

Chemical Analysis of Passivated and Oxidized Layers on FeCr and FeTi Alloys by Soft X-ray Absorption Spectroscopy

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The chemical differences between passivated and oxidized layers on 17.5 at.% FeCr and 5 at.% FeTi alloys are analysed by means of soft x-ray absorption spectroscopy (XAS). The relative absorption strengths were used to obtain a quantitative estimation of the composition of the layers. In FeCr, the passivated layer shows a relative Cr enrichment of 34 at.% with respect to the oxidized surface. In addition, Cr_2O_3 has been identified as the main oxide formed in the passivated layer of FeCr. By contrast, in FeTi, the results are consistent with the formation of a ternary oxide. The potential of XAS in the study of oxidation and passivation is discussed.

INTRODUCTION

The purpose of this work is to analyse the chemical differences between passivated and oxidized layers on FeCr and FeTi alloys by means of soft x-ray absorption spectroscopy (XAS). This problem has attracted a lot of attention in the past owing to its technological relevance. Not surprisingly, passivation and oxidation processes in these alloys were often studied by using surface-sensitive techniques like XPS and AES.^{1–12} However, there are some questions, such as the precise chemical state of some species in the layers, that still have to be answered. We show below that soft XAS is particularly suited to address these questions and, in some cases, XAS is able to distinguish between ternary oxides and mixtures of binary oxides.

Soft x-ray absorption spectroscopy is well known for its site- and symmetry-selective character.^{13–15} These characteristics allow detailed element-specific studies in heterogeneous systems. Since the absorption strength is proportional to the concentration, XAS can be used to provide valuable quantitative information. This is illustrated below for FeCr alloys and the results are compared to previous XPS studies. However, the main advantage of XAS derives from its sensitivity to chemical properties such as valency, hybridization and crystal field effects.^{16–18} We will conclude that this sensitivity makes XAS a very useful tool in the analysis of passivation and oxidation processes.

Depending on the material and the absorption edge studied, some XAS spectra are influenced by the interactions of the core hole with the outer band electrons. In those cases, the spectra show sharp multiplet structures dictated by the symmetry of the ground state and they cannot be explained by means of DOS calculations. These quasi-atomic structures are element specific and very sensitive to crystal field effects,¹⁹ allowing a detailed study of the different elements in the compounds. In this work, we analyse the transition metal 2p edges, which correspond to transitions from 2p to narrow 3d orbitals at the transition metal sites. These spectra are very sensitive to the bonding of the 3d electrons and allow us to determine the chemical state of the metal in the different layers.

The oxidation of FeCr alloys by means of dry oxygen and by oxygenated water has been studied by Olefjord.⁵ The oxides formed by both methods were found to have different compositions. In the presence of water the oxide is richer in Cr and a thin overlayer of chromium hydroxide ($\text{Cr}(\text{OH})_3$) is also formed.⁵ For dry oxygen the oxide formed is mainly Fe oxide, but when diffusion is induced by heating, or after a long period of time, enrichment of Cr oxide at the surface is also produced.⁵ By measuring the XPS binding energy of the Fe 2p core level in FeCr alloys with different Cr contents, Asami *et al.*⁸ found that those with a Cr concentration of > 12 at.% were more resistant to further oxidation. Recently, Kirchheim *et al.*¹⁰ proposed a mechanism for growing passivation layers in FeCr alloys. The model was based on preferential dissolution of Fe into the electrolyte and the lower mobility of Cr, which produces an enrichment of Cr in the passivating layer.¹⁰ FeCr alloys have also been studied by means of extended x-ray absorption fine structure (EXAFS) techniques by Kruger *et al.*^{20,21}

