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Oxidation Processes in Magneto-Optic and Related Materials

Paul A. Lee#, Neal R. Armstrong, James L. Danziger and Craig D. England

Department of Chemistry
University of Arizona
Tucson, AZ 85721

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ABSTRACT

The surface oxidation processes of thin films of magneto-optic materials, such as the rare-earth transition metal alloys have been studied, starting in ultrahigh vacuum environments, using surface analysis techniques, as a way modeling the oxidation processes which occur at the base of a defect in an overcoated material, at the instant of exposure to ambient environments. Materials examined have included FeTbCo alloys, as well as those same materials with low percentages of added elements, such as Ta, and their reactivities to both O_2 and H_2O compared with materials such as thin Fe films coated with ultrathin adlayers of Ti. The surface oxidation pathways for these materials is reviewed, and XPS data presented which indicates the type of oxides formed, and a critical region of Ta concentration which provides optimum protection.

I. INTRODUCTION

Oxidation and/or corrosion of magnetic and magneto-optic materials has become of considerable interest, since oxidation of these materials leads to loss of critical magnetic properties and thus, a loss of encoded data. Many of the materials in use or under consideration for MO data storage consist of binary, ternary and quaternary mixtures of transition metals and rare earth metal's (RE/TM), all of which react readily with ambient gases to form oxides with large heats of formation [1]. The RE/TM family is composed of TbFe, TbFeCo, GdFeCo, or TbFeCoM, where M is another metal such as Gd, Ti, Zr, Ta, Pt, etc., that has been added to enhance its stability towards oxidation and corrosion[1-9]. A systematic study of the various oxidation pathways in these materials has been carried out for certain systems[6-8,10,11].

The reaction of these materials can be classified as primarily surface oxidation processes under low and high humidity conditions, and "pitting corrosion". The former process appears to be primarily caused by the reaction with oxygen, and other strong oxidants in the atmosphere, and can occur uniformly along a metal surface, wherever contact with the atmosphere has been allowed (i.e. at the base of a defect in a protective overlayer used to generally protect the medium). Pitting corrosion represents a more destructive process, in that it generally involves the formation, dissolution and massive migration of oxides of the metals within the MO material. This process is facilitated by trace water in the environment, which can condense in defect sites, and by trace halides or other elements which accelerate the dissolution of oxides of many of the metals used in the RE-TM alloys[12].

Other recently developed MO materials consist of multilayers of two transition metals such as Pt/Co or Pd/Co which, due to the less reactive nature of Pt and Pd, and the lower reactivity of Co with respect to Tb, may promise to be more stable than RE-TM alloys[13-16] with the potential added cost of processing multilayer materials.

It has now been well documented that the addition of small levels of a fourth metal to the RE/TM alloys alters the oxidation pathways sufficiently to provide highly desirable protection of these materials, although the exact mechanism is still debated [2-9]. The addition of these metals, while satisfying the technological requirements for enhancing stability of the RE/TM alloy, without serious deterioration of the magneto-optical properties, poses more basic questions regarding the oxidation processes occuring at the surface of the material.

Many other methods have been used to protect the media from oxidation and subsequent corrosion, which include a variety of overprotection schemes[17-19]. With real materials, however, pinholes and other defects always develop, which expose the media to ambient conditions (albeit on a small distance scale initially) and there is no real way to prevent various forms of oxidation from occuring. Protection afforded by overcoating, and especially by an added fourth element, at low concentrations, can slow the process to bring it within technologically acceptable limits.

In our program, we have elected to model the initial steps of the corrosion process, which might occur at the base of a freshly produced defect site in a protective overlayer. We assume that, at the instant of formation of the defect, there is nearly clean and quite reactive metal alloy exposed, which undergoes rapid reaction to form oxides of various sorts, which ultimately control the stability of the RE-TM alloy in the vicinity of this defect. This initial reaction process can be modeled by producing a clean surface of the alloy, in ultrahigh vacuum conditions, and then exposing to low partial pressures of either O_2 or H_2O (or both), and systematically increasing their pressures until atmospheric conditions are achieved. X-ray photoelectron spectroscopy (XPS) is primarily used to characterize the extent of near surface reactions, as well as the molecular nature of the oxides formed, which confines the extent of our understanding to the first ca. 100Å of the RE-TM surface[20].

