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# **Protection of titanium alloys against high temperature oxidation during closed-die forging: structural analysis of the boro-silicate glass coating / Ti-6Al-4V alloy interfacial region by correlative imaging**

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## **Abstract**

We analyse herein the interfacial region formed between a borosilicate glass coating and Ti-6Al-4V alloy after a transient **of 8 hours** at 1150 °C. The correlation of two optical and electron microscopy methods (Raman and Backscatter Electron Diffraction imaging) enabled an accurate description of this particular interface. This interface is composed of five different phases, namely Ti<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub>, TiB, Ti<sub>5</sub>Si<sub>3</sub> and Ti<sub>6</sub>Si<sub>2</sub>B, and it proves to be protective against oxygen permeation. Finally, this study also enabled the development of a Raman database for Ti borides, silicides, and borosilicides, in part from experimental and more completely from theoretical (DFT computations) data.

## **Keywords**

A. Titanium, A. Glass, B. Raman spectroscopy, B. EDX, B. EBSD, C. High temperature corrosion

## **1. Introduction**

Titanium (Ti) alloys have been widely used in aeronautical application for years essentially due to their high corrosion resistance, high specific strength and low density. Among them, Ti-6Al-4V is the most used and studied alloy. Structural elements, which are required to exhibit specific mechanical properties, essentially come from forged parts. It is reported that the mechanical properties of the

final product are largely dependent of its microstructure, which is mainly driven by the thermomechanical history during forming. Titanium and Ti-alloys have two allotropic forms: the low-temperature hexagonal-close-packed (HCP) phase, named  $\alpha$ , and the high temperature body-centered-cubic (BCC) one, named  $\beta$ . In case of Ti-6Al-4V alloy, forging of the parts is classically achieved in the  $\alpha+\beta$  domain, around 950 °C. One of the main objectives of the MAMA (Metallic Advanced Materials for Aeronautics) project [1] is to develop the  $\beta$  forging of such parts in order to use the greater workability of the material in the  $\beta$  domain.  $\beta$  forging process therefore implies to raise the forging temperature up to the  $\beta$  stability domain of Ti-6Al-4V alloy, which means at least 1000 °C. At such high temperatures, the material surface is subject to microstructural and composition changes due to its chemical reaction with the surrounding atmosphere. Obviously, high-temperature (HT) oxidation of the alloy has to be considered in those conditions.

The most common surface alteration during forging processes is the formation of an oxide scale and an underlying  $\alpha$ -rich layer, known as “ $\alpha$ -case”, essentially formed and stabilized by oxygen ( $\alpha$ -gene element) diffusion within the metallic matrix. Contrary to the oxide scale, the main part of  $\alpha$ -case does not spall off during the forging process and remains in forgings. The presence of relatively high amounts of dissolved oxygen within this area is known to lead to a local increase in mechanical strength and elastic moduli, accompanied by a loss of ductility, which can be detrimental for the part machinability and the mechanical behaviour of the final component. It is known that the use of lubricant coatings in closed die forging processes, generally based on borosilicate glasses, allows to reduce such a surface alteration, by significantly limiting the oxidation of the materials and the extension of the of  $\alpha$ -case layer [2].

The protective effect of glass or glass/ceramic composite coatings against high temperature oxidation of Ti and its alloys has been documented in a few works [3–11]. It would be due to two main contributions. First, the presence of a continuous layer of glass at the metal surface strongly isolate it from a direct contact with the surrounding gaseous atmosphere, therefore preventing it from severe oxidation phenomenon. Second, the inward oxygen diffusion, concomitant to the oxidation process, would be substantially limited by some corrosion products of the glass/metal interaction. Indeed, similarly to the corrosion of steels by molten salts in the nuclear and solar fields, the reactivity of titanium alloys with potentially oxidating and boronising glasses at high temperature represents a corrosion phenomenon. Indeed, the silica, *i.e.* one of the main components of the glass, was found to react with Ti to form, most probably among other phases, the Ti silicide  $Ti_5Si_3$  at the metal/coating interface. This Ti silicide  $Ti_5Si_3$  would act as an oxygen diffusion barrier and further limit the metal oxidation [3,4,6,7], though there are no indications regarding its morphology, *i.e.* whether it forms a continuous layer or not. From a general point of view, most of these works do not give a complete description of the metal/coating interface. More, very little is known for the protectiveness of borosilicate glass coatings used as forging lubricants against high temperature oxidation of titanium alloys, especially above 950 °C, in the temperature range of  $\beta$  forging processes.

Thus, the purpose of the present study was to provide a detailed description of the structure of the borosilicate glass/Ti-6Al-4V alloy interface formed at high temperature, as a first attempt to understand the protectiveness of such glass coatings against high temperature oxidation of Ti alloys during the forging processes. Such a detailed description of the phases composing this glass/metal interfacial region, even at an extended reaction stage, is still lacking in the literature, and would certainly bring decisive information regarding the protectiveness of borosilicate glasses against high temperature oxidation of titanium alloys.

As a first step of a more comprehensive study, we propose herein several measurement protocols (~~including unsupervised and supervised ones~~), allowing to identify which phases are formed in the interfacial region between the glass and the metal after exposure at high temperature. To date, these protocols have been used very little for the analysis of this type of complex interface. For this reason, one specific sample was selected and thoroughly analysed throughout this study.

Usually, glass coatings are several hundred microns thick and the analysis of phases precipitating at the glass/metal interface cannot be done using conventional methods such as X-Ray Diffraction (XRD). Spatially resolved technics of structural analysis, applied at samples cross-sections, must be used in such a configuration. Among them, and after some preliminary testing, Raman spectroscopy, which can be operated down to the sub-micron scale, appeared as a first good candidate. In addition, Raman spectroscopy can be operated in mapping or imaging modes, giving access to the spatial distribution of each compound, providing they effectively give a characteristic spectrum. Although Raman scattering gave some specific features of the compounds that are present in the probed area, the severe lack of experimental Raman reference data for the system investigated here, which at least implies Ti, Si, B, O, was a significant barrier for the compounds identification. As a matter of fact, from the beginning of this work, a first literature survey showed that this system was poorly documented from a spectroscopic point of view [12–15]. This bibliographical survey gave only partial information, mainly based on DFT computations, without clear experimental evidences.

From this point, and because Raman imaging effectively gave characteristic signal that could not be assigned initially, it was first necessary to build a complete Raman spectral library for the ternary Ti, Si, B system, either from experimental acquisitions providing pure phases when available, or more theoretically (DFT computations) when the phases were difficult to synthesize. This library has been easily extended for Ti oxides from literature data, see for examples references [16–18]. Thus, this study also enabled the development of a Raman database for Ti borides, silicides, and borosilicides.

Secondly, Raman imaging was used to analyse particular areas of the sample considered in this work. Again, because the signatures of the different phases present in this sample were not known, the raw image data files were first examined in a blind way, using so-called "unsupervised" methods. These methods have indeed allowed to extract some particular, characteristic spectra, which could be compared with those present or computed in the spectra library. After identification, these signatures were used to build the images of the spatial distribution of the different phases.

