

ION-INDUCED CARBIDE FORMATION OF TiFe: EVIDENCE FROM XPS AND AES STUDIES

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Summary

X-ray photoelectron and Auger electron spectroscopic studies on TiFe demonstrate that ion bombardment of the alloy not only results in sputter cleaning or even destruction of the surface but also leads to the formation of compact carbide layers. Such carbide species are of considerable importance in elucidating the reaction mechanism of hydrocarbon synthesis. They are also expected to play a significant role in the hydrogen sorption properties of materials. A better understanding of the nature of sputtered carbon is needed for its use as protective (against corrosion) thin films in magnetic recording applications. A comparison of photoelectron and Auger electron spectra of the surface carbides of TiFe would also be of interest since it is unusual for both types of data to be produced on the same samples where chemical shifts are involved.

1. Introduction

Electron spectroscopy for chemical analysis (ESCA) has been commonly used to monitor alterations in the surfaces of many technologically important materials after exposure to ion (noble gas) bombardment. This treatment results, in many cases, in reduction to the corresponding metals or lower oxides in addition to preferential sputtering [1, 2]. During ion bombardment, not only does complex destruction of the surface molecules take place, but also fragments combine to form new species [2]. Ion bombardment has been a potential method of producing a fresh surface from contaminated ones. It is also used extensively, in conjunction with many other surface analysis techniques, to obtain compositional information as a function of depth below the surface. For example, changes in the surface composition caused by inert gas ion bombardment have been studied by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS) and secondary ion mass spectrometry (SIMS), which can

provide detailed elemental and isotopic compositions [3-7]. Ion bombardment also serves as an excitation source in ISS [8] and SIMS [9].

Changes in surface composition produced by energetic particle bombardment have been attributed to a variety of processes including differential sputtering of constituent elements [10], ion-induced diffusion [11], migration resulting from ion neutralization [12], chemical reaction with the incident ions [13] and gross surface heating due to the surface material interacting with these high energy ions [14]. In alloys, for example, surface enrichment of one of the components must also be explained by considering the above complications [15, 16] and not simply by interpreting the measured concentrations. Because of the unique sensitivity and inherent chemical specificity, XPS has been the most useful method for characterizing the complex surface oxide layers on various metal and alloy surfaces [1, 15, 17].

Argon ion bombardment of surfaces may also result in the formation of new compounds. The formation of carbides through the bombardment of contaminated surfaces and the ion-induced formation of single compounds from a mixture of different phases are a few examples [2]. A defect structure of excess oxygen (Ni_2O_3 on NiO) could be generated by oxygen ion bombardment [1], indicating that materials with unusual properties can be prepared in this way. In many substrates, carbon is readily introduced as carbides during ion bombardment. The contamination layers and gaseous impurities in the analysing chamber as well as the impurities in the argon gas used for sputtering are the main sources of carbon. Such carbide species will affect the core level analysis of the metals which in turn restrict the results based on this interpretation. Hence, the defects introduced during sputtering must be considered. Incidentally, the formation of carbides is relevant to the mechanisms involved in the methanation reactions [18, 19] as well as their role in the hydriding reactions of TiFe [20]. However, a basic understanding of sputtered carbon is crucially important because hard carbon films are used as abrasion-resistant overcoats for magnetic recording materials [21].

As part of our laboratory's work on the surface properties of hydrogen storage intermetallics, the effect of atmospheric gases such as oxygen, water vapour [22, 23] and carbon dioxide [24] as well as the influence of argon ion bombardment [25] has been studied. The consequences of such processes on the hydrogen storage characteristics have been discussed elsewhere [26] in terms of surface segregation, oxidation, activation and deactivation mechanisms. In the present investigation we use XPS and AES to characterize the carbide layers formed on TiFe alloy on argon ion bombardment. The results clearly suggest that ion bombardment induces the formation of additional undesired carbide species which are known to pose problems at various stages in different contexts [25], and as discussed below.

2. Experimental procedure

XPS and AES measurements were made using an ESCALAB Mark II instrument (VG Scientific, U.K.) at a residual gas pressure less than 5×10^{-9} mbar. Magnesium K_α (1253.6 eV) was used for excitation with a pass energy of 50 eV.

