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Analysis of liquid metal embrittlement in materials

Eugene D. Shchukin and Vladislav I. Savenko*

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation. E-mail: visavenko@phyche.ac.ru

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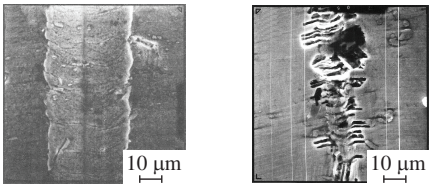
For studying initial surface damages in metals together with the effects caused by active media, the microsclerometry method has been combined with the electrochemical reduction of an active component on the tested surface. The method made it possible to detect a liquid metal embrittlement (LME) effect in the absence of a liquid metal phase.



plasticizing effect embrittling effect

A well-known microscratching test method[1] can be used in the area of the environment-sensitive mechanical behavior (ESMB) of solid surfaces. The method becomes particularly informative with small indenter loads used in the ultramicrosclerometry tests.[2] Under the smallest loads, this method allows one to observe a gradual transition from the pure elastic behavior of materials to nano- and microplastic deformations in a contact zone. A transition to the brittle behavior of material takes place during the subsequent load increasing.[3] The corresponding statistical methods characterize quantitatively such transitions in ionic crystals (NaCl, LiF), metal single crystals (Mo), covalent crystals (GaAs), and amorphous solids (quartz) depending on pH, surfactant additives in aqueous solutions, *etc.*[4]

However, the microscratching method is difficult to use for studying the most severe and important manifestations of the ESMB – the embrittlement of solid metals and alloys by a surface-active liquid metal (LME effect[5–7]). These difficulties include experimenting at elevated temperatures, the reliable wetting of solids with liquid phases, the subsequent removal of used liquid metal phase for the observation of surface damages, *etc.*

Here, we propose to use the LME effect under special boundary conditions without imposing the liquid phase of an active metal component on the solid surface. In these experiments, the test metal sample was a cathode in an electrochemical cell, and a combination of scratching and the electrochemical reduction of a surface-active ionic component adsorbed in the area adjacent to the indenter/sample contact zone was used. This combination can be universally applied in various studies of the ESMB including hydrogen embrittlement and particularly LME effect.

The device is schematically shown in Figure 1. Sample *1* is immersed in an electrochemical cell with electrolyte solution *2*. The sample is covered with hard hydrophobic varnish film *12* (nitrocellulose zaponlak-NC62), except area *4* used for scratching. Potential between sample *1* (cathode) and electrode *3* (anode) is maintained by potentiostat *11*, under potentiostatic conditions. The effective current densities (through the open surface area) were of several mA cm^{-2}, which is very small compared with the current densities usually applied in the known electrochemical treatment of metals. The load applied to indenter *5* (with a standard diamond pyramid as a tip) in vertical direction *6* ranged *P* from 10^{-2} to 1 N (for scratching super hard materials). For more precise microscratching tests, the load was reduced to $P = 10^{-4}$–10^{-5} N for the observation of first individual nucleation of dislocations in soft crystals. Synchronous electromotor *8* and reducer *9* control the horizontal movement of indenter *7* with a constant velocity (10–100 mm min^{-1}). Special Luggin-type microelectrode *10* can be placed closely to the indenter tip for observing changes in the electrochemical parameters in the zone of surface damage. The experimental information from working *1* and auxiliary *3* electrodes, microelectrode *10*, and a silver chloride reference electrode was processed with a computer.

The advantages of this method are the following: the experiments are running at room temperature under comparable conditions in the presence of active mobile atoms with the exact control of the amount of this component and in the absence of a liquid phase, that is, without the screening of surface damages. A significant advantage of the method is also the opportunity to remove an oxide film from the metal under cathode polarization, thus, dealing with perfectly clean, original surfaces.[8]

A very strong effect of strength reduction and embrittlement in aluminum under the influence of liquid gallium is well known.[5–7,9,10] With the device described, we performed the microscratching tests of aluminum (99.999%) in a 10 wt% aqueous solution of gallium sulfate. The indenter load *P* was 0.1 N and the indenter tangential velocity was 10 mm min^{-1}. Figure 2 shows the SEM images of two microgrooves on a sample surface in the absence of electric current and with an effective

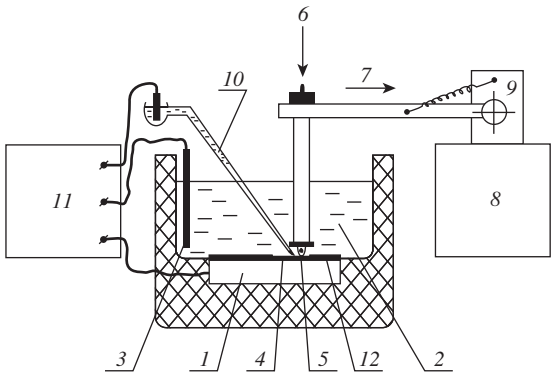


Figure 1 Schematic diagram of the experimental device: (*1*) working electrode (cathode), (*3*) anode, (*5*) scratching indenter, and (*10*) Luggin microelectrode. The further designations are explained in the text.