Finally, it remained to ensure that Raman imaging effectively gave a correct description of the sample. For such a purpose, another structural analysis technique had to be used to ascertain the information extracted from Raman imaging. Electron Backscatter Diffraction (EBSD) was selected for this purpose. As often, preliminary elemental analyses were performed using Energy Dispersive Spectroscopy (EDS) to address the analysis of the information available from these two methods.

As we will see, the combination of these two methods of optical and electronic microscopy, close to the so-called correlative imaging techniques, allowed a rather precise description of the glass/metal interface.

## **2. Materials and Methods**

### **2.1. Glass coated and uncoated samples**

Ti samples consisted in cubes of Ti-6Al-4V alloy provided by Aubert & Duval, of about 40 mm x 40 mm x 40 mm in dimensions. Faces of the cubes were grinded using P80 SiC paper. The detailed alloy composition is given in Table 1.

The cubes were coated with a commercial forging lubricant glass. This coating consists in a borosilicate glass (with a Si/B weight ratio of approximately 5.5) containing several addition elements whose nature and respective content cannot be further detailed for confidentiality reasons. Consequently, in what follows, the evolution of the glass during the thermal treatment will not be described. **The coating was applied by spraying uniformly the commercial water-based lubricant onto the grinded cubes pre-heated at 200 °C.**

Annealing of the samples was carried out in a Carbolite 1600 muffle furnace under ambient atmosphere for 8 hours at 1150 °C, *i.e.* for a temperature representative of the most stringent forging conditions. When necessary, uncoated annealed samples were available as well.

After heat treatment, the cubes were cross-sectioned to extract smaller specimens of around 20 mm x 20 mm x 5 mm. These specimens were thereafter embedded in phenolic resin, prior to be grinded and polished up to the mirror state, to enable their analysis.

## 2.2. Reference materials for the development of the Raman database

According to the isothermal sections of the Ti-Si-O, Ti-B-O and Ti-Si-B ternary systems at 1150 °C, see in particular references [19,20] for the Ti-Si-B system ternary diagram, potential compounds that may be present in the borosilicate glass/Ti-6Al-4V alloy interface are given in Table 2. It is seen that they are all limited to binary compounds of Ti with O, Si or B, within the exception of one ternary compound involving Ti, Si and B ( $\text{Ti}_6\text{Si}_2\text{B}$ ), which was only recently taken into account in the Ti-Si-B ternary diagram. Here, in a first step, the main alloying elements (Al and V) were not considered. We will see later that this was not necessary for the description of the sample under study. If required, they can be taken into account later on.

As described in what follows, these compounds constituted the first “library” used for indexing Raman spectra as well as the diffraction patterns given by the EBSD analysis.

Five of these potential materials,  $\text{TiO}_2$  (rutile) and  $\text{TiO}_2$  (anatase) (provenance unknown),  $\text{Ti}_2\text{O}_3$ ,  $\text{TiB}_2$  and  $\text{Ti}_5\text{Si}_3$  (supplier Alfa Aesar, 99.8 % purity, maximum grain size 45  $\mu\text{m}$ ) were already available and/or commercially available. They were further used and/or analysed (to get their characteristic Raman spectrum) as received.

Two of the possible titanium borides, namely  $\text{TiB}$  and  $\text{Ti}_3\text{B}_4$ , were not commercially available, they had to be synthesized, here by means of reactive sintering, following the protocol proposed by Rou and Chandran [21]. Two mixtures of pure Ti (supplier GoodFellow, 99.5 purity, 150  $\mu\text{m}$  maximum particles size) and  $\text{TiB}_2$  powders were prepared, in proportions reflecting the respective stoichiometries of  $\text{TiB}$  and  $\text{Ti}_3\text{B}_4$ . The two different powders mixtures were then treated in a Dr. Sinter 2080 unit (SPS Syntex Inc., Japan), available at the Plateforme Nationale de Frittage Flash (PNF2 - CNRS), located at the Université Toulouse 3 Paul Sabatier. An 8 mm inner diameter graphite die was used, lined with a 0.2 mm thick graphite foil (PERMA-FOIL® Toyo Tanso). Sintering experiments were conducted under vacuum (< 10 Pa) for an uniaxial pressure of 10 MPa, applied from the beginning of the process. The temperature, monitored by an optical pyrometer, was first raised to 600 °C and maintained for 3 min.

A heating rate of  $100\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  was then applied to reach the targeted temperature of  $1800\text{ }^{\circ}\text{C}$ , which was finally maintained for 2 hours. The two sintered pellets were cross-sectioned for elementary and structural analyses. They were then embedded in phenolic resin, prior to be grinded and polished up to the mirror state.

Most of the Ti silicides and the borosilicide that may be present in the system studied here were either commercially unavailable or difficult to synthesize. Density Functional Theory (DFT) calculations were therefore performed to provide, among other information, the zone-center frequencies of the Raman-active modes of these compounds. For comprehensiveness purposes, the computations concerned all stable borides, silicides, and borosilicide.

### 2.3. DFT computations

DFT computations were performed using the Vienna *Ab initio* Simulation Package, VASP [22]. Simulations were carried out within the Perdew-Burke-Ernzerhof generalized gradient approximation of the exchange and correlation functional (PBE) [23] to the density functional theory [24,25]. Projector augmented wave (PAW) pseudo-potentials [26] were used, and a kinetic energy cut-off of 600 eV for the plane-wave basis set was adopted to compute energies. Calculations of energies were performed on primitive cells. A 600 eV energy cut-off and  $\Gamma$ -centered Monkhorst-Pack [27] sampling of the Brillouin zone (BZ) showed good convergence for structural relaxations. Results were obtained at zero pressure.

To compute inter-atomic force constants (IFC), and thus the vibrational band structures plotted along high symmetry q-point and the vibrational projected density of states, additional calculations were carried out. The finite displacement method using the *phonopy* package [28] were performed on supercells (see Table 2 for the supercells used). The complete result of these computations is given in Appendix A (Table A.1 and Table A.2). Throughout this paper, we will only use the zone-centre ( $\Gamma$  point) frequencies, assuming crystalline phases, as evidenced by the first examinations of the sample.

The space groups of the different phases considered, and their respective lattice parameters, experimental as well as computed, are given in Table 3. The agreement between the experimental and computed lattice parameters is usually a first indication of the reliability of the computation. It is seen from Table 3 that the agreement is excellent.

### 2.4. Optical microscopy: metallographic observations and Raman spectroscopy

Preliminary metallographic observations were conducted using a Keyence VHX7000 digital microscope.

Then, micro-Raman measurements were performed using a Renishaw InVia spectrometer. Most of the measurements were conducted at 532 nm. Excitation at 785 nm was used occasionally to ensure that some observed specific signatures were indeed Raman vibrational modes. 50x and 100x (numerical aperture or NA = 0.75 and 0.9 respectively) objectives were systematically used to focus the laser at the sample surface and collect the scattered light.

Frequency calibration was performed using a silicon standard, whose frequency was set at  $520.5\text{ cm}^{-1}$ . Using the present set-up, the spectral resolution (*i.e.* the accuracy on the frequency determinations from line fitting procedures) was about  $0.1\text{ cm}^{-1}$ .