The alloy, TiFe, used in this study was a commercial sample (Ergenics Division of MPD Technology Corporation, U.S.A.). All the measurements were made at room temperature in the as-received and air-exposed conditions. The sample was subjected to argon ion bombardment at 5×10^{-6} mbar pressure with a beam voltage of 8 kV and a filament current of $60 \mu\text{A cm}^{-2}$ at different time intervals. All binding energy values in this work were calibrated with respect to the reference silver metal ($3d_{5/2}$ level) at 368.2 eV and the carbon (1s) level of adventitious carbon on the sample at 284.5 eV. Carbon (1s) and carbon (KLL) signals were recorded in the XPS and AES modes respectively. Both measurements were made on the same area of the sample. Further experimental details are given elsewhere [16, 22].

3. Results

3.1. XPS studies

The evolution of carbon (1s) spectra as a function of sputtering time is shown in Fig. 1. The spectrum in Fig. 1(a) shows a dominant feature at 284.5 eV (used as a reference), which is due to the background carbon arising out of the residual gas (mainly hydrocarbons) from the spectrometer chamber. The contamination layers could have also been produced by exposing the samples to the atmosphere. The removal of such species from the surface occurs by argon ion bombardment. Following extended sputtering, the high binding energy portions of the peaks (adventitious carbon) disappear with a smoothly decreasing tail extending to the higher binding energies. As can be seen from the spectra in Fig. 1, lines (b)–(e), sputtering also results in the formation of a new signal to the left of the contamination signals, which probably accounts for a carbide-like species. This can be clearly recognized from their chemical shifts (about 2–3 eV in the lower binding energy side). That is, carbon from the contamination layers and/or from the residual gas could have been implanted in the segregated metal and/or the oxidized metal surface by the influence of energetic heavy ions on sputtering.

From the variation in the binding energies of carbon (1s) spectra, on ion bombardment, one can draw a conclusion about the formation of metal–carbon bonds. It could be due to pure carbide species or oxycarbide-like species, or both could be responsible. The oxycarbide formation may be facilitated by the surface oxides present initially [22]. The component elements of the TiFe alloy, *i.e.* iron and titanium, are known to form carbides [27] and titanium, even, produces an oxycarbide [28]. Our result could be further supported by the fact that ion-induced formation of metal carbides, such as those of silicon, chromium, manganese and zirconium, has been reported [2, 29, 30] and hence similar behaviour is expected in this instance. The peak positions were confirmed from the binding energy values of pure carbides [31], carburized nickel samples [32], carbides formed from the decomposition of carbon dioxide on polycrystalline iron films [33] and adsorbed carbon (carbide carbon) from the decomposition of formic acid on TiFe itself [34]. Although the carbide formation affects the metal core level positions, they could not be identified because of the complex nature of the spectra caused by the various lower valent oxides [22] appearing in the same region.

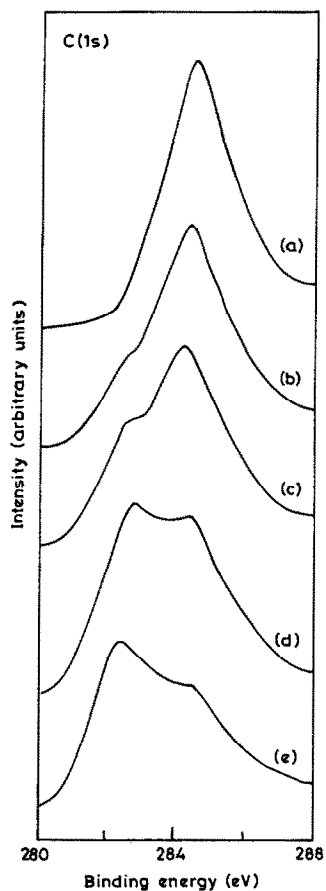


Fig. 1. XPS signals from the TiFe surface: (a) initial state (as-inserted); (b) sputtered for 60 s; (c) sputtered for 210 s; (d) sputtered for 510 s; (e) sputtered for 1410 s.

As can be seen from Fig. 1, the spectra consist of two lines: the dominant hydrocarbon line (at about 285.0 eV) and a second line (at about 282.0–283.0 eV) originating from a carbide-like species. In all cases (such as in AB_5 and A_2B systems [25]), the carbide-like lines were found at a lower binding energy than the hydrocarbon line, indicating that carbon in carbides has a lower binding energy than in saturated hydrocarbon or graphite or oxygen-bonded carbons. The energy shift implies that electron transfer takes place from the metal to carbon in carbides, suggesting that carbide formation must have been stimulated by the ion beam. That is, during sputtering, the adsorbed carbon species as well as the target material is activated, thereby facilitating the formation of the carbide layers. From Fig. 1, it is also clear that with increasing sputtering time, a feature appears at the low energy side (about 2–3 eV). This feature grows with time, relative to the reference carbon signal.

