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DEVELOPMENT OF A SURFACE ULTRASONIC WAVE TECHNIQUE FOR THE STUDY OF H ENTRY INTO METALS

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Abstract. - Rayleigh acoustic waves were propagated along the surface of sheet samples of Ni and Fe alloys during cathodic charging. The waves were propagated at frequencies from 2 to 8 MHz, and their velocity and attenuation were measured. Attenuation and velocity both decreased during charging, and then increased again after the charging current was removed. These effects could arise from H entering solid solution or from such extraneous phenomena as the influence of bubbles on wave propagation, the formation or decomposition of films on the metal or polarization effects in the electrolyte. A series of experiments are described which establish that the attenuation and velocity changes were in fact due to H entry upon charging and H egress after charging. The process dominating the changes is the interaction of H atoms with dislocations within the outer 100 to 1000 Å of the sample surface region.

I. Introduction. - Internal friction measurements have been employed [1] in the study of H solubility and H embrittlement (HE) in alloys, but they are of limited use when H enters a sample from a liquid electrolyte because of large background damping. To overcome this difficulty an ultrasonic technique has been developed [2] in which Rayleigh surface waves (RW) are propagated on a material from a transmitting transducer to a receiving transducer while the material is undergoing cathodic charging with H (Figure 1). The change of amplitude of the wave is inversely related to its attenuation (or internal friction) change during charging. Changes in transit time of the wave between the two transducers of fixed distance of separation are related to changes in the RW velocity. The RW penetrates approximately one wavelength \( \lambda \) of the surface, but its intensity decays exponentially with depth [3]. Consequently the wave samples the near-surface region preferentially and is sensitive to changes in attenuation \( \alpha \) and velocity \( v_R \), occurring at depths as small as \( 10^{-1} \) to \( 10^{-4} \lambda \) [4].

For a typical ferrous material, \( v_R \approx 3 \times 10^3 \) m/s [5], so that at a typical test frequency \( f \) of 3 MHz, \( \lambda = v_R f = 10^{-3} \) m; thus the technique can yield information about processes occurring within the first \( 10^{-6} \) m (one μm) of the sample surface. This high resolution, along with the capability for

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Fig. 1: Surface Wave-Polarization Cell.
in situ measurements, were the basis for the charging studies described in this note.

2. Experimental. - The studies were conducted on strips of hot-rolled, low-carbon steel (0.08C, 0.53Mn, 0.011P, 0.008S), and on 50% cold-worked (cw) sheet material of HASTELLOY Alloy C-276 (16% Cr, 16% Mo, 5% Fe, 4% W, 2.5% Co, 0.35% V, 1% Mn, 0.08% S, 0.02% C, balance Ni). The strips were 170 mm x 25 mm x 1.8 mm thick, and were bent to an L shape to be accommodated in the fixture. The surfaces of the strips were polished to a 6 μm diamond finish to eliminate surface roughness as a variable.

As is described in Reference 2, RW transducers (Automation Industries, Type SMZ) were bonded to the strips with stopcock grease (Fisher Nomaq). The ultrasonic signals at frequencies from 2.5 to 8 MHz, were generated, received and recorded by means of a commercial system (MATEC, Inc. Warwick, R.I., USA). The system was tuned, with the sample in air, to maximum received signal amplitude. The electrolyte, 1% H_2SO_4, was then poured into the cell, the sample was activated cathodically at 2mA/cm^2 for 3 min. to clean the surface. Then α and v_R were determined as a function of cathodic current density to 5.5 mA/cm^2 and charging time to 3h. Solutions containing As^3+ were injected into the electrolyte to evaluate this ionic species' effectiveness as a charging promotor (H recombination poison). In addition, Cu^{+2} was added to determine the influence of an extraneous metal ion on α and v_R.

3. Surface Wave Behavior. - As is presented in summary form in Reference 2, two types of waves may propagate along the surface of a material. If the material is thin, of order a few times λ, then a Lamb wave (LW) may propagate. The velocity v at which a LW propagates depends upon the physical properties of the material; moreover it decreases as the thickness of the material and the frequency of propagation increases. The RW, in contrast, propagates on the surface of bodies of thickness much greater than λ, with v lower than the LW velocity and independent of f.