To prevent overheating effects, the power density at the specimen was first reduced down to a few  $\text{mW}/\mu\text{m}^2$ . Nevertheless, it was observed that such a power density was still too high to safely analyze particular areas of the samples, and most of the standards available as powders. Such an overheating was revealed by strong line shifts and broadenings, or even by a complete sample oxidation in the case of the boride and silicide powders. To solve, or at least minimize this issue, the line mode of the spectrometer was also used. In this case, the laser beam was focused along a line of about 20 or 50  $\mu\text{m}$  long, depending on the objective magnification, and about 1  $\mu\text{m}$  wide. Then, the line was imaged at the CCD camera. Using such focusing conditions, it was possible to use power densities well below  $500 \mu\text{W}/\mu\text{m}^2$ , still keeping reasonable acquisition times, a few tens of seconds at most, depending on the signal/noise (S/N) ratio needed. The final criterion was to select a power density for which controlled evolution of the line shape of the spectra versus power density and/or time were achieved. We will come back to this point below.

From this point, both point and line modes were used for Raman imaging of the samples. The Raman images were systematically constructed with a measurement step of about 1  $\mu\text{m}$  or below, that is a point spacing close to the actual spatial resolution of the method. Data pre-processing mainly consisted in spikes elimination and, when necessary, a so-called “base-line” subtraction. In such case, base-lines were fitted with polynomial functions mainly using the higher wavenumber range, beyond  $800 \text{ cm}^{-1}$ , far from the Raman signals of the sample, taking care not to modify the overall line shape of the Raman spectra. For some of the computations, the data sets, *i.e.* all individual spectra, were normalized to unity.

To create the 2D spectral images, the spectra were processed in different ways [29,30]. Here, the information being sought was only the nature of the phases that are present in a particular area of the sample. As we shall see, the overlap of the characteristic spectra of each phase can be more or less important. As an immediate direct consequence, it was difficult or even impossible to isolate and use a specific Raman line of a given phase to draw its corresponding Raman map. Thus, so-called multivariate methods, which consider the whole frequency range of each spectrum, had to be privileged. Different image creation methods have been used, that use either supervised or unsupervised algorithms [29]. As a rule, for such computations, the raw data set is represented as a matrix, where each collected spectrum occupies a row in the data matrix. This matrix has dimension  $m \times n$ , where  $m$  is the total number of spectra from the data set and  $n$  is the number of wavenumbers at which the intensities are collected. The aim of each of these multivariate methods is to reduce this raw data matrix into submatrices  $C$  and  $S$  according to Eq. 1:

$$D = C \cdot S^t + E \quad (1)$$

Here,  $D$  is the  $m \times n$  data matrix composed of  $m$  spectra and  $n$  wavenumbers,  $C$  is the  $m \times p$  concentration or “scores” matrix with  $p$  the number of pure reference spectra,  $S$  is the  $n \times p$  matrix consisting of “pure phase spectra” or “loadings” corresponding to unit concentration,  $E$  is the  $m \times n$  model residual noise matrix.  $t$  stands for matrix transpose.

In the supervised approach, a library of reference spectra, *i.e.* spectra that correspond to pure phases, is used. Then, each individual spectrum from the raw data file is expressed as a linear combination of those reference spectra. Obviously, the method assumes that the library contains all the possible reference spectra, *i.e.* the spectra of all the phases that may be encountered during data collection. In other words, the sample has to be perfectly known. As stated above, some of these reference spectra have been obtained from acquisitions on pure components. Otherwise, these reference spectra have been extracted from the raw data set after identification from the predictions of DFT calculations. This approach, which requires looking at all the individual spectra, can be prone to errors or omissions in the case of an unknown system, or of files containing a very large number of spectra.

Because the system investigated was not known from the beginning of this work, initial guesses were obviously necessary. To assist and guide the supervised analysis, two different classes of unsupervised algorithms were used as well, namely principal component analysis (PCA) and multivariate curve resolution (MCR). Their descriptions most probably fall outside the scope of this paper, we refer the reader to references [31,32] for such a purpose. In short, PCA analyzes data variance [31]. One of the main interests of PCA lies in its ability to condense the information from thousands of spectra into a few orthogonal principal components (PCs), usually known as “loadings”. Then, the corresponding “scores” can be used for image visualization and subsequent spectral feature extraction. Because each PC is obtained by maximizing the amount of variance it explains, it does not correspond to a specific chemical species or a specific crystallographic phase. However, such an analysis allows to visualize the different areas of interest in a given Raman image quite immediately. Then, because each particular region contains a characteristic “true Raman fingerprint”, the method may provide a way to go back to the individual signatures of each particular phase present in the sample, in an indirect way however. MCR is the generic denomination of a group of techniques whose aim is to retrieve the spectral signatures, here the Raman spectra, of the pure chemical species that are present in the experimental data file. Here, no prior knowledge on the composition of the mixture and the location of the different phases is necessary [32], meaning that this iterative method can be used even when the sample or the system is not known. This is clearly the strength of this method. Generally, the method works rather well when some of the components are present in pure form somewhere within the dataset. In the present work, data processing was mostly achieved using the commercially available Wire 5 software package.

A particular area of the sample has first been identified and located to allow the correlation of Raman images with compositional Energy Dispersive X-rays Spectrometry (EDS) and structural Electron Backscatter Diffraction (EBSD) images. These measurements were performed sequentially. In a second step, other regions of the same sample were further analyzed with adapted acquisition conditions.

## **2.5. SEM/EDS/EBSD analyses**

Scanning electron microscopy (SEM)-based observations and characterisations were performed on a JEOL JSM-7100TTL LV Field Emission Gun – Scanning Electron Microscope (FEG-SEM). Elementary analysis was performed by EDS analysis using a 100 mm<sup>2</sup> SDD Ultim-max detector (Oxford Instruments). Structural analysis was done by EBSD analysis using a Symmetry S2 CMOS EBSD camera (Oxford Instruments). The information sought here is the local diffraction pattern, for phase identification purposes and grain morphology characterisation. The potential grain orientation or texture effects will not be analysed in the present paper.

It is obvious that the spatial resolution of electron microscopy-based techniques, about 100 nm for EBSD, also allowed to precisely locate the different phases and gave access to their morphologies. For phase identification, combined EBSD and EDS maps were acquired at 10 kV accelerating voltage, in order to reduce the interacting volume, using TruMap option with a step size of 100 nm.

## **3. Results**

### **3.1. Metallography**

The first preliminary characterisation consisted in the evaluation of the protective capacity of the glass coating in the  $\beta$  stability domain of Ti-6Al-4V alloy. For such a purpose, cross sections of both glass coated and uncoated samples were chemically etched with the Kroll reagent to reveal the  $\alpha$ -case area,



according to known procedures. Resulting optical micrographs are presented in Figure 1. As evidenced in Figure 1, Kroll chemical etching revealed the presence of a thick  $\alpha$ -case region of about 700  $\mu\text{m}$  in the uncoated sample, represented by the bright region composed of large acicular grains at the surface of the sample. On the contrary, no clear evidence of its presence could be found in the analogous glass coated sample. As the  $\alpha$ -case formation is directly linked to the oxygen ingress at high temperature [33], increasing locally the  $\beta$  transus temperature, the absence of  $\alpha$ -case formation when the glass coating is used clearly illustrates its protective effect, even in the very high temperature range considered in this work.