Most of our attention has been recently focused on the characterization of the differences in reactivity of RE-TM alloys (FeTbCo) to which have been added various amounts of a fourth element modifier[21,22]. Elements such as Zr, Ta, Nb, Ti, etc. are known to form stable, and stoichiometric oxides, which can act as a diffusion barrier to O_2 and H_2O. Migration of these metals has been seen in some cases, in reponse to exposure to O_2. Migration of both Fe and Tb is almost always observed, once their oxidation begins. It is of interest to determine if this simple protocol we have developed can lend some predictive capability to the determination of an optimum amount of the fourth element modifier, in addition to providing some mechanistic detail as to the corrosion protection mechanism. As will be discussed below, tantalum as a modifier can be quite efficient in its reaction with O_2, but it appears that there may be a critical Ta concentration which provides the best protection. Higher levels of Ta may actually form oxides which disrupt the microstructural environment sufficiently as to facilitate diffusion of O_2, and actually increase near surface reactivity.

2. EXPERIMENTAL

A number of methods have been used to study oxide film formation on a clean surface of the MO material in question, under highly controlled conditions (starting with UHV), and have been described elsewhere[21,22]. We have studied a number of metals directly and indirectly related to M-O systems using a combination of Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectrometry (RBS). These metals and alloys include Fe, FeTi, TbFeCo, TbFeCoM (where M = Zr, Ta, or Pt).

Exposure of the MO materials to oxygen and water was carried out by first removal of a thin Al protective coating (300Å) used to provide stability during transfer from the sputter deposition system. This sputtering step also removed small amounts of oxidized metal, to expose the alloy in as clean a state as it was produced (which means that there is always a few atomic percent oxide in the film to begin with). Dosing with O_2 and H_2O could then occur, between analysis by XPS and AES, at partial pressures of 1×10^{-7} to 1×10^{-5} torr, through a leakvalve, for Langmuir exposures of 1-10,000 L (where 1 langmuir = 1×10^{-6} torr-sec).

Clean Fe and FeTi thin films were made by evaporation from Fe and Ti wires. TbFeCo and TbFeCoTa were produced by both single and multiple target sputtering on doped Si wafers for RBS and XPS/AES analysis Analysis by RBS indicated that the films all had ca. 65-70% Fe, 19-21% Tb and 7-11% Co, and 1-5% Ta. Typical samples consisted of 1000Å of metal or alloy protected with 300Å of Al.

3. RESULTS AND DISCUSSION

3.1 Oxidation/Corrosion Processes, An Overview:

The reactions of O_2 and H_2O with clean, single element, metal surfaces have been extensively studied, and several excellent reviews exist detailing the present understanding of those processes[1,23-30]. Surface oxidation processes, through the reaction with O_2, occur either through the formation of $O_2^{=}$ or $O_2^{-\cdot}$, depending upon the partial pressure of O_2 at the interface with the ambient, which controls the concentration of anion states formed by the reduction of oxygen (Figure 1). Incorporation of the oxide next occurs by a place exchange mechanism, and subsequent growth of the oxide can occur by diffusion of the oxygen anion, and/or by diffusion of metal cations through the growing oxide. Both processes are field assisted, and therefore decrease in rate with time, since the concentration of anions at the surface of the material is fixed by the partial pressure of the oxidant, and the increasing thickness of the oxide decreases the field strength at the interface where oxide formation is occuring[24]. Secondary growth of the oxide can also continue through pores or other surface defects. The formation of this passivating oxide in some metal/alloy systems helps to prevent or inhibit the interdiffusion of oxidant to the metal/oxide interface.

