samples are analyzed. Both effects are found to cause a significant enhancement in metal microhardness (up to 20%); therefore, in a qualitative sense, these effects are considered equivalent.

Keywords: contact potential difference, electric potential, microhardness of metals

I. INTRODUCTION

At present, it has been found that external energetic actions on solids are capable of changing their strength and plastic characteristics. The most well-known is the effect of short pulses of high amplitude electric current treatment, which can substantially reduce the deformation resistance [1-3]. The essence of the current impact is rather complicated. It involves a number of interrelated effects, such as electron-plastic, ponderomotive action or pinch-effect, skin effect, Joule heating. The problem of singling out the specific contribution of each component to the materials plasticizing is not obvious and far from being solved. On the one hand it is complicated by the fact that the conduction electrons of metals and alloys shield any electrostatic effects. On the other hand it is for this reason the metal systems easily change the surface state by changing its electrical potential. The surface potential value controls the most practically important processes, such as various types of corrosion, wear and endurance in hazard environments and materials behavior under loading.

Since the mechanical properties of materials are sensitive to the state of thin near-surface layers, it can be expected that the change in the density of the surface energy caused by an electrical potential can substantially influence characteristics such as its microhardness. This effect (the change in the strength when a metal surface is charged) is associated [4–9] with the formation of a double electrical layer that changes the specific surface energy. It was assumed in [7, 8] that the intensity and the sign of the change in the microhardness are determined by the magnitude and the sign of the Hall coefficient, i.e., the conduction type of a metal. This assumption has not been examined for a wide class of materials until now. The aim of this work is to study the changes in the microhardness of metals with different Hall coefficients under low electrical potentials. The aim of this work is to determine the effect of low electric potentials and contact potential difference on the microhardness of metallic materials.
II. MATERIALS AND METHODS

For this reason, the probable manifestations of the same effect [5, 7] were investigated by measuring metal microhardness \( H \) (see, e.g. Mott [10]) for the test sample with the aid of a microhardness tester ‘AFFRI DM-8’. Depending on the kind of material, the indenter load varied in the range \( 0.1 \leq P \leq 1 \) N; in what follows this is specified for each particular case. Experimental checks showed that the microhardness values obtained for one and the same material were practically unaffected by the variation in the indenter load. The test samples were subjected to the action of electric potential from a DC voltage source (i) and of contact potential difference due to two connected metals having different electron densities [11] (ii) (see Fig. 1 a and b, respectively).

![Fig. 1. Scheme of applying electric potential to the sample by measuring material microhardness: (a) from a DC source; (b) – by connecting a contact metal. 1 – sample; 2 – insulation; 3 – indenter; 4 – metal in contact; P – indenter load](image)

Shielded copper wire 0.5 mm in diameter was connected to the test sample to provide for electric contact with a contact metal plate; during the testing the sample was isolated from both the microhardness tester and the earth. In case (ii) the mass of contact metal \( m_{Me} \), might vary. Of particular interest is the method of setting up the problem: this enables one to define the critical minimal mass of contact metal, which provides for a significant enhancement in the microhardness of the tested metal.

The observed effect of microhardness variation due to potential difference can be conveniently estimated using the dimensionless ratio

\[
Q = \frac{\bar{H}_E - \bar{H}_0}{\bar{H}_0},
\]

where \( \bar{H}_0 \) and \( \bar{H}_E \) are, respectively, the average initial microhardness of material and the average microhardness of the same material subjected to the action of potential difference. The resultant microhardness values are expected to be low; therefore, to estimate the effects observed in cases (i) and (ii), statistical data treatment involves the use of a routine procedure [12].
The average microhardness value is

\[ \bar{H} = \frac{\sum H_i}{n}, \]  

(2)

Where \( n \geq 30 \) is the number of measurements.

In all the cases the standard deviation was estimated for the average microhardness value \( \bar{H} \) as

\[ s_n = \pm \sqrt{\frac{\sigma_n^2}{n}}, \]  

(3)

Where \( \sigma_n^2 = \frac{\sum (H_i - \bar{H})^2}{n-1} \) is the variance of measured \( H_i \) values for \( n \geq 30 \).

By matching \( \bar{H}_E \) and \( \bar{H}_h \) values, the statistical significance of the difference between the two values was estimated using Student’s t-test, i.e.

\[ \hat{t} = \frac{\bar{H}_E - \bar{H}_h}{\sigma_{n_E+n_h} \sqrt{\frac{n_E+n_h}{n_E+n_h}}}. \]  

(4)

The difference is significant, if \( \hat{t} > t_{\alpha, n} \). Here \( t_{\alpha, n} \) is the fractile of Student’s t-distribution; \( n \) is the number of degrees of freedom and \( \alpha \) is the confidence level.

