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Near Surface Modification Affected by Hydrogen Interaction: Global Supplemented by Local Approach

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The current study is centered on elastic-plastic solid interaction with hydrogen. Here, the environment is free hydrogen, from either external or internal origins providing as such aggressive effects. In this context, near surface displacement occurred, beside microcracking onset or growth, significant interfacial weakening, as critical forms of mechanical degradation. Metastable austenitic stainless 316L steel was selected, in order to provide a comprehensive study on bulk surfaces. Global findings on hydrogen effects were supplemented by nanoscale information. Only for the nanosection, Ti/Cu thin films were also included, namely an additional small-volume case. Samples have been charged with hydrogen under low fugacity conditions and the outcoming effects have been sorted out by mechanical response tracking assisted by contact mechanics methodology. Nanoindentation and continuous scratch tests were utilized supplemented by Scanning Probe Microscopy (SPM) visualization. Local resolution provided remarkable input to the global findings, in terms of dislocation nucleation aspects, near surface modification, plastic localization and microfracture onset. In thin layers, the effective work of the adhesion was reduced indicating significant degradation that could be expressed quantitatively. Global/local benefits of the stainless steel system under study made it possible to apply multiscale models describing complex micro-mechanical processes.

Keywords: metastable austenitic steel, hydrogen interaction, nanotests, continuous scratch tests, crystal plasticity.

Introduction. Hydrogen/metal interactive effects have significant implications on surface behavior including structural integrity aspects due to crack stability transition. Regardless the specific enhancing damage origins, irreversible displacement, microcrack initiation and growth beside delamination require special concern from nano-, meso- up to macrostructural scale. The striking point in the current study is based on small-volume experiments and is mainly focused on how hydrogen affects small-volume mechanical behavior. An appropriate factor in analyzing the basic interaction of hydrogen was attributed to variations in the length scale. In elastic-plastic solids with no hydrogen, consistent trends of the length scale have been already established. On this background, hydrogen interaction could be screened for length scales regarding toughness or hardness. The small-volume activity was mainly conducted in a metastable stainless steel system with some findings in hydrogen affecting Ti/Cu thin film. However, a very extensive background was previously established as related to AISI 316L [1–3] regarding possible events that are enhanced by hydrogen. Plastic displacement might have the end result of fracture processes, namely embrittlement or load-bearing capacity limitations. Moreover, surface modification caused by environment introduces issues regarding tribological contact insights. Nanotests also promise new experimental options with implications on quantification of early wear. These elements are highly accentuated in a metastable system in which phase stability is dominated by mechanical or chemical aspects.

Experimental Procedures. *Global Approach*. Macrostudies in austenitic stainless steel included AISI 304, 316 and 310 steels. Mechanical response was studied using fracture mechanics methodology [1–3]. In metastable systems with no hydrogen, austenite decomposition occurred below the *Md* temperature. However, presence of hydrogen enhances martensitic transformation, resulting also in delayed microcracking and ductility reduction [4–6]. Austenite products were identified using X-ray diffraction and the Mossbauer spectroscopy analysis.

Local Approach. For 316L metastable stainless steel nanotests were conducted on top of global tests. Thus, indentation tests to a prescribed load of 100 μN were performed with Hysitron nanoindentation instrument using conical indenter with 400 nm tip radius curvature. Tests were performed prior to hydrogen charging, instantly, post charging and one day after charging. Beside nanoindentation, lateral continuous scratch tests were performed. Hydrogen was also charged by 1MNaOH cathodic charging under current densities in the range of 10 to 500 mA/cm^2. Fine features' visualization was carried out by Scanning Electron Microscopy (SEM) and by Atomic Force Microscopy (AFM). In addition, other experiments regarding thin films affected by hydrogen were conducted. Here, thin films on SiO_2 substrate with and without hydrogen were probed allowing some classification of Cu and Cu/Ti/SiO_2 interfacial bonds to be assessed.

Experimental Results. *Macromethodology*. It became evident that hydrogen provided either by electrolytic cathodic charging or by high-temperature pressure gaseous charging preserves fundamental findings of transformation and alternative fracture modes. The transformation reaction was identified resulting in hexagonal close-packed and body-centered-tetragonal martensitic products. Mechanical response degradation with hydrogen became apparent in all parameters starting with significant surface relief. Delayed microcracking, hydrogen affected near surface layer and modification, as well as enhanced crack growth and degradation of the fatigue strength, were established.

Local Findings. Reproducible displacement excursions at an average load of 200 μN were observed for the noncharged samples. This finding based on nanoindentation load-displacement curves was attributed to plasticity initiation since unloading prior to the excursion load yielded no residual deformation. In contrast, yield initiation in charged specimens occurred at 100–650 μN. One day after charging the yield point ranged between 300–350 μN (Fig. 1). With regard to the scratch test, hydrogen interaction increased localized plasticity along given slip bands by as much as a factor of three. These direct results become highly relevant in the near surface modification evolution in the dynamic sense. In principle, quantitative local strain arguments could be based on measurements of the surface slip height habits (h) and the spacing (s). Surface ultrafine features along the scratch pile-up as well as perpendicular to the scratch pile-up indicated dramatic effects of hydrogen on microplasticity. Even under low fugacity charging, significant variations were measured providing eventually building blocks for multiscale modeling efforts. The Cu/SiO_2 thin film result is shown in Fig. 2 by emphasizing the increase of delamination area affected by the hydrogen environment.