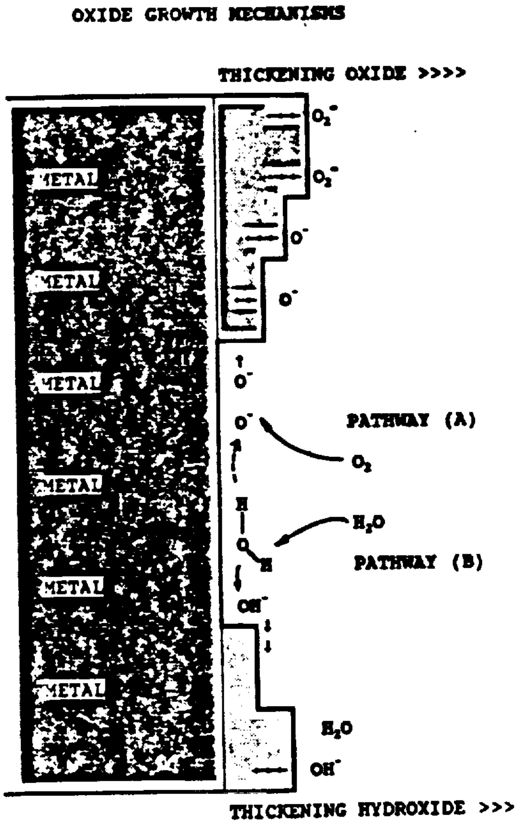

Fig. 1 Oxidation pathways for oxygen and water on a metal surface.

Given the tendency of metals such as iron and cobalt to form relatively stable oxides by this process, it might be expected that such near surface oxidation would not be a significant problem for the RE-TM alloy MO technologies[16,17,29,30]. The presence of the rare earth metal however, coupled with the extremely thin films normally used, can add significance to this oxidation pathway. Surface oxides can often be formed, during exposure to atmospheric pressure O_2, which extend 100Å or more into the material, which can be an appreciable fraction of the total film thickness in a MO disk[6-8]. The oxides of the rare earth metals, which have a chemistry similar to calcium, can often support diffusion of both anions, cations, and even the zero valent metal itself, as has been shown previously by our studies of various alkali and alkaline earth metals[28].

The reaction of H_2O with these clean metals is believed to proceed by way of the chemisorption of molecular water (only seen at extremely low temperatures) and the subsequent formation of a surface hydride, and a hydroxide ion, followed by the further dissociation of the hydroxide to form another hydride and incorporated oxide anions (Figure 1)[1]. It has been our experience that many of the pure metals, and the metal alloys, show a significantly lower reaction tendency toward water than oxygen, in the gas phase, at low partial pressures, which we believe to be due to the presence of surface hydrides already present at near saturation levels under most vacuum and atmospheric characterization conditions. Only under conditions of high partial pressures of gaseous H_2O (i.e. the "wet oxidation" conditions described in other reports[9]), is appreciable reaction seen. This should not be construed, however, as inconsistent with the important role that H_2O plays in pitting corrosion, where the presence of condensed water acts to enhance diffusion of anions and cations in a microcorrosion cell, and supports the electrical double layer, which supports the electric field, which drives the pitting corrosion process[33]. When hydroxides are formed, as the result of the reaction with water, it is generally assumed that such hydroxide films are not chemically as stable as stoichiometric oxide films, and do not provide the type of diffusion barrier to O_2, etc. that stoichiometric oxide films provide. It is therefore essential to understand the nature of the reaction of both gaseous O_2 and H_2O, as the initial steps in the corrosion process.

The oxide layer, once formed, regardless of stability, can be an environment for further corrosion processes. In moist environments water condenses in microscopic regions on the surface of the metal or metal-oxide. Soluble species can then form (especially in the presence of halides) that leave pits upon dissolution, thus opening the surface of the alloy to further oxidation, a phenomenon known as pitting corrosion. Solution pH within the microscopic corrosion cell is often a controlling factor in the rate of pitting corrosion, as are mechanical stresses introduced into the metal film, and/or one of the protective overlayers[32].