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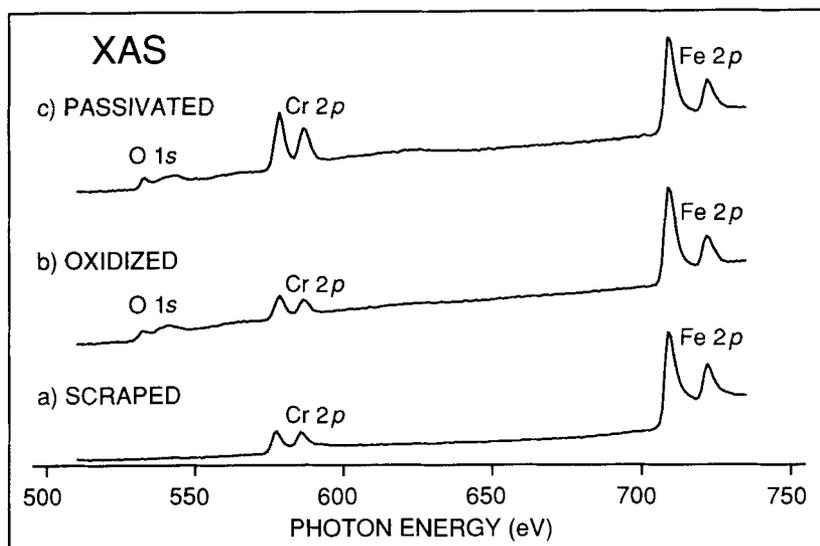


Figure 1. Broad XAS spectra of 17.5 at.% FeCr alloy: (a) scraped *in situ*; (b) oxidized; (c) passivated.

These studies also provided very interesting information about the crystal structure and the bonding lengths of the oxides formed in these alloys.

EXPERIMENTAL

The experiments were performed at the SX700/I beam line in the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY).²² The spectra were recorded in total electron yield mode in a vacuum of better than 5×10^{-10} Torr. The detector consists of three biased grids placed in front of a channeltron; more details can be found elsewhere.²³ The throughput of the monochromator is essentially structureless in the regions of interest. The photon energy scale was calibrated by using the known peak position of the O 1s spectra in TiO₂²⁴ and the Fe 2p and Ti 2p spectra in metallic Fe and Ti.²⁵ In most cases, a very good signal-to-noise ratio was achieved in one scan of <10 min. Only the Ti 2p spectra required multiple scans because of the lower cross-section and the smaller concentration of Ti in the FeTi alloy.

The alloys used in this work were prepared from the pure elements by arc melting. The Cr content in the FeCr alloy was 17.5 at.% while the Ti content in FeTi alloy was 5 at.%. Three different spectra were taken for each alloy. In both cases, the native oxide layer formed on top of a polished surface provided the first spectra. Afterwards, the samples were scraped *in situ* with an alumina file to obtain the reference spectra of the clean surface. The passivated layers were produced in another sample by controlled anodic oxidation in a 1 N H₂SO₄ electrolyte at +700 mV (SHE) for 1 h and then rinsed and dried in air. More details on the passivation method can be found elsewhere.¹⁰

The spectra were normalized to the maximum peak heights because an absolute normalization is not possible in photoyield methods. The mean probing depth of XAS measured in total electron yield (20–40 Å) is slightly larger than that of XPS.²³ Thus, the XAS spectra will be less sensitive to the contamination layer

formed while transferring the sample from the passivation cell to the spectrometer. The spectra taken by illuminating different portions of the samples were consistent in all cases. The entire experiment was repeated a second time using a different set of samples in order to ensure reproducibility.

RESULTS AND DISCUSSION

FeCr alloy

Quantitative analysis. The overview spectra of the passivated, oxidized and clean 17.5 at.% FeCr alloy are shown in Fig. 1. The structures in the spectra are attributed to the different absorption edges. The assignments are made by taking into account the binding energies of the relevant core-level electrons. In this way, the strong features observed in Fig. 1 at 530, 575 and 710 eV are attributed to the O 1s, Cr 2p and Fe 2p absorption edges, respectively.