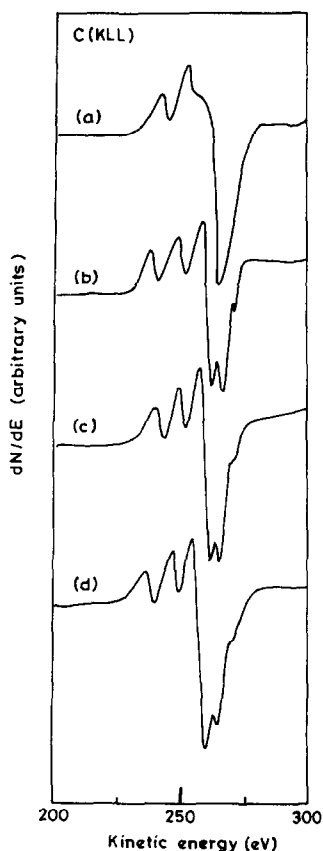


Fig. 2. AES signals from the TiFe surface: (a) initial state (as-inserted); (b) sputtered for 30 s; (c) sputtered for 390 s; (d) sputtered for 990 s.

3.2. AES studies

Carbon Auger signals of sputtered TiFe exhibits a fine structure typical of bulk or pure carbides [35, 36], suggesting a sputtering-induced effect (Fig. 2). The structure differs from that of the carbon peak of the sample in the “as-received” condition (Fig. 2(a)), which corresponds to absorbed carbon (amorphous or graphite nature) [29, 37, 38]. On sputtering, the carbon coating is removed, as can be seen from Fig. 2. A number of interesting changes in the spectrum shape have been observed owing to alterations in bonding. In each case, a distinguishable spectral change is observed which is sufficiently distinctive to identify the various forms of carbon at the surface. The spectra associated with carbides are usually characterized by a sharp fine structure (Fig. 2, lines (b)–(d)) at about 265–270 eV [35, 36]. Further, spectra from metallic carbides are characterized by the two low energy peaks (at about 240–250 eV) that are almost absent in data for pure or adsorbed carbon [29, 35, 36, 38] (Fig. 2(a)).

Supporting evidence for the ion-induced behaviour of TiFe comes from the spectra obtained from the sputtered samples of various metals, alloys and oxides [36, 39–41]. The AES line shapes (Fig. 2) have been compared with previously reported spectra of carbon in different forms, *i.e.* amorphous, graphite, diamond, carbon monoxide and carbides [35–42]. The carbon Auger line shape of “as-inserted” TiFe (Fig. 2(a)) is similar to that of amorphous carbon or graphitic carbon [29, 36–38] and the spectra of sputtered TiFe (Fig. 2, lines b–d) are characteristic of carbidic carbon [35, 36, 39–41]. Fine structures in Auger spectra can be seen frequently from both metals and non-metals, and originate either in chemical effects or in final state effects. The more commonly observed fine structure due to chemical effects, however, arises in one or more possible chemical states. One of the most striking examples is that of the Auger spectrum of carbon in different chemical situations [29, 35, 36, 42]. For example, typical carbon spectra show that both the overall appearance of the Auger peak shape and the associated fine structures change markedly on going from graphite to various carbides.

4. Discussion

Although ion bombardment is used universally for surface cleaning of materials, either by itself or with heating, the potential user should be aware of the artefacts that it can introduce. These take the form of either chemical or morphological changes, or both, at the surface. To overcome carbide formation during depth profile analysis, the following condition could be helpful. The rate of removal of the adsorbed impurities by ion bombardment on the surface must be greater than the adsorption rate of the residual gas molecules; its presence can easily be identified by monitoring the corresponding photoelectrons and Auger electrons of carbon. Ion-induced carbide formation was observed on metals such as titanium, chromium, zirconium and manganese [2, 29, 30]. It was also noticed on sputtered TiO₂, and the electron beam produces a similar effect, although to a lesser extent [29]. Thus, both ion and electron beams give rise to apparent reduction effects and their combined action stimulates carbide formation. Since the carbide formation of many elements is exothermic, the production of a metal–carbon bond after implantation seems likely, because of the high excess energy of the implanted carbon species.