3.2 Surface Oxidation Processes of Clean FeTbCo, FeTbCoTa:XPS Results

The reactions with O_2 and H_2O, of the clean metals, as would proceed at the base of a freshly opened defect site, have been largely studied by XPS, and compared with previous studies of pure Fe, and Fe films modified with adatom metal layers such as Ti[22].In the studies of the RE/TM alloys, the XPS core level spectra for the Fe(2p) and O(1s) transitions have been most revealing of the types of chemical processes ongoing during exposure to O_2 or H_2O. The photoelectron spectra for Tb or the other rare earths are complicated, show subtle shifts during the oxidation process, and cannot generally be used as an indication of the real growth of oxide films in the alloy. Fourth element modifiers such as Ta also have large enough XPS sensitivities as to provide for an additional monitor of oxidation processes.

A wide range of materials including Ti, Al, Ta, Zr, Au, Ag, Pt etc., have been used to try to inhibit surface oxidation and pitting corrosion[1-9]. Studies of Ti modified thin films showed a significant decrease in pitting corrosion[4,5]. In our initial studies we chose to model the protection afforded by trace levels of Ti in the RE-TM alloy to both surface oxidation and the initial phases of pitting, by addition of discontinuous adlayers of Ti to a pure Fe surface, exposed to both O_2 and H_2O in the gas phase[33]. The initial oxidation of Fe is critical to the pitting corrosion process, and any protection which reduces the reactivity of Fe toward both O_2 or H_2O, and/or which may provide a diffusion barrier to those reactants. Thin Fe films were evaporated from resistively heated Fe filaments onto a Mo substrate and a 3-10 Å discontiuous layer of Ti was deposited over it. In Ti films greater than 10 Å the overlayer apparently became continuous and bulk oxidation properties were observed.

At Ti coverages of 3 Å some modification of the oxidation process for Fe did occur as shown in Figure 2. The three Fe(2p) XPS spectra show the lineshapes for the clean Fe (or FeTi) surface, and that same surface after exposure to low amounts (600L) of O_2, for both the bare surface, and one which had been modified with the 3Å Ti adlayer. For the unprotected surface there is extensive oxidation, as expected from several previous studies[25,26]. For the Ti-modified material, the extent of oxide formation has been reduced by ca. 50%, as deduced from the lower oxide film thickness on this sample (ca. 27Å versus 13Å on the unmodified Fe surface). In these studies the Ti overlayer is completely oxidized to TiO_2, and an exposure of 5L of O_2 to this Ti-modified Fe film is nearly enough to oxidize the entire Ti metal overlayer, which indicates how aggressive such a modifier can be in reacting with an incoming oxidant. Our previous work, along with that of several other investigators, has shown that the type of oxides formed on the Fe surface are combinations of FeO, Fe_3O_4, and at high enough oxygen exposures, Fe_2O_3[26]. This is essentially the type of oxidation pathway taken for Fe in the RE-TM alloy thin films, as seen below.

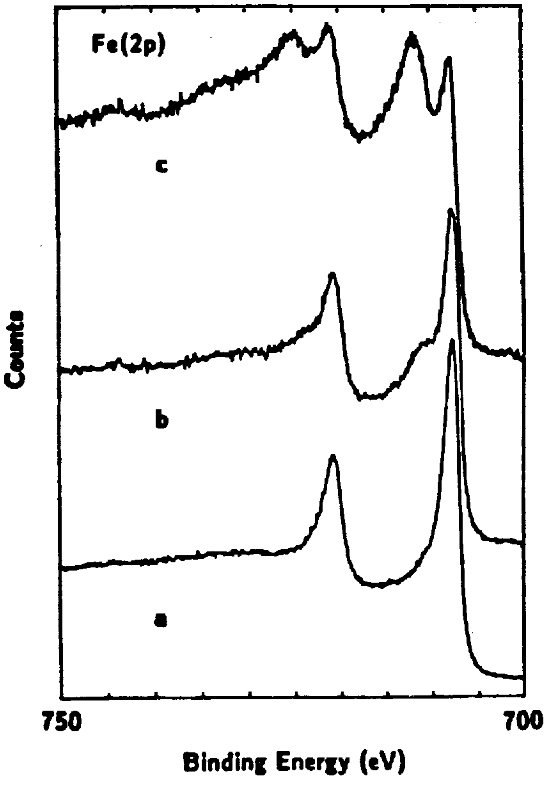

Fig. 2 Fe(2p) XPS lineshapes for 3Å of Ti on Fe. a) "Clean" Fe/Ti, b) after exposure to 600L O_2 and c) Clean Fe exposed to 600L O_2

Low levels of water exposure to the Ti-modified Fe thin films does little to oxidize the Fe, but results in a range of oxidation states for the Ti, unlike the case for O_2 exposures (Figure 3). This wide range of oxidation states of Ti suggests that a very heterogeneous oxide will result from the reaction of H_2O with the modifier, which would be unlikely to provide a diffusion barrier (or an electronic barrier) toward further oxidation processes.