### 3.2. EDS mapping

EDS maps of the main compounds of the system, namely Ti, Al, V, O, Si and B, obtained on glass/metal interface of the sample, are shown in Figure 2. The EDS analysis indicates that the interfacial area is essentially composed of Ti, O, Si and B, distributed among different regions that can be identified thanks to the contrast of the Ti element distribution map. On the contrary of Ti, O, Si and B, no quantifiable levels (i.e. over 1 at.%) of Al and V could have been detected, except within the alloy. They were thus not considered in the following process of interfacial compounds identification.

From the glass to the alloy matrix, the first layer, closest to the glass, appears discontinuous and mainly composed of Ti and O, and most probably corresponds to one or several Ti oxides. Then, Si and B are detected within the interfacial region, along with Ti. The contrast of these Ti, Si and B element images suggests the presence of at least two, or even three phases composed of Ti, Si and/or B. Finally, O is not detected in the lower part of the images, another proof of the protective effect of the glass against oxygen ingress during the high temperature heat treatment.

Looking at Figure 2, the area of interest for Raman imaging is therefore limited to a region of thickness of only about 15  $\mu\text{m}$ .

### 3.3. Raman Spectroscopy

#### 3.3.1. Construction of the spectral library

As expected from the phase diagrams, and subsequently confirmed by the EDS analyses, the interfacial region between glass and Ti potentially contains different oxides, borides and/or silicides. As most of the Raman spectra of these materials were not known, it was first necessary to generate the spectral library, for identification purposes. To this end, spectra were recorded on standards when available, otherwise spectra, more exactly the expected zone-center Raman frequencies were computed. In the latter case, *first-principles* methods are reliable enough to give a precise idea of the expected zone-center frequencies. As mentioned in section 2.2 and confirmed from the EDS mapping information, the alloying elements were not considered. Obviously, if necessary, they could be taken into account afterwards.

The symmetry of the different Raman-active zone center modes was determined from the DFT computations (using phonopy code [28]). Therefore, the corresponding Raman tensors are known from the character tables of each symmetry group. Nevertheless, in what follows, we simply give the Raman spectra and/or the computed frequencies, without going into the details of the consequences of the mode symmetries, not useful here. As a matter of fact, the polarization of the scattered light was not analyzed, and more, the orientation of the crystallites in the interfacial region was not known, even if this information is available in the EBSD data, see below. Moreover, the relative intensities of

the different lines of each compound cannot be computed accurately by the computation protocol used in this work. Therefore, one expects to observe some differences in the relative intensities of the lines for a given compound, depending on the orientation of the grains relative to the propagation and polarization directions of the incident laser beam. This means that line intensity ratios cannot be completely considered and discussed in what follows. To ensure that all frequencies were effectively observed, many spectra have been recorded on each available compound. In what follows, typical spectra are given. The main trends are described in Figures 3a-c. The computed frequencies are indicated by the vertical bars in the figures.

The spectra of the main titanium oxides ( $\text{TiO}_2$  rutile and anatase,  $\text{Ti}_2\text{O}_3$ ) were already known, see for example references [16–18]. Four ( $A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$ ), six ( $A_{1g} \oplus 2B_{1g} \oplus 3E_g$ ) and seven ( $2A_{1g} \oplus 5E_g$ ) Raman-active modes were expected, respectively. The corresponding spectra are given in Figure 3a. They correspond in all respects to those widely reported in the literature, it is seen that they can be easily distinguished.

On the other hand, as already mentioned, the spectra of Ti borides, silicides and borosilicides were not known experimentally: it was first necessary to compute them. The computed frequencies, along with the corresponding mode symmetry, are given in Tables A.1-9. When possible, they are compared to the few data available in the literature [12,14–18]. In most cases, our results are very close to those of Wdowik et al. [12,14,15]. This is not unexpected insofar the overall computation protocol is the same.

The examination of Tables B.1-9 shows that these spectra can be constituted of many lines, because of the more or less important number of atoms in the primitive cells that are characteristic of each phase.

Thanks to the different titanium borides reference materials (synthesized or commercially available), the three Ti borides could be directly examined. Their corresponding spectra are given in Figure 3b, along with the computed frequencies (detailed in Tables B.7-9). Note that it was impossible to record a clear spectrum for  $\text{TiB}_2$ , whatever the acquisition conditions used. It can be seen that the computation reproduces the experimental spectra quite faithfully. Moreover, Figure 3b demonstrates that the spectra of the different Ti borides can be easily discriminated, if needed.

Concerning Ti silicides, only  $\text{Ti}_5\text{Si}_3$  could be analyzed. Its spectrum is given in Figure 3c. Again, it is seen that the correspondence between the experimental spectrum and the calculated one is rather good. The broad signal around  $800 \text{ cm}^{-1}$ , which was not observed systematically, most probably comes from the spectrometer's optics when high acquisition times are to be used. We will not consider this signal in the following. On the other hand, the examination of the Tables B.1-5 suggests that the other phases cannot be discriminated as easily, without some knowledge about the line intensities. The only exception is  $\text{TiSi}_2$ , a compound for which the experimental spectrum is known. In this case also, the model vs experiment agreement was found to be satisfactory [14].

The last compound considered was  $\text{Ti}_6\text{Si}_2\text{B}$ . The expected frequencies are also given in Table B.6., along with those extracted from reference [15]. Likewise, the two data sets are in agreement.

From Table 1, it is seen that borides can be discriminated from silicides. Because of the low boron mass, specific Raman modes are effectively expected at much higher frequencies, while the cut-off frequencies of the silicides spectra are lower than  $\text{ca } 450 \text{ cm}^{-1}$ .

### 3.3.2. Analysis of the glass-coated sample.

Because the phases present in the interfacial layer were not known *a priori*, there were different ways to address the analysis of the sample. The first one was obviously to record spectra on the sample at random, or more conveniently with the help of the contrast of the optical image. Here, the main issue was that most of the experimental spectra turned out to be the result of the superposition of several "pure phase" spectra. This was partly due to the small grain size of the crystallites that constitute the interfacial area. Nevertheless, these first analyses allowed to isolate without too much ambiguity the Raman signature of four different phases, namely  $\text{Ti}_2\text{O}_3$ , TiB,  $\text{Ti}_5\text{Si}_3$  and  $\text{Ti}_6\text{Si}_2\text{B}$ , see Figure 4. In the figure, the red traces are the reference spectra already given in Figure 3, while the blue traces are the spectra obtained for the sample cross-section, close to the interfacial region. According to the figure, the first three phases ( $\text{Ti}_2\text{O}_3$ , TiB and  $\text{Ti}_5\text{Si}_3$ ) are therefore unambiguously identified. One can also see on this same figure that the characteristic spectrum of  $\text{Ti}_2\text{O}_3$  recorded in the sample is downshifted from the reference spectrum, which reflects a local heating under the focused laser beam. This justifies the choice to use the line mode of the spectrometer to limit local overheating when recording Raman images.

The last identified phase was  $\text{Ti}_6\text{Si}_2\text{B}$ , as shown by the comparison of the experimental spectrum and the computed frequencies. Again, the agreement was satisfactory, even if only one mode was seen to have a significant intensity.

Among these compounds, only  $\text{Ti}_5\text{Si}_3$  had already been clearly detected or merely suggested in similar systems [3,7,8,34–38]. Nevertheless, this first approach did not ensure that all the present phases were actually detected.