These kinds of spectra are very useful because they show at once the elements that are present in the near-surface region and their relative concentrations. As expected, the O 1s absorption edge is completely absent in the spectrum of the clean surface. The spectra were normalized to the Fe peak height in order to compare the relative Cr content. Figure 1 shows clearly that the passivation process has given rise to relative enrichment of Cr in the surface region with respect to the oxidized sample. This conclusion is in qualitative agreement with previous XPS and AES studies.^{6,9,10} It is worth noting that no appreciable enrichment of Cr is produced in the oxidized surface, which is also in agreement with previous data.⁶

One can take the relative Cr 2p/Fe 2p absorption intensity in the clean spectrum and the known composition of the alloy to derive an approximate value for the relative sensitivity factor for these edges. Assuming that this factor is not severely affected by the formation of the different Fe and Cr oxides, it is possible to obtain a quantitative estimation of the Cr enrichment value in

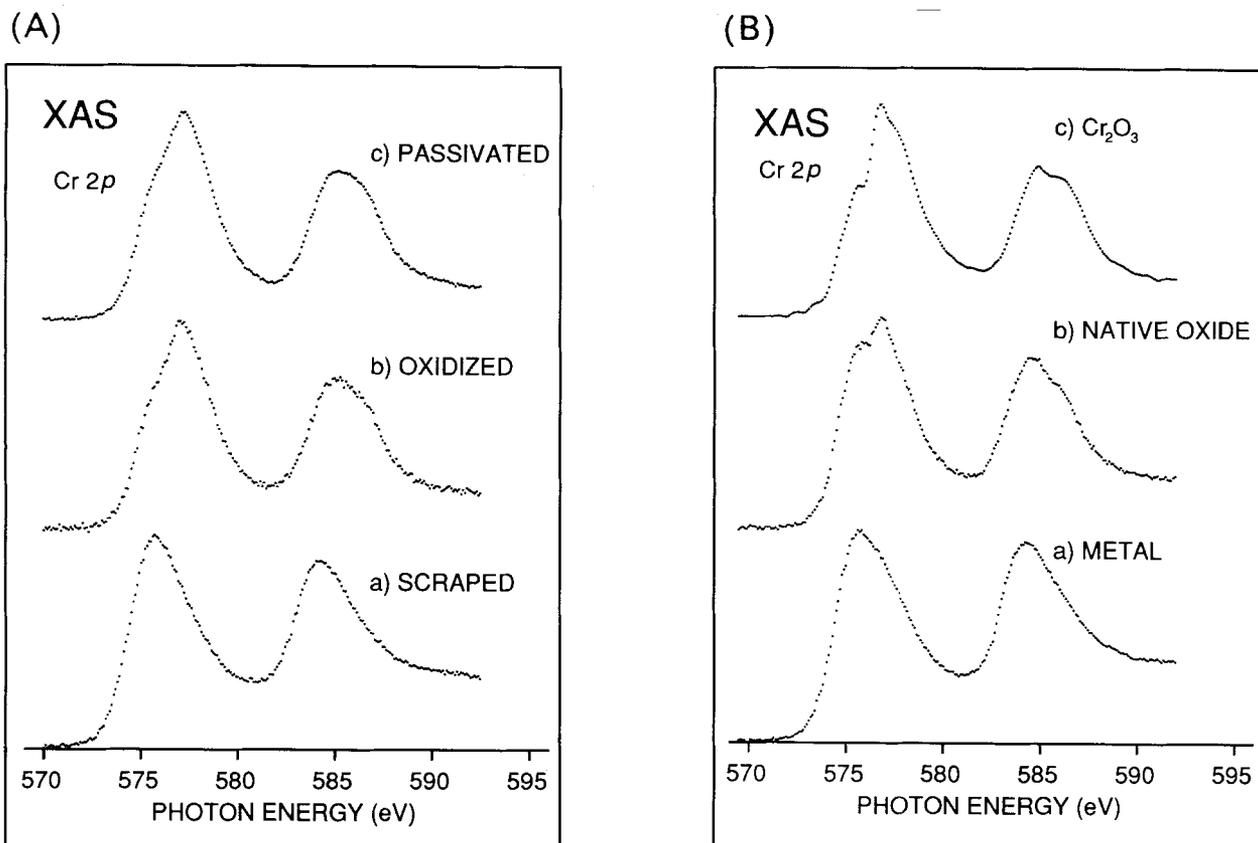


Figure 2. (A) Cr 2p edge XAS spectra of 17.5 at.% FeCr alloy: (a) scraped *in situ*; (b) oxidized; (c) passivated. (B) Cr 2p edge XAS spectra of some Cr standards: (a) clean Cr metal; (b) air-exposed Cr metal; (c) Cr_2O_3 .