It has been widely reported that exposure of TbFeCo to O_2 typically results in initial oxidation of the Tb (in our studies to a depth less than 50Å), followed by oxidation and surface migration of Fe[10,11]. From these studies it appears that the surface of the oxidized TbFeCo thin film is composed of a terbium oxide layer over a mixed terbium/iron oxide at the interface with the unreacted metal alloy. Oxidation of the RE-TM thin film by H_2O results in the formation of a Tb oxide and hydroxide layer but does not oxidize the Fe appreciably, consistent with the results shown above for the Ti-modified thin films. This oxidation by H_2O still causes the migration and enrichment of Tb in the near-surface region[7].

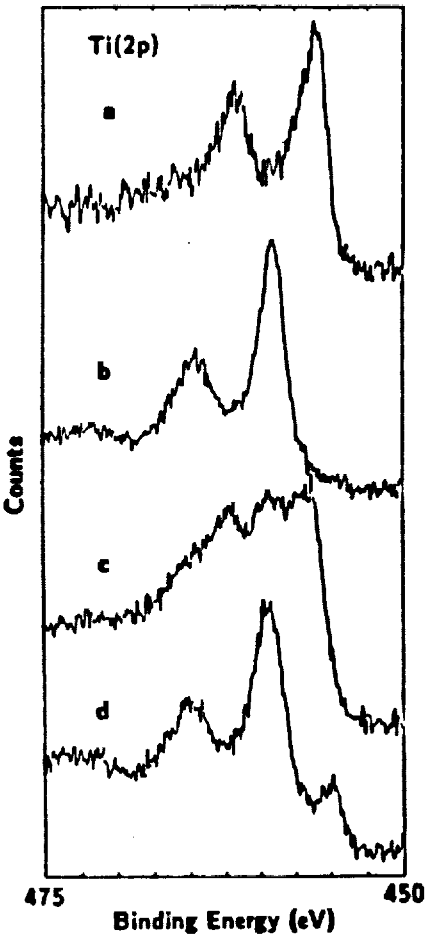

Fig. 3 Comparison of Ti(2p) Lineshapes for 3Å of Ti on Fe. a) Clean, b) 600L O_2, 600L H_2O, and 5L O_2 followed by 600L O_2.