Because v_R is frequency-independent and because the RW can be made to sample thin sub-surface regions through the use of high frequencies (small λ), the wave is an excellent probe for surface properties and surface phenomena. Theoretical treatment indicates that material changes within a layer of less than 0.2 λ have the most pronounced effect RW propagation.

The objective of these experiments is to relate H behavior during cathodic charging to changes in RW behavior. Since RW, LW or hybrid transition waves may propagate on the sample surface during the 10^-4 s transit times involved, it was necessary to establish that RW conditions exist. This was accomplished in experiments that showed that the waves propagating had minimum velocity which was independent of the propagation frequency.

In Figure 2 are displayed α and relative velocity as a function of f for a C-276 L-bend specimen in the electrolyte at the rest or corrosion potential. The velocity data are relative to a handbook value [5] of the RW velocity, v_o = 2.9 x 10^5 cm/s, so a decrease in pulse arrival time manifests itself as an increase in the ratio of velocity v to v_o.
For the one mm sheet material used in these experiments, \( v \) becomes independent of \( f \) above 6 or 7 MHz. At lower \( f \), \( v \) increases with \( f \), so LW conditions must prevail. The predicted penetration depth at any \( f \) is essentially \( \lambda \), i.e. \( v/f \), which may be calculated for any combination of \( v \) and \( f \) employed. These measurements are consistent with the calculated values which indicate that below 6 MHz, the wave penetration depth is greater than 0.5 mm and therefore that Lamb rather than Rayleigh conditions obtain. These data show that surface wave theory generally describes wave behavior in this experimental system and that for the material and geometry employed, RW conditions are established at frequencies greater than 6-7 MHz.

Also evident from Figure 2 is that \( \alpha \) increases (i.e. pulse amplitude decreases) as \( f \) increases. In fact then, the thinner the region sampled by a wave of fixed input energy, the greater the attenuation of the wave. Since most material-dependent acoustic wave damping losses increase with frequency \([6]\), the attenuation data suggest that the waves are sampling intrinsic damping processes within the near-surface region of the alloy.

4. Extraneous Losses vs. Hydrogen-Related Losses. The data on the unpolarized alloy sample suggest that RW can be propagated in the system described and that their behavior provides information related to physical processes occurring in the alloy of interest. On the other hand, once a sample has been polarized, a number of extraneous acoustic energy processes not related to the structure or properties of the alloy may influence RW behavior. These processes have been documented in the literature and include the influence of gaseous phases (e.g. \( \text{H}_2 \) or \( \text{O}_2 \) bubbles) and formation and decomposition of thin films (e.g. passive films). In Reference \([2]\) it is shown that these processes do not dominate H-related behavior in this technique. Several experiments which underscore the sensitivity of the RW system to H-related phenomena are emphasized here.

Typical attenuation-time behavior before, during and after polarization is shown in Figure 3. When cathodic polarization \( E \) of about 250 mV\(_{\text{SCE}}\) is applied (corresponding to an applied current density of 4.2 mA/cm\(^2\)), received pulse amplitude instantaneously increases, and correspondingly \( \alpha \) decreases. At fixed current density, \( \alpha \) gradually decreases further over a 5 min. period, although fluctuation or noise in the signal is observed. At higher current densities, both the instantaneous and the graduate decrease in \( \alpha \) are even larger; thus it is clear that cathodic polarization causes \( \alpha \) to decrease. These attenuation changes are reversible. When the cathodic
potential is removed, $\alpha$ increases instantaneously, then further increases gradually as it recovers toward its original value. These data strongly suggest that the decrease in $\alpha$ is associated with H entry into the Ni alloy and the increase is related to the reversible H egress.

Data on the steel lead to similar conclusions [7]. At a given polarization, $\alpha$ decreases markedly when 2 mg/l of As$_2$O$_3$ is added to the electrolyte (Figure 4a). An identical effect was observed for the Ni alloy [2] and both effects are consistent with the known H-recombination poisoning effects of As, which promote the entry of H atoms into the sample surface.