the surface layers. The relative Cr/(Fe + Cr) concentration estimated in this way is ~ 34 at.% in the passivated layer and 18 at.% in the oxidized layer. These values must be compared with 17.5 at.%, the relative Cr concentration expected in the bulk. Thus, the relative composition in the native oxide layer hardly changes while in the passivated layer there is a large Cr enrichment.

The relative Cr enrichment found here is consistent with previous XPS and AES studies.^{6,9,10} For instance, Olefjord and Fischmeister⁶ found, using XPS, that for 17.5 at.% FeCr left in oxygenated water for 1 h at 25 °C the Cr concentration rises to 25 at.%, while at 70 °C the Cr concentration rises to 31 at.%. Accordingly, Leygraf *et al.*⁹ found that for 18 at.% FeCr passivated for 1 h in 1 N H_2SO_4 at 900 mV the Cr concentration is 65 at.% using XPS and 56 at.% using AES. These estimations are larger than the value obtained here, but there is no serious discrepancy if one takes into account that the mean probing depth in XPS and AES is smaller than in XAS. This example illustrates clearly the potential of XAS for both element and quantitative analysis in this kind of system.

Chemical analysis. We now turn to the chemical information that can be obtained from detailed studies of the peaks. The O 1s region is less useful in this case, because when mixtures of oxides are present their peaks overlap. Instead, we will concentrate on the metal 2p edges, which can be interpreted easily in a qualitative way.

The Cr 2p spectra of passivated, oxidized and clean 17.5 at.% FeCr are shown in Fig. 2(A). For comparison

purposes, we illustrate in Fig. 2(B) the Cr 2p edges of Cr_2O_3 , the native oxide grown on Cr metal and the spectrum of clean Cr metal. The spectra exhibit two strong absorption features that are related to the spin-orbit splitting of the Cr 2p level. The spectrum of Cr metal shows rather smooth, broad features with an asymmetric tail towards higher photon energies. This kind of spectrum is generally found in pure metals and alloys. By contrast, the spectrum of Cr_2O_3 presents a richer structure, with shoulders and unresolved multiplets. This kind of spectrum is characteristic of narrow band materials, such as transition metal oxides.

First, we note the similarity between the spectra of clean Cr metal and FeCr alloy. This suggests that the local density of unoccupied states at the Cr sites hardly changes upon alloying. Secondly, we note that the Cr 2p spectra from both the oxidized and the passivated layers are characteristic of oxides and not of Cr metal or FeCr alloys. Although the probing depth of XAS is only slightly larger than the thickness of the oxidized and passivated layers, typically 20–30 Å thick, we do not think that the Cr 2p spectra of these layers are significantly influenced by metallic Cr in the bulk because this would not explain the shoulder in the high-energy side of the Cr 2p_{3/2} peak. In fact, the general features of the oxidized and passivated spectra are similar to those of Cr_2O_3 , although the spectral structures are broadened. This broadening suggests some modification of the primary Cr_2O_3 oxide structure in the oxidized and passivated layers. This modification could be due to both the presence of a very thin overlayer of chromium hydroxide ($\text{Cr}(\text{OH})_3$), as suggested

