

THE DECREASE OF LATTICE PARAMETER OF THIN FILMS CAUSED
BY CATHODIC CHARGING OF HYDROGEN

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The phenomena that take place when some b.c.c. metals are cathodically charged with hydrogen are being studied by x-ray diffraction, and some preliminary results and a plausible explanation have been reported (1). Briefly, the lattice parameter calculated from Bragg peaks obtained from diffraction by metal near the surface of the sheet opposite the charging surface increases at a rate that is extremely low in view of the known diffusivity of hydrogen in the metal. In addition, different Bragg reflections lead to different values of lattice parameters and to different time dependencies; also, grain rotation occurs. The suggested mechanism for these phenomena involves large amounts of plastic deformation caused by stress generation caused by hydrogen concentration gradients. We report here an additional phenomenon that occurs in thin metal films sputtered upon a much thicker metal substrate when the latter is cathodically charged with hydrogen. A provisional explanation is offered.

Experimental

Upon a 0.5 mm-thick sheet of annealed polycrystalline Ti-30 Mo alloy, Ta is sputtered in an environment of 90% argon and 10% oxygen, forming an amorphous TaO_x layer of about 75 nm thickness. Sputtering of Ta is continued in argon at 4×10^{-3} Pa, producing a metallic tantalum layer about 200 nm thick. The specimen is annealed to produce a layer of bcc tantalum of normal lattice parameter. The resulting three-layer specimen is mounted in a cathodic charging device fitted into a Siemens 500 D diffractometer. From a solution of 5 volume % H_2SO_4 , hydrogen is charged at a charging current density of $250 A/m^2$ into the alloy side of the specimen. The opposite side, that bearing the thin Ta layer, is exposed to air and subjected to x-ray diffraction during the charging operation. Bragg reflections from both the alloy substrate and the overlying Ta film are followed during the charging. The x-ray beam covers about 40% of the surface of the sample, representing about 7000 alloy grains.

Results and Discussion

Fig. 1 displays the results of such a procedure. The increase of lattice parameter, a , of the Ti-30 Mo alloy substrate as calculated from various Bragg diffractions has been observed before, and has been previously discussed (1). The decrease of the lattice parameter of the Ta film is unexpected and is the subject of this note. If Ta metal is sputtered onto the Ti-30 Mo sheet, without an intervening oxide layer, similar results are obtained. One can deposit TiO_x and Ti upon the alloy (Fig. 2), or b.c.c. iron (Fig. 3), and qualitatively similar results are obtained. The lattice parameter of the overlying thin film decreases concurrently with the increase in the lattice parameter of the substrate.

It is difficult to conceive of possible physical causes for the shrinkage of the lattice parameter of the thin metal layers that withstand close scrutiny. One might, for example consider that the bond between the thin metal film and the substrate persists unbroken during the hydrogen charging, and as the substrate expands because of the hydrogen absorption the film is thereby forced to expand in the lateral direction. This causes a Poisson contraction in the dimension normal to the plane of the film, which is the dimension that affects the Bragg diffraction. However, this explanation is not consistent with the observation that the absolute value of the negative Δa of the film can be as large or larger than the positive Δa of the substrate at any one value of duration of charging. Nor is it consistent with the observation that if the cathodic charging is done on the film side the Δa of the film is negative and the Δa

of the substrate is positive. This observation also disposes of another conceivable hypothesis, that the negative Δa of the film is due to an overall bending of the specimen produced by the hydrogen-caused expansion of the substrate alloy just below the input surface. Finally, the effect of hydride formation in the metal film should be considered. Although diffraction lines from hydrides either of the film metal or of the substrate metal have not been observed, one might argue that they exist in the film but have escaped observation. However, it seems very difficult to conceive how such a second-phase precipitation could generate a lattice contraction in the direction normal to the free surface. Nevertheless, the possibility of hydride formation in Ta and Ti was the motivation for our use of iron as the overlying film since iron does not form hydrides. Our finding that an iron film also exhibits a negative Δa upon cathodic charging rules out hydride formation as having any relevance to the phenomenon.

One possible explanation remains that cannot be dismissed out of hand. We offer it in the spirit of a working hypothesis to be examined by further work. We note that the cathodic charging of Ti-30 Mo alloy is accompanied by much plastic deformation caused by H-concentration-induced stresses (1). Fig. (4) shows slip markings on the alloy surface opposite the charging surface of the sheet specimen. Clearly, the overlying film of metal will be moved relative to its original plane by the up and down thrusts represented by the slip bands. If various slip systems are operating within any one grain, as is most probable, the result will be to produce a mesa-like microtopography so that the metal film is broken up into discrete islands such that cross-sections of the film have been converted to free surfaces. Such a configuration would provide the film metal with a much larger surface/volume ratio than does the initial planar film.