The second method was to get some first Raman images of the sample, and to analyze the data files using unsupervised methods. This second method is probably more efficient since it ensures that no information is forgotten. In particular, it allows to confirm or refute that all the phases present in the sample have been detected by simple visual inspection of the sample, as long as they effectively give a Raman signal.

Several Raman images were recorded for this particular sample. All gave the same trends. The main issue was to work using low to very low incident power, that is with rather weak signals, in order to avoid the strong overheating of a particular phase,  $\text{Ti}_2\text{O}_3$ , which was consequently seen differently by the algorithms, depending on its location in the vicinity of the glass/metal interface. This was clearly a concern here because most of the detected phases gave only weak Raman responses. This is why the analysis in line mode had to be privileged in a first time, at the expense of a slightly lower spatial resolution.

The example detailed in Figure 5 refers to the area already analyzed using EDS, see Figure 2. For this particular example, the image file contains 2774 spectra. The measurement step was  $1.3\ \mu\text{m}$  both in x and y directions, the analyzed area ( $85 \times 48\ \mu\text{m}^2$ ) is highlighted in the SE image. In a first step, PCA has been used, in order to have a first quick review of the data set in a totally blind way. The analysis showed that this dataset could be reconstructed using 8 to 10 components, which described more than 99 % of the variance in the dataset. Again, these components, all orthogonal to each other, have no particular physical meaning, as such they were just used to reconstruct the data set. Images of the corresponding "scores" of five of these components are shown in Figure 5. They effectively allowed to visualize all the different areas of interest in the sample, *i.e.* the glass/metal interfacial area in particular. They are given in false colors to increase their contrast and simplify their reading.

Focusing on the particular area depicted in the PCs images, the images tend to exhibit different strata or different nodules that are recognized and described differently by the algorithm. Looking at the signals obtained in these particular regions, one finds again the four different characteristic signatures of  $\text{Ti}_2\text{O}_3$ , TiB,  $\text{Ti}_5\text{Si}_3$ ,  $\text{Ti}_6\text{Si}_2\text{B}$ . Such an analysis also tends to show that these are the only signatures present in the data set, in the interfacial area. The interfacial area can thus be described by at least four different phases. Here, it is obvious that a compound which do not give a specific signature will not be definitely identified here. Nevertheless, the algorithm will still detect areas without specific signals, and differentiate them from the other areas providing their respective signatures are significantly different from each other. This means that an important criterion is the signal/noise ratio of the measurement, which must be high enough to allow to discriminate all the different spectra. Here, this first simple analysis suggests that only very little information may be missing.

In a second step, the multivariate curve resolution alternating least square (MCR-ALS) algorithm was used, as an attempt to retrieve the pure spectral contributions that are present in the data file. Here, eight components were required to describe the dataset. Quite unexpectedly, the algorithm computed signatures close to the spectra of  $\text{Ti}_2\text{O}_3$ , TiB,  $\text{Ti}_5\text{Si}_3$ , see Figure 6. In the figure, the red traces are the spectra of the  $\text{Ti}_2\text{O}_3$ , TiB and  $\text{Ti}_5\text{Si}_3$  standards, while the blue traces are the computed spectra. One note here that  $\text{Ti}_2\text{O}_3$  is seen in two slightly different ways as their two characteristic spectra differ greatly both in frequency and line width, which again translates a strong local heating of this phase, despite the precautions made while working at the lowest possible incident power. The fourth computed spectrum is more difficult to interpret, even if it exhibits one of the expected frequencies for  $\text{Ti}_6\text{Si}_2\text{B}$ , the frequency of its most intense mode. Again, the remaining three signals (not shown here) gave the signals recorded in the glass and the metal. In the interfacial area, the MCR algorithms show that each experimental spectrum can be seen as a linear combination of these four computed spectra. The coefficients of these linear combinations are plotted as an image in Figure 5b. These images indicate the potential distribution of these phases in the interfacial layer.

From this point, it is possible to reconstruct the data set in a supervised way, with the assumption that each experimental spectrum is a linear combination of the pure phase spectra recognized above, namely  $\text{Ti}_2\text{O}_3$ , TiB,  $\text{Ti}_5\text{Si}_3$  and  $\text{Ti}_6\text{Si}_2\text{B}$ , while introducing in the computations the different signals recorded in metal and in glass so that it converges to a physically correct solution. Another way to proceed could be to mask the uninteresting areas, here glass and metal. In the end, both solutions gave the same trends. The resulting images are given in Figure 5.

Looking at Figure 5, one observes that all three methods partly converge to a same sample description. In particular, the spatial distribution maps obtained by both supervised and unsupervised approaches exhibit the same details. By contrast, the MCR algorithm could not recognize and clearly extract the  $\text{Ti}_6\text{Si}_2\text{B}$  signal. This is partly due to the fact that this compound has a rather weak Raman response. As we will see in the following, it was possible to improve its detection by slightly modifying the acquisition conditions. Nevertheless, it is seen that Raman imaging gives access to the spatial distribution of these four phases.

In the last two computations, the intensity of all spectra was normalized to unity. This allowed to smooth the strong differences in intensity observed in the data set. It also allowed to use intensity scales ranging from 0 (absence) to one (pure phase), which simplifies the reading of the images.

This approach effectively allowed to describe the sample. However, one has to keep in mind that this is only an approximate solution. In particular, each reference spectrum is assumed to perfectly

correspond to those that may be found in the data file. In practice, for a lot of reasons (strain, crystallographic texture and/or grain orientation...) this is obviously not feasible. Nevertheless, if the errors in a reference spectrum are small compared with the overall signal values, this approach remains a fair approximation. It is also understood that the mixing coefficients do not lead to true volume fraction calculations, due to strong differences in scattering cross-sections of the different pure phases and/or strong differences in optical properties. They are simply an indication of the presence or absence of a given phase at a given location in the area analyzed. Finally, the data obtained here do not allow to simply quantify a possible hypo- or hyper- stoichiometry of these phases, which is always a crucial information when transport properties are concerned.

The Raman analysis suggests that the interfacial region is composed of 4 different phases, namely  $\text{Ti}_2\text{O}_3$ , TiB,  $\text{Ti}_5\text{Si}_3$ , and  $\text{Ti}_6\text{Si}_2\text{B}$ .  $\text{Ti}_2\text{O}_3$  was rather found in the glass, and/or close to the glass/metal interface, whereas  $\text{Ti}_6\text{Si}_2\text{B}$  as detected in the bottom of the interfacial layer as a more or less continuous layer of around 3  $\mu\text{m}$  thick. Most of the interfacial region is made of  $\text{Ti}_5\text{Si}_3$ , along with some TiB inclusions.

In order to confirm these first results, the same area was subsequently analyzed by EBSD.

### 3.3.3. Electron backscatter diffraction

Here, in a similar way, indexing was conducted on the basis of the phases potentially present in the interfacial layer, see Table 1. In addition, the  $\alpha$ -Ti and  $\beta$ -Ti phases composing the initial alloy matrix were introduced in the database. The crystalline structures of the compounds potentially present are sufficiently dissimilar to ensure the discrimination of the different associated phases.