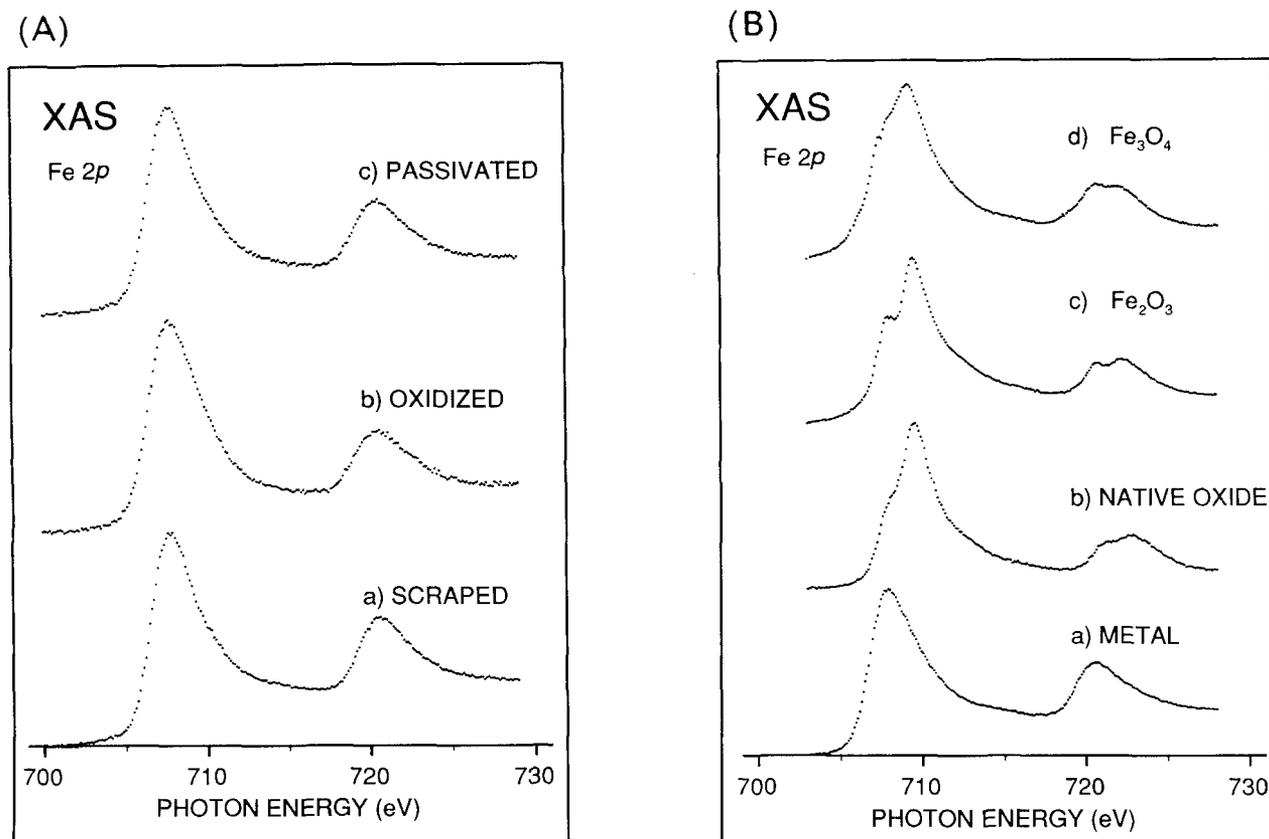


Figure 3. (A) Fe 2p edge XAS spectra of 17.5 at.% FeCr alloy: (a) scraped *in situ*; (b) oxidized; (c) passivated. (B) Fe 2p edge XAS spectra of some Fe standards: (a) clean Fe metal; (b) air-exposed Fe metal; (c) Fe₂O₃; (d) Fe₃O₄.

by Olejford and Fischmeister,⁶ and defects such as vacancies or even the presence of some isolated Fe²⁺ ions in the Cr₂O₃ matrix. The main conclusion here is the formation of primary Cr₂O₃ in the oxidized and passivated layers, in agreement with the conclusions of previous XPS and AES studies.⁶