III. RESULTS OF MICROHARDNESS MEASUREMENT

Fig. 2 demonstrates that the imposition of an electrical potential \( \Delta \phi \) can both increase and decrease the microhardness. Thus in the case of aluminum, an increase in the absolute value of electric potential would cause the microhardness to decrease, while in the case of zirconium, the microhardness is enhanced significantly.

![Fig. 2. Dependencies of material microhardness on electric potential: Zr sample (curve 1; indenter load 1 N) and Al sample (curve 2; indenter load 0.1 N)]
The experimental evidence for the existence of the above effects is listed in Table 1 (contact metals are given in parentheses); the scheme used is illustrated in Fig. 1 b. The data obtained suggests that an increase in the microhardness of material would vary in the range $0.025 \leq Q \leq 0.16$ for different pairs of metals. The $Q$ values were evaluated using Student’s t-test. The number of degrees of freedom being $n = n_x + n_y - 2 = 30 + 30 - 2 = 58$ and the confidence level $\alpha = 0.95$, the fractile of Student’s t-distribution is $t_{\alpha, n} = 2.0$. It is assumed that the corresponding values $\bar{H}_0$ and $\bar{H}_E$ that are members of the pair belong to samples from different populations, with the difference between $\bar{H}_0$ and $\bar{H}_E$ being greater than the confidence level 0.95 (Table 1).

Table 1: An increase in metal microhardness due to contact potential difference

| Metal tested (metal in contact) | Initial microhardness $\bar{H}_0$ (MPa) | Microhardness for electrical potential $\bar{H}_E$ (MPa) | Relative unit $Q = \frac{\bar{H}_E - \bar{H}_0}{\bar{H}_0}$ | Student’s-test values for the pair $\bar{H}_0$ and $\bar{H}_E$ |
|--------------------------------|------------------------------------------|-------------------------------------------------|-----------------|-----------------|
| Al (Sn)                        | 319                                      | 368                                             | 0.16            | 6.4             |
| Al (Cu)                        | 248                                      | 286                                             | 0.15            | 21.0            |
| Al (Zr)                        | 202                                      | 228                                             | 0.13            | 21.1            |
| Zr (Al)                        | 1668                                     | 1831                                            | 0.1             | 17.8            |
| Fe-3wt.%Si (Zr)                | 1922                                     | 1969                                            | 0.025           | 3.6             |

In view of the above it might be of interest to investigate the probable dependence of microhardness on contact metal mass, $Q(m_{Me})$. A series of experiments was carried on for different metal pairs. The results obtained suggest that the dependence of microhardness on contact metal mass is an extreme one in character. Thus in the specific cases of Al, Zr and Fe-3wt.% Si alloy the dependencies $Q(m_{Me})$ show extremums $Q_{max} \approx 0.14$, $Q_{max} \approx 0.04$ and $Q_{max} \approx 0.025$, respectively, for $m_{Zr} \approx 4$ g, $m_{Al} \approx 6$ g and $m_{Zr} \approx 2$ g, respectively.

This evidently testifies that due to contact potential difference, the microhardness of metal would increase (see Fig. 3 and Table 2).

Table 2: Dependence $Q(m_{Me})$ obtained for tested metals

| Metal tested (metal in contact) | $Q_{max}$ | $m_{Me} \cdot 10^3$, kg |
|--------------------------------|-----------|-------------------------|
| Al (Zr)                        | 0.14      | 4                       |
| Zr (Al)                        | 0.04      | 6                       |
| Fe-3wt.%Si (Zr)                | 0.025     | 2                       |

In the light of the above evidence the possible effect on microhardness of contact metal mass $m_{Me}$ might be of significant interest. It has been found that microhardness is really
determined by the value \( m_{Me} \). Fig. 3 demonstrates variation in the microhardness of Al (1) and Zr samples (2) as a function of contact metal mass, i.e. Zr and Al, respectively. It can be seen that with increasing contact metal mass, the effect is enhanced. By applying a potential from an energy source, effects of the opposite sign are observed for aluminum and zirconium.

Fig. 3. Material microhardness as a function of contact metal mass: (1) Al sample (contact metal Zr; indenter load 0.2 N); (2) Zr sample (contact metal Al; indenter load 1 N); (3) Fe-3%Si sample (contact metal Zr; indenter load 1 N);

However, the effect on microhardness of contact potential difference is found to be more complex than the effect of potential from an energy source. Thus the function \( Q(m_{Me}) \) obtained for contact metal mass varying from 0 to 20 g has extreme character. It follows from the specific cases of \( Q(m_{Me}) \) dependence presented in Fig. 3 that the extremums \( Q_{\text{max}} \approx 0.14 \) and \( Q_{\text{max}} \approx 0.04 \) are observed for aluminum and zirconium, respectively, with \( m_{Zr} \approx 4 \) g and \( m_{Al} \approx 6 \) g, respectively, and \( Q_{\text{max}} \approx 0.025 \) is observed for the pair Fe-3wt.%Si – Zr with \( m_{Zr} \approx 2 \) g. Evidently, the above effects suggest an enhancement in the microhardness of the studied metals.