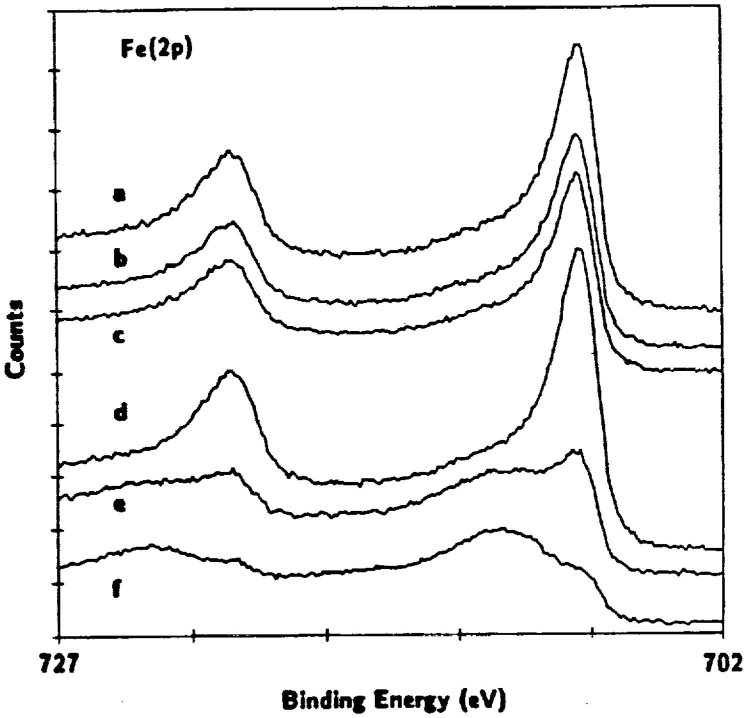

Fig. 4 Fe(2p) XPS lineshapes for TbFeCoTa 1% and 4% exposed to oxygen and water. a) "Clean", b) 1% Ta exposed to 1000L H_2O, c) 4% Ta exposed to 1000L H_2O, d) "Clean", e) 1% Ta exposed to 1000L O_2, f) 4% Ta exposed to 1000L O_2.

Oxidation studies of TbFeCo-Ta films, with Ta loadings of 1% to 4%, show that there are significant differences in the amount of protection associated with different Ta loadings in these thin films. From the Fe(2p) XPS spectra in Figure 4, it can be seen that there is considerable reaction of Fe with O_2 for both films, but that the extent of formation of the Fe^{+2} and Fe^{+3} oxides is lessened in the films with 1% Ta versus those with a 4% or higher loading. The Ta(4f) spectra for these samples (Figure 5) both show that extensive oxidation has occured to the Ta incorporated into these films, with the 1% Ta having been virtually completely oxidized by this low exposure to O_2 or by residual oxidants. Some migration of Ta occurs along with this sacrificial oxidation. The reasons for the better protection afforded by the lower Ta loading are not known, but since this is a consistent observation, it is tempting to suggest that the higher Ta loadings react with O_2 sufficiently to cause some microstructural changes in the near surface region, as a result of Ta migration to form its oxide, which actually open up sections of the RE-TM alloy to O_2 which might otherwise have remained protected.

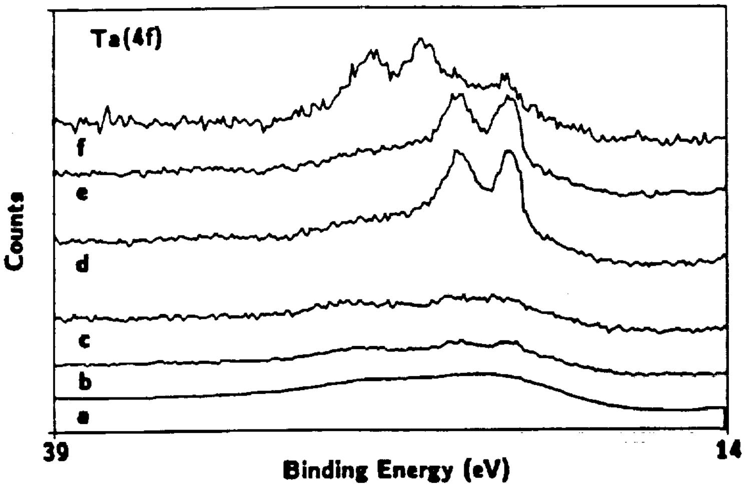

Fig. 5 Ta(4f) lineshapes for TbFeCoTa 1% and 4% Ta materials exposed to oxygen an water. a) "Clean" 1% Ta, b) 1% Ta exposed to 1000L H_2O, c) 1% Ta exposed to 1000L O_2, d) "Clean" 4% Ta, e) 4% Ta exposed to 1000L H_2O, f) 4% Ta exposed to 1000L O_2.