The Fe 2p spectra of passivated, oxidized and clean 17.5 at.% FeCr are shown in Fig. 3(A). The spectra of clean Fe metal and some Fe oxides are presented in Fig. 3(B) for comparison. It is clear that Fe is not present as Fe₂O₃ or Fe₃O₄ in the passivated and oxidized layers; the spectra of the Fe oxides present a low-energy shoulder in the Fe 2p_{3/2} region that is absent in the spectra of the oxidized and passivated alloys. In fact, the alloy spectra seem to exhibit metallic characteristics in all cases, because of the similarity to the spectrum of clean Fe metal. However, the shape of the Fe²⁺ XAS spectrum is very similar to that of the Fe metal, and Asami *et al.*⁸ found that the Fe atoms are mainly in an Fe²⁺ oxidation state for Cr contents of >12 at.%. Thus, we conclude that the Fe 2p spectra of the oxidized and passivated layers are mainly due to the metallic Fe in the bulk alloy and Fe²⁺ ions in the overlayers.

Finally, we note that the peaks of the metal 2p spectra are slightly narrower in the clean alloys than in pure metals. For instance, the full width at half-maximum (FWHM) of the Fe 2p_{3/2} peak in the pure metal is 3.7 eV, while in the clean alloy it is only 3.4 eV. In addition, the FWHM for Cr 2p_{3/2} in the pure metal is 4.3 eV, being 4.1 eV in the clean alloy. This effect is related to the narrowing of the metal 3d bands in the alloys, caused by the decrease in the overlap with the

wave functions of the neighbouring atoms; a similar behaviour has been observed already in other transition metal alloys and silicides.^{26,27}

FeTi alloy

We now illustrate a case in which one can identify the presence of a ternary oxide, even for a low concentration of transition metal. To this end, we have chosen the Ti 2p spectra of passivated, oxidized and clean 5 at.% FeTi shown in Fig. 4(A). These spectra can be compared with the edges of FeTiO₃, TiO₂ (in the rutile structure) and clean Ti metal presented in Fig. 4(B).

First, the spectrum of the clean alloy exhibits metallic characteristics; however, it is different from the spectrum of pure Ti metal. The latter presents some structure due to the inherent unoccupied electronic structure in Ti metal, matching the electron energy-loss spectra of clean Ti obtained by Fink *et al.*²⁵ In this case, alloying does affect the unoccupied electronic structure around the Ti atoms, in contrast with the behaviour observed in the Cr alloy. This is due to stronger metal-to-metal interactions in the Ti alloy, caused by the larger size of the Ti 3d orbitals. Secondly, the spectra of the passivated and oxidized surfaces resemble those of Ti oxides and not of Ti metal or alloy.

The shape of the peaks in TiO₂ is more complex than in the other oxides. In particular, one of the peaks splits into two, as marked by the vertical arrows in Fig. 4(B). This splitting is caused by distortions in the octahedral environment around the Ti ions,¹⁹ and illustrates the