Band contrast map, *i.e.* the electron backscatter pattern (EBSP) quality measured by the software (based on the contrast or sharpness between the Kikuchi bands and the background) and the indexed phases map are presented in Figure 7a and Figure 7b respectively. Black areas correspond to unindexed regions associated to very weak band contrast. This can be the case for amorphous/poorly crystallised compounds, or for submicronic grain sizes. In particular, the black areas in the upper part of both figures correspond to the glass. First, according to Figure 7a, the band contrast map appears to reflect rather faithfully the FSD micrograph, see Figure 5, indicating that most of the glass/metal corrosion products are crystallised. This rather high crystallinity was already suggested by the quality of the Raman spectra observed in this particular region of the sample. Second, the indexed phases map presented in Figure 7b confirms the sequential arrangement of the glass/metal corrosion products evidenced by Raman spectroscopy, with a much better spatial resolution however. In particular, EBSD confirmed the presence of small quantities of TiB, in the form of submicronic acicular grains, dispersed within the two first layers of corrosion products and the first micrometers of the metal matrix just beneath them.

The first layer of corrosion products, contiguous to the metal matrix, is confirmed to be a  $\text{Ti}_6\text{Si}_2\text{B}$  layer. EBSD also revealed that this layer was continuous and dense. More, it is composed of a single row of equiaxed grains of around 3  $\mu\text{m}$  in diameter. The next layer, about 15  $\mu\text{m}$  thick, is confirmed to be mainly  $\text{Ti}_5\text{Si}_3$ , containing small dispersed acicular grains of TiB, as mentioned above. EBSD also evidenced the additional presence of small dispersed nodular grains of  $\alpha$ -Ti of around 1  $\mu\text{m}$  in diameter within this  $\text{Ti}_5\text{Si}_3$  layer.

Unlike Raman spectroscopy, EBSD revealed an additional discontinuous layer of  $\text{TiB}_2$  next to the  $\text{Ti}_5\text{Si}_3$  one, in the form of small grains of hundreds of nanometres dispersed within the first few micrometers

of glass. The  $\text{TiB}_2$  layer was finally followed by another discontinuous layers of  $\text{Ti}_2\text{O}_3$ , whose grains also appeared dispersed within the first micrometers of glass next to the  $\text{TiB}_2$  grains. As mentioned above,  $\text{TiB}_2$  did not give a clear Raman signature, thus not allowing to detect this phase without ambiguity.

Nevertheless, neglecting the small contribution of  $\text{TiB}_2$ , both Raman spectroscopy and EBSD gave a similar description of the sample. The observed phases are located identically by both techniques.

### 3.3.4. Additional Raman analysis

Following the EBSD results, other Raman measurements were conducted on the same sample, in different regions, to validate and improve the analysis protocol, and to confirm the first trends. In order to improve the convergence of Raman and EBSD descriptions of the sample, these additional measurements were conducted at a higher spatial resolution, here  $0.6 \mu\text{m}$ , *i.e.* the highest resolution that can be reached with the line mode of the spectrometer. A 100x optic, not available at the beginning of this study, was used for this purpose. Here, the analysis of the image data set was conducted in a supervised manner. Reference spectra, that correspond to the four phases evidenced, were extracted from particular areas of the image, for a better convergence of the computation. Again, the glass and metal signals were taken into account.

The composition images are given in Figure 8. The results are in all respect similar to those described in Figure 5, with a much better spatial resolution, which allows a better discrimination of the different detected phases. This figure does not give any additional information concerning the interfacial area, it simply shows that the method allows to clearly distinguish spatially the different phases. One also sees that the contrast of the optical image is now high enough to distinguish the more or less continuous  $\text{Ti}_6\text{Si}_2\text{B}$  layer.

More, it was possible to distinguish and use two very slightly different signals in the sample area that correspond to the Ti alloy. These two images are also given in Figure 8. It is seen that they closely mimic the distribution of the  $\alpha$  and  $\beta$  phases of Ti, as described in the EBSD image given in Figure 7. At present, we do not have a clear explanation for the origin of these two slightly different signals or responses, as it is generally accepted that metals do not give strong specific signals. Nevertheless, Raman scattering by electrons in elemental metals such as Al, Mo, Nb, Zr, Ta, Ti, V, or W was reported in a few works [39]. Here, the elementary electronic Raman scattering process in the metal consists in the excitation of an electron from below to above the Fermi level. Generally, the Raman scattering response consists in a continuous signal smeared over a wide range of frequencies (few hundreds or thousands of  $\text{cm}^{-1}$ ) and it is usually rather low in intensity, much lower than signals arising from vibrational origins. This is why this type of signal is often discarded as a “noise” or sometimes assimilated to a luminescence “background”. This may be a first explanation, without formal proof however. Other factors, such as a simple variation in reflectivity between the two phases can also be considered. Anyway, this will probably be a direction to explore in further studies.

## Discussion

The main purpose of this paper was to characterize the interfacial reaction taking place between Ti-6Al-4V alloy and a borosilicate glass at high temperatures,  $1150 \text{ }^\circ\text{C}$  in the present study. For such a purpose, we focused on the description of a particular sample.

From an experimental point of view, the protocol proposed here, allowed a precise determination of the different phases that are present in the interfacial zone, between the glass and the metal. This illustrates the potential of the so-called correlative imaging techniques, here the coupling of two methods that allow the identification of particular crystalline phases, even if the measurements were not made in a single instrument. In this particular case, the protocol works well because all the different phases are crystalline. Regarding the Raman part, this work is also an illustration of the contribution of unsupervised methods for the analysis of unknown samples. Indeed, they allow to isolate quite immediately the different regions of interest on an unknown sample, and to extract their different spectral characteristics. These characteristics can then be compared with databases, either experimental ones, or theoretical ones as this had to be the case in this work. Indeed, the DFT methods allow to obtain the vibrational spectra of solids with a great reliability.

For the temperature considered in this work (1150 °C), the borosilicate glass reacts with Ti-6Al-4V to form a number of intermediate phases, including  $Ti_2O_3$ ,  $TiB_2$ ,  $TiB$ ,  $Ti_5Si_3$  and  $Ti_6Si_2B$ . Both  $Ti_5Si_3$ ,  $Ti_6Si_2B$  were observed as quite continuous layers, while  $Ti_2O_3$ ,  $TiB_2$ , and  $TiB$ , were rather detected in the form of sub-micrometric inclusions.

Presence of titanium oxide at the glass/metal interface results from the oxidation of titanium by the glass components ( $SiO_2$  and  $B_2O_3$  mainly). However, formation of titanium sesquioxide  $Ti_2O_3$ , rather than  $TiO_2$ , indicates that the glass coating drop the oxygen activity down to at least  $10^{-22}$  at the glass/metal interface. The dispersed state of  $Ti_2O_3$  within the first micrometers of the glass would be due to its partial dissolution within the glass, as observed for  $TiO_2$  by Podor et al. [40].

Boron and silicon released by titanium oxidation can then diffuse toward the alloy surface and react with titanium to form titanium boride  $TiB_2$  [40] and titanium silicide  $Ti_5Si_3$  [3,7,8,34–38] under low oxygen activity conditions. Analogously to  $Ti_2O_3$ , the dispersed state of  $TiB_2$  would be due to its partial dissolution within the glass network.