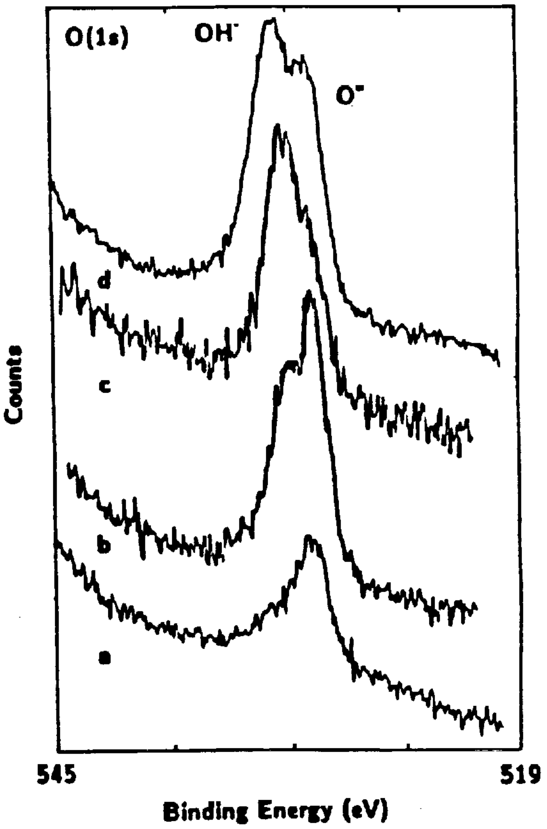

Fig. 6 O(1s) XPS lineshapes for water dosing on TbFeCo and TbFeCoTa 1% and 4% Ta films. a) Typical "Clean" film, b) 4% Ta exposed to 1000L H_2O, c) 1% Ta film exposed to 1000L H_2O and d) TbFeCo film exposed to 600L H_2O.

Oxidation of Ta-modified TbFeCo by water in this same near surface region results only in differences in the types of oxides seen in the 1% Ta film vs. the 4% Ta film. The difference is most exemplified in the O(1s) lineshapes of Figure 6. Unmodified TbFCo thin films exposed to low levels of H_2O show the existence of both oxide and hydroxide forms in the oxide layer, with the hydroxyl form being the most dominant. The assumption is that the oxide forms arise from reaction with both Tb and Fe (minimal reaction with Fe is seen in these cases) and that the hydroxides arise strictly from Tb. The 1% Ta material exhibited the same behavior as the unmodified FeTbCo films. Interestingly, in the 4% Ta materials the oxide formed was in greater proportion to the hydroxide than in the unmodified, or lower Ta content films. Since Ta will not readily form hydroxides, it is assumed that those hydroxides detected are strictly from the formation of Tb-hydroxides, and that these are favored in the lower Ta-content films.

4. CONCLUSIONS

The protection afforded a RE-TM alloy by a fourth element modifiers such as Ta may be viewed from a relatively simple perspective, even though the actual surface chemistries ongoing in the near surface region may be quite complex. There is a strong desire to add modifiers which will react preferentially with both O_2 and H_2O, migrate preferentially to the near surface region, and form protective barriers which prevent both diffusion of Tb outwards, and diffusion of O_2 and H_2O inwards, toward the unreacted metal. In the reactions with O_2 it is clear that it may be possible to select refractory oxide-forming metals such as Ta, Zr, and Nb which will fulfill most of those requirements. At high Ta loadings, however, the Ta oxidation chemistries may disrupt the microstructural environment sufficiently to actually increase the reactivity of the entire material in the vicinity of a newly formed defect. This question needs to be addressed in further experiments. The reaction with H_2O appears to be considerably more complicated. The fourth element modifiers that we have examined to date do not appear to affect the extent of oxide formation, as far as the XPS data for Fe reveal, but do play some role in the distribution of oxide versus hydroxide. The reasons for this change in distribution are still not clear, but may be important if it is assumed that the hydroxides formed are less passive than the stoichiometric oxides. Clearly one would like to have reactions involving H_2O proceed, as in Figure 1, so as to lose both hydrogens to hydride or H_2 formation, leaving the stoichiometric oxide. Except for the most reactive alkali metals, such as pure Li[28], this is rarely found to occur. The issue of oxide stability in the presence of water and halides has yet to be addressed in these studies, but is recognized as perhaps the central feature in determining the rate of pitting corrosion. Another alternative to protection is the addition of more noble metals such as Pt, which do not form stable oxides under the conditions cited here, but which may nevertheless change the reactivity of these RE-TM alloys, possibly through a purely electronic effect (e.g. change of surface work function). Detailed analyses of such processes are currently underway.

5. ACKNOWLEDGEMENTS

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APPENDIX L