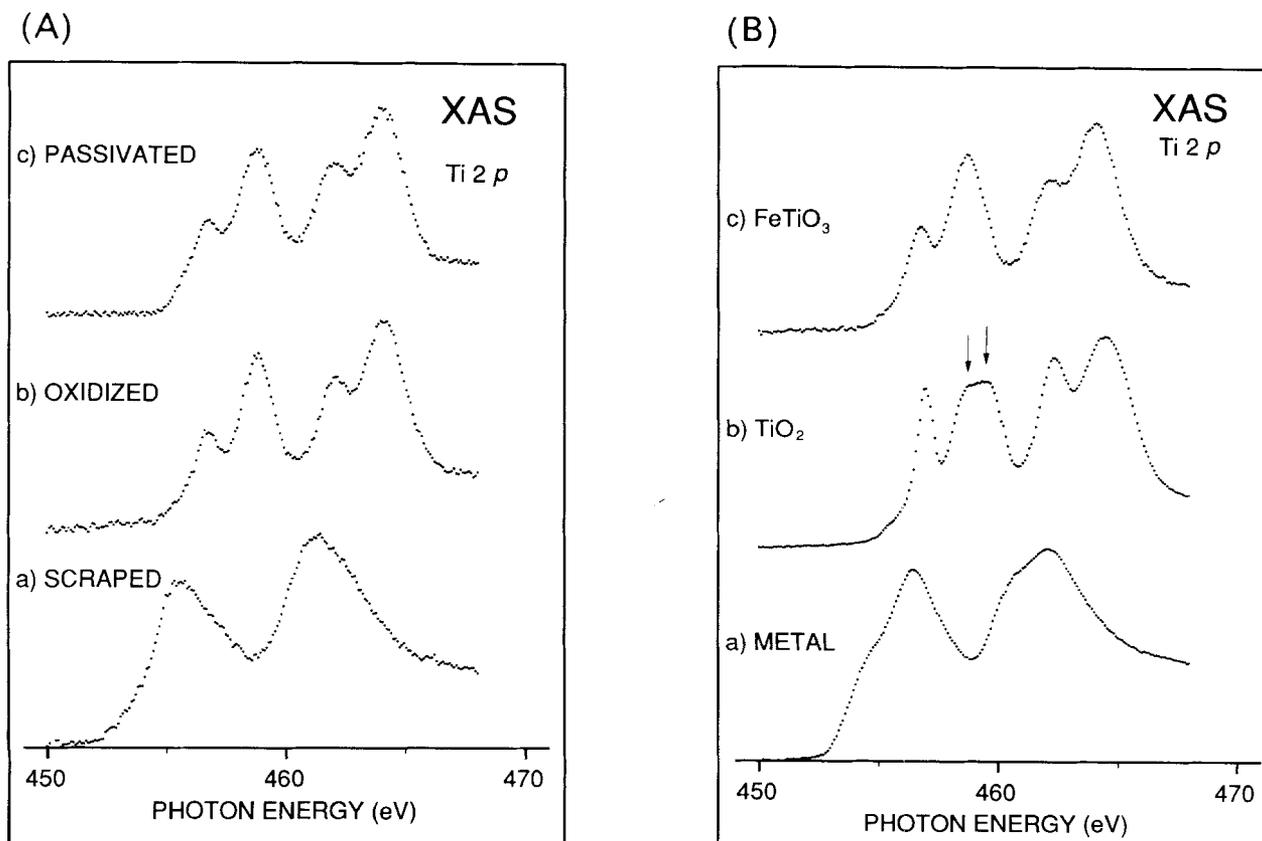


Figure 4. (A) Ti 2p edge XAS spectra of 5 at.% FeTi alloy: (a) scraped *in situ*; (b) oxidized; (c) passivated. (B) Ti 2p edge XAS spectra of some Ti standards: (a) clean Ti metal; (b) TiO_2 ; (c) FeTiO_3 .

sensitivity of XAS to this kind of effect. The spectrum of FeTiO_3 is relatively simple in appearance and does not present such splitting, indicating a more symmetric oxygen environment in this material. We can see that the Ti 2p spectra in the oxidized and passivated layers do not resemble that of TiO_2 and are consistent with the spectrum of FeTiO_3 . These results rule out the possibility of a binary oxide in the oxidized and passivated layers, suggesting, instead, the formation of a ternary oxide.

SUMMARY AND CONCLUSIONS

In summary, we have illustrated the potential of XAS in the study of oxidation and passivation processes in alloys. This potential includes qualitative and quantita-

tive capabilities, although the major advantage is given by its extreme sensitivity to chemical properties. The oxidized and passivated layers of 17.5 at.% FeCr are mainly formed by the relatively isolated Fe^{2+} ions dissolved in a Cr_2O_3 matrix. The Cr enrichment in the passivated layer is ~ 34 at.%, while the relative composition in the oxidized surface hardly changes. By contrast, the results in 5 at.% FeTi rule out the possibility of a binary oxide in these layers, suggesting, instead, the formation of a ternary oxide.

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