Surface oxide layers form on most materials at room temperature. The presence of these contamination layers makes it very difficult to analyze the oxygen content of the bulk material. We have shown experimentally that for example the use of an air jet to prevent carbon contamination on sensitive nitride specimens can lead to dramatic in situ oxidation phenomena. On the most sensitive specimens (HfN, ZrN) such phenomena can even be observed without the use of an air jet: the mere positioning of the electron beam on the specimen can already start this (continuous) oxidation process. However, apart from these dynamic oxidation phenomena, which can easily lead to erroneous interpretations, there is also a problem related to the presence of native oxide skins on sensitive metals like T, Zr, and Hf or their alloys.

It is not usually realized how large the influence of a 5nm-thick TiO$_2$ layer on an otherwise oxygen-free piece of titanium can be on the experimentally O-Ka count rate. If the presence of a Ti-oxide skin is ignored and all the O Ka counts are attributed to an alleged bulk oxygen content, most bulk matrix correction programs would translate this to something like between 1 and 2 wt.% oxygen, no matter which accelerating voltage is used. Very large errors in the bulk oxygen content can be made under these circumstances. These problems find their origin in the fact that the O Ka emission volumes in metals like Ti are extremely shallow (approx 200 nm) due to the large absorption of O Ka x rays. (The mass absorption coefficient of O Ka in Ti is of the order of 2000 cm$^2$/g). An oxide skin of even a few tens of nanometers can therefore occupy a surprisingly large portion of the total emission volume and its influence on the total O Ka count rate can be disproportionally large due to the relatively low self-absorption of the O Ka intensity. It follows that when efforts are undertaken to measure low bulk levels of oxygen in titanium or its alloys, it is vital to know the oxide film thicknesses on each of the specimens in order to subtract the count rates from these films from the total observed O Ka count rate.

From a chemical point of view it might be expected that the oxide skin thickness is related to the titanium content and will thus vary from one compound to another. Therefore, it is necessary to use thin-film analysis software, coupled with analyses over a wide range in voltages, in order to distinguish surface from bulk effects.

It was necessary to use thin film analysis procedures in our attempts to measure bulk oxygen contents in ternary Ti-Si-O and Ti-Al-O phases produced during diffusion bonding of metal-ceramic joints. Our preliminary results indicate that in the analysis of the solid solution of oxygen in titanium, the apparent bulk oxygen content is doubled by the presence of an oxide skin. This means that errors of up to 100% in the bulk oxygen content can easily be made if the presence of an oxide skin on the specimens is not taken into account.

**Experimental**

In order to establish the variation of oxide skin thickness with Ti-content in the Ti-Si-O system, a binary Ti-TiSi$_2$ diffusion couple was prepared from (presumably) "oxygen-free" starting materials by diffusion bonding in a vacuum furnace, and subsequently annealed for a prolonged period on time at 900 C. After annealing, the couple contained the Ti$_3$Si, Ti$_5$Si$_3$, Ti$_5$Si$_4$, and TiSi compounds in parallel layers between the unreacted Ti and TiSi$_2$ starting materials.

The oxygen measurements were carried out in a JEOL 733 Superprobe, equipped with a W/Si multilayer crystal (2d-spacing 59.8 Å), with natural hematite (Fe$_2$O$_3$) as a standard. Standard and sample were mounted in copper-filled conductive polymer and no conductive coatings were applied. Measurements of 0 Ka were made for each titanium-silicon compound and the Fe$_2$O$_3$ standard at accelerating voltages of 2, 3, 4, 5, 6, 8, 10, 12, and 15 kV. The measured k-ratios for 0 Ka were processed with our thin-film program ("TFA"$^2$), assuming that the oxide skins consist exclusively of TiO$_2$ and that all O Ka counts can be attributed to this surface layer.

**Results and Discussion**

The results for the unreacted Ti specimen are shown in Fig. 1. The open circles represent the measured k ratios for Ti as a function of the accelerating voltage. The thin-film program ("TFA") was used to calculate k ratios. The major input parameters were the accelerating voltage and the assumed thickness.
The oxidation of titanium at low temperatures has been studied by a number of investigators using Auger and x-ray photoelectron spectros-

copy. Early photoemission results showed the formation of a layer of TiO₂, which was thicker than the photoelectron sampling depth. The sub-

sequent literature gives conflicting results from oxide film thicknesses less than two monolayers to 40 Å and the presence of inhomogeneous oxides. However, the Ti oxidation studies are carried out in clean vacuum systems that may not simulate oxide formation after metallographic polishing in the laboratory.

It is possible, and perhaps even likely, that any adhering atmospheric oxygen is inadvertently included as a contribution to the total film thickness of TiO₂. However, the very small thickness of the TiO₂ film makes it impossible to do meaningful EPMA measurements that are completely contained inside the film, even at the lowest accelerating voltages applied.

Alloying the titanium with 16.35 wt.% of Si as in the Ti₅Si₁ compound (Fig. 2) reduces the oxide skin to 43 Å. This trend is continued in the Ti₅Si₃ (42 Å) and Ti₅Si₄ (38 Å) compounds. The lowest value of 36 Å so far has been found on the TiSi compound (Fig. 3). (TiSi₂ was not measured.) All efforts to reduce the surface oxide skin thickness by mechanical polishing procedures and/or chemical etching techniques have proved futile. Apparently the presence of such skins cannot be avoided. It is therefore all the more important that the influence of such a skin on the measurements of bulk oxygen contents is not underestimated or neglected. The work presented here is a necessary prerequisite for a correct evaluation of the O Kα microprobe data in order to arrive at the correct ternary phase relationships in the Ti-Si-O and Ti-Al-O systems.

At the moment investigations based on Auger and XPS techniques into the nature and thickness of the oxide skins on the various phases in both systems have been started. Apart from backing up our EPMA results we also hope that these techniques will supply more detailed information on the exact nature and layer sequence of oxides on top of the surfaces in case more than one oxide is involved.

References