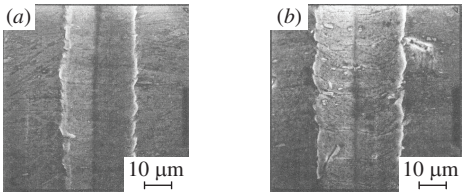


Figure 2 SEM images of microscratches on an aluminum sample made in a 10 wt% aqueous solution of gallium sulfate (*a*) in the absence of electric current and (*b*) under conditions of cathode polarization with the effective current density of 6.8 mA cm^{-2}. Indenter load P = 0.1 N.

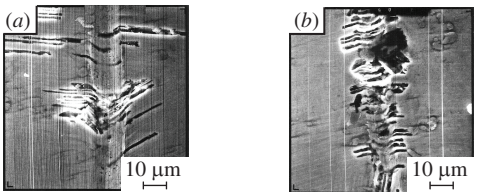


Figure 3 SEM images of microscratches on the surface of a titanium aluminide sample made in a 10 wt% aqueous solution of mercury nitrate under conditions of cathode polarization with effective current densities of (*a*) 2.6 and (*b*) 4.7 mA cm^{-2}. Indenter load P = 0.2 N.

current density of 6.8 mA cm^{-2} at the working electrode potential E = –0.62 V. In the second case, the microgroove width increased by about 20% with no visible cracks. This result indicates the predominance of an adsorption plasticizing effect with respect to the embrittling one due to the specific contact conditions of the relatively soft loading regime and the extremely high initial plasticity of very pure metal.[2,4,11] The hydrogen embrittlement was not observed in these experiments (at the working electrode potential E = –0.62 V).

A popular intermetallide compound, titanium aluminide, is an extremely hard material. The SEM micrographs (Figure 3) show two neighbor microscratches on the sample surface made in a 10 wt% aqueous solution of mercury nitrate with an indenter load of 0.2 N under cathode polarization conditions with effective current densities of 2.6 and 4.7 mA cm^{-2}. In the first case, discrete damage areas are observed, spreading out of the groove lateral faces. In the second case, more severe damages fill the entire length of a groove, and they are localized mainly inside it. The role of a critical amount of an active component in the fracture zone is probably observed here. Experiments with electrochemical reduction of cadmium on titanium aluminide showed increasing damageability during microscratching. Note that the standard electrode potentials of the pairs Hg^{2+}/Hg and Ga^{3+}/Ga are E^0 = +0.854 and –0.53 V, respectively. However, any noticeable evolution or extraction of hydrogen was not observed in both cases. In the latter case, at the working electrode potential E noticeably lower than E^0, this phenomenon was probably due to the high over voltage required for the evolution of hydrogen at the aluminum and titanium aluminide cathodes.

Along with applying to metal ions, this method allows one to observe the effects of reduction of other cations (*e.g.*, hydrogen) in connection with studies on the exclusive hydrogen embrittlement of steels. In principle, the same method makes it possible to use anodic polarization with surface oxidation and adsorption of corresponding active anions. In addition to the aqueous solutions, various low-melting-point salts and eutectic mixtures can be used.

References

1 *ASTM Standard G171-03, Standard Test Method for Scratch Hardness of Materials Using a Diamond Stylus*, ASTM International, West Conshohocken, PA, 2017.
2 E. D. Shchukin, V. I. Savenko and A. I. Malkin, *Prot. Met. Phys. Chem.*, 2013, **49**, 40 (*Fizikokhimiya Poverkhnosti i Zashchita Materialov*, 2013, **49**, 44).
3 L. A. Kochanova, V. M. Kuchumova, V. I. Savenko and E. D. Shchukin, *J. Mater. Sci.*, 1992, **27**, 5516.
4 E. D. Shchukin, L. A. Kochanova and V. I. Savenko, in *Modern Aspects of Electrochemistry*, eds. R. E. White, B. E. Conwey and J. O'M. Bockris, Plenum Press, New York, 1993, vol. 24, pp. 245–298.
5 *Embrittlement by Liquid and Solid Metals: Proceedings of the Symposium Metallurgical Society of AIME*, ed. M.H. Kamdar, Metallurgical Society of AIME, Warrendale, PA, 1984.
6 D. G. Kolman, in *ASM Handbook*, ASM International, OH, 2003, vol. 13A, pp. 381–392.
7 E. Shchukin, Z. Polukarova and V. Savenko, *Liquid Metal Embrittlement in Solids (LME-effect)*, Lambert Academic Publishing, Riga, 2018.
8 Yu. D. Gamburg and G. Zangary, *Theory and Practice of Metal Deposition*, Springer, New York, 2011.
9 S. P. Lynch, in *Stress Corrosion Cracking: Theory and Practice*, eds. V. S. Raja and T. Shoji, Woodhead Publishing, Kirjastus, 2011, pp. 90–130.
10 *Environment-Sensitive Mechanical Behavior*, eds. A. R. C. Westwood and N. S. Stoloff, Gordon and Breach, New York, 1966.
11 *Surface Effects in Crystal Plasticity*, eds. R. M. Latanision and J. T. Fourie, Nordhoff, Leiden, 1977.

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