IV. DISCUSSION OF RESULTS

Due to contact potential difference, a charge exchange would occur between the double electric layers on the surface of both metals with a resultant change in the surface energy density and, consequently, in the mechanical properties of materials, in particular, microhardness. Using this idea for interpretation of noted results a qualitative similarity between contact potential difference and potential created by an electric energy source. This might be accounted by the fact that (i) the above effect is produced by the absolute value of potential no matter what its sign; (ii) the most significant effect is observed for a potential ≤ 1 V; (iii) mechanical properties of aluminum and zirconium are affected adversely by potential.

In what follows we shall discuss the following regularities established herein: (i) the same effect as related to the surface state and (ii) effects of opposite signs observed for aluminum and zirconium (Fig. 2).
It is maintained that the effect of electric potential is equivalent, in a qualitative sense, to the action of metals with different electron work functions. Two regularities have been established for investigated metals, i.e. relation of the effect in question to material surface condition and a difference in the behavior of the said characteristic observed for Al and Zr (Fig. 2).

Variation in metal microhardness due to electric potential is thought to be related to a change in the state of double electric layer on the metal surface. The opposite effect of potential might be due to aluminum and zirconium having different conductivities. Thus a difference in the behaviors of the said characteristic is observed for aluminum and zirconium (see Fig. 3 a), with the shape of $Q(m_{N})$ dependence remaining unchanged. This might be attributed to the metals having different conduction mechanisms. This point of view can be confirmed by the data on the sign of the Hall constant values, $R$, which are obtained for aluminum and zirconium [8] from the expression for the Hall electromotive force

$$E_H = R \cdot j \cdot B$$

Where $B$ is the magnetic induction and $j$ is electric current density.

It is well-known [10] that $R_{Al} < 0$ and $R_{Zr} > 0$, which corresponds to electron and hole conduction. Provided the tests are performed according to the scheme illustrated in Fig. 1 b, microhardness of material might either increase or decrease, depending on the signs of the Hall constants $R$ observed for the main metal and the contact metal.

It should also be noted that upon withdrawal of electric potential and upon removal of contact metal, relaxation of microhardness would occur in accordance with the equation $H \sim \exp(-t/\tau)$ (here the time constant $\tau \approx 5 \times 10^3$ s) so that microhardness assumes its initial value (see Fig. 4). For the area $S \approx 10^{-4}$ m$^2$ and the electrode spacing $d \approx 10^{-10}$ m, the electrostatic capacitance of metal surface layer $C_e = \varepsilon_0 \varepsilon S/d \geq 10^{-5}$ F (here $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon$ is the dielectric constant). Hence for any reasonable value of electric resistance $R$, the inequality $\tau >> RC_e$ would be valid. Thus, variation in metal microhardness under the above conditions might be related to the long-lived changes in surface layer state, which are initiated by events occurring in the double electric surface layer, e.g. adsorption phenomena [6] or surface film polarization [14] on a free surface.

Evidently, the effect of electric potential and of contact potential difference on the microhardness of a metal is mostly due to a change in its surface energy density, which favors initiation of plastic shears and nucleation of different kinds of defects. In particular, it might affect mechanical characteristics of metals, e.g. creep rate [4, 9] and microhardness [9].
Fig. 4. Microhardness relaxation with time observed upon withdrawal of the contact metal Zr from the test sample of Fe-3%Si alloy (Zr mass 4.4 g; indenter load 1 N)

The results discussed herein (see Fig. 3 b) suggest that the effect of contact potential difference on microhardness cannot be considered unambiguous. First, the magnitude of the effect is determined by the contact metal mass: for all the studied pairs of metals the maximal effect is observed for $m = 5 \pm 2$ g. Second, contact potential difference would have a softening effect on aluminum only in case the mass of contact metal (zirconium) is $> 20$ g; for lower $m$ values, the microhardness of aluminum would increase. At the present stage of research the latter facts cannot be accounted for.

CONCLUSION

The results obtained in the present study strongly suggest that the electronic structure of metals and their mechanical properties are closely related. Such a relationship was established with the aid of simple experimental methods. Thus the macro-scale characteristics of localized plastic deformation are found to be affected by a change in the number of electrons per unit cell of metal, which might be regarded as a manifestation of the above relationship [15]. Evidently, such effects are extremely complicated in character; therefore, their origin calls for further investigation. These must be taken into account, e.g. by addressing dislocations motion in metals under the action of electric field and by the interpretation of electric migration phenomena [16-18].

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