We suggest that the thermodynamic surface stress (2,3) of the film metal is of tensile character, so that the contractile force in the surfaces of the plasticity-caused protuberances puts the interior atoms of the protuberances into compression. This is the same phenomenon whereby the lattice parameters of extremely small particles of silver (4,5) and of gold (6) are smaller than those of the same metals in large sizes. Thus, the observed lattice parameter of the film metal continues to decrease with time of hydrogen charging because with increasing amount of surface rumpling an increasing fraction of the film volume lies within protuberances of large ratio of area to volume, and hence in the compressive stress field produced by the tensile surface stress. Clearly, the reason why this phenomenon is not observed for the substrate metal as its surface is rumpled by the cathodic charging is that the contribution to the x-ray diffraction intensity from atoms far from the surface (penetration distance of the x-rays is more than 2 μm) overwhelms that from atoms affected by the surface stress about protuberances.

The surfaces of the protuberances have a complex chemistry. Since the metal film is in contact with air there is undoubtedly an air-formed oxide layer, or at least, adsorbed oxygen. In addition, hydrogen from the volume of the metal may adsorb at the interface between the oxygen layer and the film metal atoms. The magnitude and sign of the surface stress are controlled by that chemistry. To estimate the mean protuberance dimension needed to obtain the decrease in lattice parameter observed we may use $\sigma_s \approx 1 \text{ N/m}$ as a reasonable value, and assume hemispherical shapes for the protuberances. The mean radius can be estimated from $r = 2(1-2\nu)\sigma_s E_y^{-1}(\Delta a/a)^{-1}$. Taking the Young's modulus, E_y , as 10^{10} N/m^2 , the Poisson ratio ν as 0.3, and $\Delta a/a$ as -2.4×10^{-3} , a typical value from our experiments, we find $r = 3 \times 10^{-6} \text{ cm}$, a not unreasonable number.

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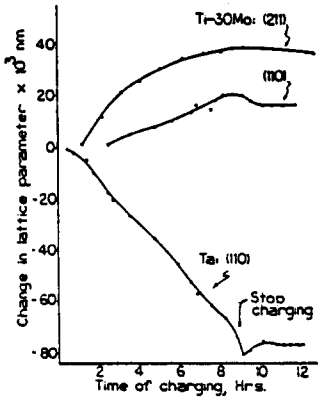


FIG. 1: Three-layer sheet specimen composed of 0.5 mm-thick Ti-30 Mo alloy, 75 nm-thick tantalum oxide, and 200 nm-thick Ta. Hydrogen was charged into the alloy side at 250 A/m², and the consequent changes with time of the lattice parameters of the alloy substrate and of the Ta film were calculated from the observed Bragg peaks from the indicated planes.

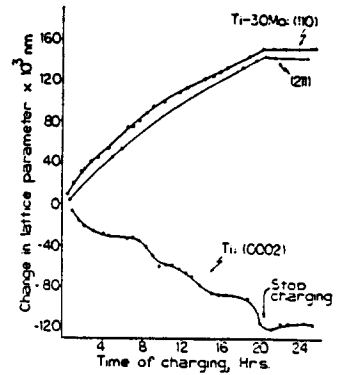


FIG. 2: Three-layer sheet specimen: 0.5 mm Ti-30 Mo, 80 nm titanium oxide, and 150 nm Ti metal. Hydrogen was charged into the alloy side at 36 A/m².

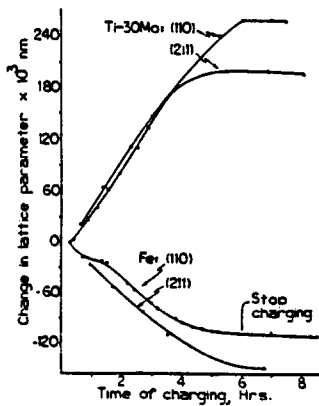


FIG. 3: Two-layer sheet specimen: 0.5 mm Ti-30 Mo and 240 nm iron (b.c.c.). Hydrogen was charged into the alloy side at 250 A/m².

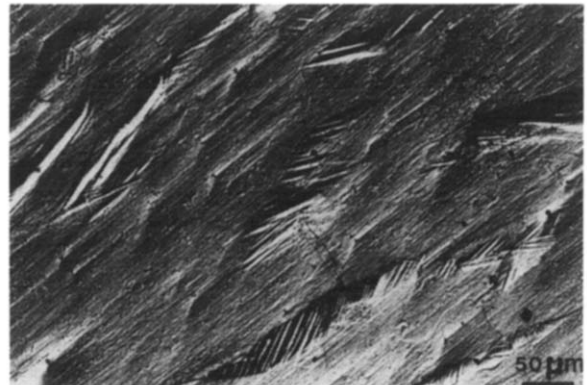


FIG. 4: Light micrograph showing slip lines on the Ti-30 Mo surface opposite the charging side of a specimen 200 μm thick. Current density for charging was 250 A/m².