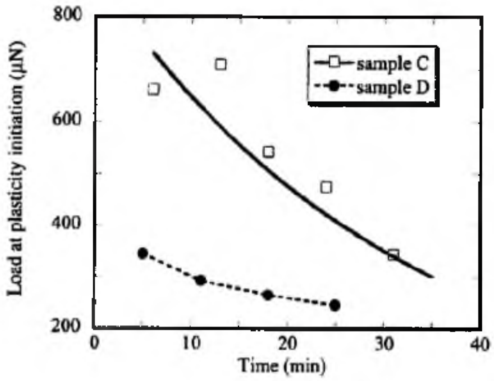

Fig. 1. Load at plasticity initiation vs. time after hydrogen charging.

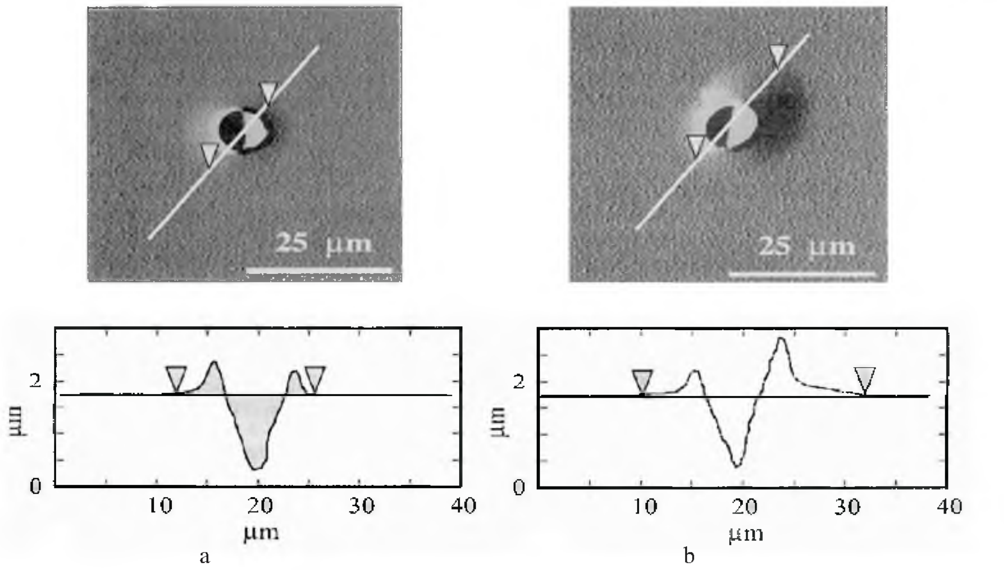

Fig. 2. Indentation induced delaminations in 500 nm Ti/Cu film on noncharged (a) and hydrogen charged (b) samples.

Discussion. Surface modification due to environmental infraction in metastable austenitic stainless steel has at least two origins: firstly, displacements caused by phase stability associated with martensitic phases and, secondly, hydrogen-enhanced localized plasticity that can be measured. These results are experimentally substantiated by the combined program of global/local approach. Pseudo-phases were identified during the transient time by consistent X-ray diffraction and the Mossbauer spectroscopy analysis, and internal friction results were obtained [7]. Moreover, extensive activities by Birnbaum [8] emphasized the local approach by sophisticated in situ Transmission Electron Microscope (TEM) observations. In this context, the current findings by nanomechanical methodology explore fundamental insights in terms of localized slip by AFM as enhanced by hydrogen uptake. Beside measured local displacements, results like microcracking and other damage factors introduce additional detrimental surface modification elements. The described investigation with local resolution of dislocation dynamics bounded to crystal plasticity reflects on wear or tribological contact. For example, Kubota et al. [9] addressed the issue of fretting fatigue in austenitic stainless steel system by concluding the significant life decrease that was caused by hydrogen interaction. Such results combined with basic inherent mechanics become more understandable and can shade light on structural integrity phenomena.

Conclusions. Viable hydrogen embrittlement models [1, 2] can be based on the microapproach input, particularly in terms of dislocation shielding mechanisms developed for the hydrogen-enhanced local decohesion model. The nanoscale results also emphasize the inclusion of microplasticity variations that can explain the wide range data on deformation/hydrogen interaction in elastic-plastic crystalline solids. The following conclusions are made:

1. Hydrogen concentration near the surface in 316L metastable austenitic stainless steel raised the dislocation nucleation load by more than a factor of two.

2. In copper thin film on silica substrate, hydrogen interaction decreases work of adhesive.

3. Nanomechanical tests combined with probe microscopy provide critical experiments resolving the scale relationship to be involved in the embrittlement phenomena.

4. In metastable stainless steel with hydrogen, austenite decomposition enhances surface relief, localized plasticity, microcracking or delimitation, which cause significant surface modification with implication to tribological contact effects.

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