The possibility exists that the decreases in $\alpha$ and $\nu$ in the presence of As are not related to H. Ionic species change the capacitance of the electrolyte at a sample surface during charging, and such changes may influence RW behavior. Moreover, As can plate out on Fe and the metallic film could influence RW behavior. For these reasons the possibility that extraneous ions may influence $\alpha$ and $\nu$ was examined by injecting a fairly concentrated solution (0.5 g/l) of CuSO$_4$ into the electrolyte. No change in $\alpha$ was observed (Figure 4b) although Cu deposition on the sample surface was visible to the naked eye. This is further evidence that the decrease in $\alpha$ and $\nu$ are related to the entry of H atoms into the sample rather than to any capacitance or plating effects.

Final evidence that the reversible changes in $\alpha$ during charging or outgassing
Fig. 5: Variation of $\alpha$ with type of polarization and H-recombination poison concentration in the Ni alloy.

Another extraneous effect which may influence $\alpha$ is the creation or degradation of passive films. During anodic polarization (Curve 2 - Figure 5), a passive film forms. If the sample is immediately polarized cathodically (Curve 3), $\alpha$ decreases, but to a much lesser extent than that observed in a sample which has not been polarized anodically. Only after several hours of cathodic polarization with attendant film removal, will the behavior observed in Curves 1, 4 and 5 be reproduced. The necessity of conducting experiments on film-free surfaces is evident, and is the basis for the cathodic pre-treatment procedure employed.

5. Hydrogen-Related Behavior. - The experiments discussed thus far show that the RW experiments allow monitoring of H-entry and egress. The internal friction process which couples H-behavior to $\alpha$ is the pinning of near-surface dislocations during charging and their unpinning during egress. Data which indicate this are summarized in Figure 6.

The dotted curve shows normalized attenuation as a function of cathodic current density after 10 min of charging. The data are presented relative to $\alpha_\infty$, the asymptotic maximum value of $\alpha$ observed after long-time recovery from cathodic charging. The gradually-changing component of $\alpha$ decreases as current density increases, an effect which is due to the entry of increasing amounts of H into the alloy surface at the higher cathodic polarizations. If H is assumed to penetrate by bulk diffusion, then 600 s of charg-
ing is sufficient for H to move $2 \times 10^{-6}$ m inward, since the diffusivity of H is about $2.5 \times 10^{-13}$ m$^2$/s in this alloy [8]. Effects in a layer of this thickness are readily measured at a RW frequency of 6 MHz.

The solid curves in Figure 6 show recovery of normalized attenuation after polarization is removed as a function of square root of $t$, the recovery time. The initial rapid recovery, presumably due to electrolyte de-polarization effects, is evident. The gradual recovery of $a$ is not described by $t^{1/2}$ kinetics expected for simple H-egress by bulk diffusion.

The lack of agreement with bulk diffusion kinetics may be related to the trapping of H atoms by dislocations. A substantial H atom-dislocation interaction has been shown to exist in austenitic stainless steels, [9] which are similar to this alloy, so H atoms introduced by charging may be segregating to dislocations. As they arrive, they may pin the dislocations and diminish the component of attenuation due to dislocation damping; thus the gradual decrease in $a$ during charging may be evidence of the H-dislocation interaction. When the cathodic potential is removed, the concentration of H on surface decreases, and H atoms may leave the dislocation and return to the electrolyte. As the atoms leave, the dislocations become unpinned, and dislocation damping (and therefore $a$) increase. Analysis of these data [2] indicates that the recovery in $a$ follows a $(\text{time})^{1/4}$ kinetic law, behavior consistent with the kinetics predicted [10] for the unpinning of dislocations as H atoms leave dislocation atmospheres.

In summary then, the RW system depicted in Figure 1 and the experimental procedures described in this paper indicate that surface ultrasonics provides a powerful tool for the study of H entry and egress in alloys. H behavior within the first 100 to 1000 Å of the surface may be monitored by way of observation of changes in dislocation damping in the near surface region.

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7. References.