During sputtering, the ion pumps are usually shut off and hence it is possible that on prolonged depth profile analysis, impurities can build up to partial pressures close to the critical limit [39]. However, for given vacuum conditions, appreciable carbide formation can be avoided or reduced by choosing optimum sputter conditions, *i.e.* working at high sputter energies which increase the sputter rate and thereby minimize carbide formation. Since the rate of removal of the contaminants is greater than the adsorption of the residual gas molecules, the possibility of the contaminants interacting at the surface is negligible. Therefore, by adopting necessary precautions, the formation of unsuitable compounds can be avoided.

Carbide formation can affect depth profile analysis in several ways. For

example, it can affect the relative amplitude of the other elements and thus interfere with the determination of the stoichiometry. It is also likely that carbide formation negatively influences depth resolution because carbides are difficult to sputter. Such carbide-like signals could be misinterpreted on bulk carbides. This is particularly important on steel and carbon-containing alloys, where an artificial carbide formation might lead to wrong interpretation of the bulk carbon (or carbide) content of such compounds. In most studies, core levels of metals and oxygen have frequently been monitored in identifying the clean surface; therefore the formation of carbides could pass unnoticed. Neither of these regions gives a clear indication of the carbides, although the metal core levels do to a certain extent. However, the metal core level signals could be misinterpreted as arising from the lower oxide species because the binding energy values for most of the suboxides and the carbides appear in the same region, thus deviating attention to the former. The energy shifts observed on charge transfer make quantitative analysis of both the XPS and AES signals difficult. Changes in shape of the Auger spectra also affect the use of AES for quantitative analysis.

It is well known that the presence of adatom impurities may drastically alter the catalytic behaviour of a metal surface. The formation of carbide or oxycarbide particles on TiFe may present a convenient "window" at the surface [20], through which hydrogen could readily enter or leave without encountering the contamination or activation problems from which these materials often suffer. Therefore, the hydrogenation of the sputtered alloy would give results that are appreciably different from those of the untreated sample. Hence, this has to be considered whenever the reaction is carried out with a sputtered surface. Whereas, for supported metal systems, the carbide layers play an important role in the hydrogenation reactions, since carbidic carbon on Group VIII metal can be readily hydrogenated in a hydrogen atmosphere. Carbide formation was found to be a promoter for the hydrogenation reaction over Fischer-Tropsch catalysts. That is, hydrocarbon formation is probably initiated by a surface reaction between atomic carbon and atomic hydrogen in the adsorbed phase. Therefore, importance has to be given to these ion-induced carbides or it should be avoided in studying the hydrogenation reaction mechanisms by XPS and AES combined with ion bombardment technique. Otherwise they will drastically affect the mechanism. As the present XPS and AES observations on TiFe alloy provide evidence for a strong interaction between sputtered atoms and/or residual gas and the target surface, a close look at the surface carbides could be useful in understanding the surface chemistry of materials. Since this type of atom-surface interaction has been little described elsewhere, new theoretical and experimental approaches are required to elucidate its nature.

5. Conclusion

XPS and AES measurements on TiFe indicate the formation of a surface carbide species on argon ion bombardment. Although the metal core level photo-

electrons eventually show no or little change, the carbon photoelectron signals and the Auger line shapes provide evidence for the existence of such species. The trend to a pattern near that for bulk carbide is consistent with the development of more ionic bonding configuration. The carbon spectra showed a bulk carbide-like state with variable binding energy contributions involving metal-carbon bonding. The examination of carbon levels is of substantial analytical value for determining surface carbide layers such as those encountered in this study. Such a compilation of the data and their comparison with controlled surface science measurements serves as a useful guide for future studies of energetic ion bombardment. Moreover, a better understanding of sputtered carbon is essential for its use as protective overcoats for thin film magnetic media.

If ion bombardment is to be applied for cleaning surfaces and for depth profiling the concentration of various species, the chemical perturbations must be clearly understood. This is essential in studying the reaction mechanisms involving the surface species, since the ion-induced carbides on the surface would give rise to a different reaction route and hence there is every chance of deviating from the mechanism. This would be an especially severe problem for the hydrogenation reactions, *e.g.* for hydrogen storage materials, hydrocarbon and methanol synthesis catalysts. It would also affect the results of carbon-containing alloys such as stainless steel and the nature of metal and suboxidic species on various metal-oxygen systems, in addition to the complications of progressive sputtering due to the hardness of the carbides.

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