Formation of  $Ti_5Si_3$  has been strongly suggested during the interaction of Ti with silicon-containing coatings (Si,  $SiO_2$ , glass, ...) in previous works [8,41,42]. The presence of other silicides was also sometimes suggested, see reference [41], and references herein. This does not seem to be the case here, at least close to the metal. In most cases, this identification was based on the elemental analysis (EDS and EPMA). To our knowledge, the effects of borosilicate glasses were less studied, and the presence of borosilicides induced by the interaction of Ti with borosilicate glass has never been reported.

One finds in the glass/alloy interfacial region the phases that are expected in the Ti-rich corner of the Ti-Si-B system, as shown in Figure 9 by the Ti-TiB<sub>2</sub>-TiSi<sub>2</sub> domain of the ternary Ti-B-Si diagram, computed using the TCTI4 database from Thermo-Calc. This phase diagram does not allow to correctly trace the diffusion path experimentally observed in Figure 7b. For instance, the TiB precipitates within the large Ti<sub>5</sub>Si<sub>3</sub> region indicates the existence of a two-phase TiB-Ti<sub>5</sub>Si<sub>3</sub> domain, which is absent on the computed diagram of Figure 9. The inconsistency can be explained by a simplified modeling of the Ti-B and Ti-Si binary systems in the TCTI4 database. Indeed, phases such as TiB<sub>2</sub>, TiB and Ti<sub>5</sub>Si<sub>3</sub> are described as stoichiometric compounds in the database, but small non-stoichiometric domains have been previously reported in the literature [43,44]. Therefore, starting from the computed version, the Ti-TiB<sub>2</sub>-TiSi<sub>2</sub> domain of the ternary Ti-B-Si has been modified as shown in Figure 10, including these features, which lead to the “appearance” of two-phase domains. The diffusion path corresponding to the observations of Figure 7b has hence been drawn, according to the conventional rules [45], starting from the TiB<sub>2</sub> layer. It is hard to tell if the TiB<sub>2</sub>-Ti<sub>5</sub>Si<sub>3</sub> interface is planar or not: the wavy shape could be due to the initial rugosity of the material or it could be due to the release of supersaturated element in the diffusion process. In the hypothesis of planar interface, the diffusion path should be parallel to

a tie-line of the  $TiB_2$ - $Ti_5Si_3$  two-phase domain, as shown in Figure 10. On the contrary, the  $TiB$  precipitates within  $Ti_5Si_3$  clearly indicates the crossing of the tie-lines in the  $TiB_2$ - $Ti_5Si_3$  domain. The complex  $Ti_5Si_3$ - $Ti_6Si_2B$  interface with the presence of  $TiB$  precipitates indicates the equilibrium among three phases, which can be represented with a dashed line crossing the corresponding three-phase domain. Finally, the  $\alpha$ -Ti phase is reached, with the presence of  $TiB$  precipitates, which agrees with the necessity to cross the  $\alpha$ -Ti- $TiB$  region, before reaching the monophasic  $\alpha$ -Ti domain, in agreement with the phase diagram of Figure 10.

As illustrated by the two comparative micrographs presented in Figure 1, the glass coating appears to prevent the  $\alpha$ -case formation in the glass coated sample. Such phenomenon is directly linked to a significant reduction of the oxygen ingress in the metal matrix. This might be due to two distinct and potentially concomitant contributions. The first one would consist in a strong reduction of the O activity at the metal surface down to around  $10^{-38}$ , which represents the lower boundary of the  $\alpha$ -Ti(O) stability domain. The second one would consist in a significant decrease of O diffusivity within the different compounds separating the metal from the atmosphere, namely the glass and the different corrosion products forming continuous interfacial layers ( $Ti_5Si_3$  and  $Ti_6Si_2B$ ).

It is difficult to go further in this discussion, as only one example has been fully analyzed. A next step will be certainly to vary the exposure times at high temperature. If the suggestions and/or explanations given above are valid, it will be necessary to go further in the elementary analysis, i.e. to use EPMA to accurately quantify evolution of the element profiles, especially those of oxygen, along the glass/metal interface down to the metal matrix.

#### 4. Summary

The main purpose of this paper was to describe the interfacial region formed between Ti-6Al-4V alloys and a specific borosilicate glass at high temperatures, 1150 °C in the present study. The correlation of two optical and electronic microscopy methods (Raman and Electron Backscatter Diffraction imaging), very little used so far for the analysis of similar systems, effectively enabled an accurate description of this particular interface at the micrometric scale or below. In addition, both techniques have provided the same information in terms of phase identification, confirming the potential of the so-called correlative imaging methods. This same protocol could be used to analyze in a more detailed way the time evolution of this particular Ti alloy/glass interface.

This specific interface was seen to be composed of five different phases, namely  $Ti_2O_3$ ,  $TiB_2$ ,  $TiB$ ,  $Ti_5Si_3$  and  $Ti_6Si_2B$ . A modified version of the 1150 °C isothermal section of the Ti-Si-B ternary diagram, attempting to account for the non-stoichiometric character of  $TiB$ ,  $TiB_2$  and  $Ti_5Si_3$ , is used to trace the diffusion path experimentally observed. It would be interesting to perform similar studies using glasses of different boron contents in order to evaluate the role of this element on the overall sample behavior.

At the same time, this study also enabled the development of a Raman database for Ti borides, silicides, and borosilicides, both from experimental and theoretical (DFT computations) points of view, while still awaiting some experimental verification for some of the silicides considered.

#### 5. Acknowledgements



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## 6. Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

## 7. Author statement

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## Appendix A

DFT calculations were performed using the Vienna *Ab initio* Simulation Package, VASP [22]. Simulations were carried out within the Perdew-Burke-Ernzerhof generalized gradient approximation of the exchange and correlation functional (PBE) [23] to the density functional theory [24,25]. Projector augmented wave (PAW) pseudo-potentials [26] were used. Calculations of energies were performed on primitive cells. A 600 eV energy cutoff and  $\Gamma$ -centered Monkhorst-Pack [27] sampling of the Brillouin zone (BZ) showed good convergence for structural relaxations. Energies minimization includes the optimization of atomic positions as well as super-cell shape and volume. Results were obtained at zero pressure. Details of the structures are presented below. Atomic structures are visualized with VESTA (Visualisation for Electronic and Structural Analysis) [46].

The main information is presented in the Table A. [Erreur ! Source du renvoi introuvable.1](#): space group, number of atom per unit-cell, Wyckoff positions and Infra-red and Raman irreducible representation.

To calculate the inter-atomic force constants (IFCs), and thus the vibrational band structures (plotted along the high symmetry q-points [47]) and the projected density of states (onto non-equivalent positions), additional calculations were carried out. The finite displacement method using the *phonopy* package [28] were used on super-cells (see Table A. [Erreur ! Source du renvoi introuvable.1](#)). From group theory [48], the infra-red and Raman irreducible representations are deduced.

For the Ti-B system, our results are very close to those of Wdowik [12], the method is the same (same code, same pseudo-potential, but here with stronger convergence criteria). In our work, these systems were all found metallic, so it was impossible to calculate the dielectric constants.

Lattice parameters are in excellent agreement with experimental ones and theoretical literature. All structures are non-magnetic except  $Ti_3Si$ , see values in Table A.1. The formation energy,  $E_f$  in eV per atom, given by Eq. A.1:

$$E_f[Ti_xSi_yB_z] = \frac{E_0[Ti_xSi_yB_z] - \frac{x E_0[Ti_{hcp}]}{2} - \frac{y E_0[Si_{diamond}]}{2} - \frac{z E_0[B_\alpha]}{12}}{x + y + z}$$

(Eq. A.1)

were computed for all structures.  $E_0$  correspond to the DFT energies of phases. The reference states are: the diamond for Si, hcp system for Ti and  $\alpha$  phase for boron [49]. Energies are listed in Table A. [A.12](#). The most theoretically stable phase, at a given concentration, is always the phase observed experimentally. The DFT approaches deployed here allow to reproduce with great accuracy the ground state properties of the studied systems, *i.e.* for Ti-B, Ti-Si and TiSi-B systems. We therefore went further in the study of these systems and studied the vibrational properties, which then allowed us to analyze the frequencies in the center of the zone ( $q=0$ , point  $\Gamma$ ), and thus to position the Raman frequencies. Above are plotted the vibrational band structures and projected densities of states for all structures. The results show that only one structure is dynamically unstable ( $Ti_3Si$ -63). It should be noted that a calculation without activating magnetism for  $Ti_3Si$ -225, leads to a calculation where the phase is unstable. In this case, magnetism stabilizes the phase.

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Table A.1: Atomic positions and their irreducible Infra-red and Raman representation, of the different studied compounds.

System	Space group	Number of atoms	Atom	Wyckoff positions	IR activity	R activity
<b>Ti<sub>3</sub>Si</b>	225	16	Ti	$8c (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ $4a (0, 0, 0)$	$T_{1u}$ $T_{1u}$	$T_{2g}$
			Si	$4b (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$T_{1u}$	
			63	8	Ti	$8g (0.3432, 0.1716, 0.75)$
			Si	$4c (\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ $4c (\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$		
	86	32	Ti	$8g (0.6819, 0.2172, 0.9959)$ $8g (0.5282, 0.6414, 0.7181)$ $8g (0.5814, 0.1073, 0.4685)$	$A_u + E_u + 2E_u$	$A_g + B_g + E_g + 2E_g$
			Si	$8g (0.5419, 0.7053, 0.2118)$		
<b>Ti<sub>5</sub>Si<sub>3</sub></b>	193	16	Ti	$4d (\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ $6g (0, \frac{1}{4}, \frac{1}{4})$	$A_{2u} + E_{1u}$ $A_{2u} + 2^*E_{1u}$	$E_{2g} + E_{1g}$ $A_{1g} + 2^*E_{2g} + E_{1g}$
			Si	$6g (0, 0.608, \frac{1}{4})$		
			<b>Ti<sub>5</sub>Si<sub>4</sub></b>	92	36	Ti
			Si	$8b (0.0443, 0.3014, 0.8135)$ $8b (0.6427, 0.7052, 0.8273)$		
<b>TiSi<sub>2</sub></b>	70	24	Ti	$8a (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$	$B_{1u} + B_{2u} + B_{3u}$	$B_{1g} + B_{2g} + B_{3g}$
			Si	$16f (\frac{3}{4}, 0.4130, \frac{1}{4})$	$2B_{1u} + B_{2u} + B_{3u}$	$A_g + 2B_{1g} + B_{2g} + 2B_{3g}$
<b>TiSi</b>	62	8	Ti	$4c (\frac{1}{4}, 0.3715, 0.6759)$	$2B_{1u} + B_{2u} + B_{3u}$	$2A_g + B_{1g} + 2B_{2g} + B_{3g}$
			Si	$4c (\frac{1}{4}, 0.8542, 0.5442)$		
<b>Ti<sub>6</sub>Si<sub>2</sub>B</b>	189	9	Ti	$3g (0, 0.2384, \frac{1}{2})$ $3f (0, 0.6004, 0)$	$A''_{2+} + 2^*E'$ $A''_{2+} + 2^*E'$	$A_1' + 2E' + E''$ $A_1' + 2E' + E''$
			Si	$2d (\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$	$A''_{2+} + 2^*E'$	$2^*E'$
			B	$1a (0, 0, 0)$	$A''_{2+} + E'$	$E'$
			<b>Ti<sub>3</sub>B<sub>4</sub></b>	71	7	Ti
			B	$4i (0, 0.3683, 0)$ $4j (0, 0.4356, \frac{1}{2})$	$B_{1u} + B_{2u} + B_{3u}$	$A_g + B_{2g} + B_{3g}$
<b>TiB</b>	62	8	Ti	$4c (0.1774, \frac{1}{4}, 0.1222)$ $4c (0.0299, \frac{1}{4}, 0.5988)$	$2^*B_{1u} + B_{2u} + B_{3u}$	$2^*A_g + B_{1g} + 2^*B_{2g} + B_{3g}$
			<b>TiB<sub>2</sub></b>	191	3	Ti
			B	$2d (\frac{1}{2}, \frac{2}{3}, \frac{1}{2})$	$A_{2u} + E_{1u}$	$E_{2g}$

Table A.12: Group symmetry, lattice parameters ( $a$ ,  $b$ ,  $c$  in Å), formation energies (in eV per atom), magnetism (in Bohr's magneton  $\mu_b$ ), stability, and size of the supercell used to compute IFC.

System	Symmetry	Method	Lattice parameters			$E_f$ (eV/atom)	$\mu_b$	Stability	Supercell size
			a (Å)	b (Å)	c (Å)				
Ti <sub>3</sub> Si	225 ( $Fm\bar{3}m$ )	PBE	6.284	-	-	-0.317	6	stable	2x2x2
	63 ( $Cmcm$ )	PBE	4.891	-	4.516	-0.463	0	unstable	2x2x2
	86 ( $P4_2/n$ )	PBE	10.156	-	5.071	-0.499	0	stable	1x1x2
		Exp. [50]	10.196	-	5.162	-	-	-	-
Ti <sub>5</sub> Si <sub>3</sub>	193 ( $P6_3/mmc$ )	PBE	7.468	-	5.131	-0.770	0	stable	2x2x2
		Exp. [51,52]	7.461	-	5.1508	-	-	-	-
Ti <sub>5</sub> Si <sub>4</sub>	92 ( $P4_12_12$ )	PBE	6.708	-	12.195	-0.791	0	stable	2x2x1
		Exp. [53]	6.713	-	12.19	-	-	-	-
TiSi <sub>2</sub>	70 ( $Fddd$ )	PBE	4.805	8.263	8.565	-0.555	0	stable	2x1x1
		Exp. [54]	4.800	8.267	8.55	-	-	-	-
TiSi	62 ( $Pnma$ )	PBE	3.646	5.010	6.536	-0.770	0	stable	3x2x2
		Exp. [55]	3.63	4.99	6.54	-	-	-	-
Ti <sub>6</sub> Si <sub>2</sub> B	189 ( $P\bar{6}2m$ )	PBE	6.787	-	3.316	-0.659	0	stable	2x2x3
		Exp. [15,52,56]	6.8015	-	3.3377	-	-	-	-
Ti <sub>3</sub> B <sub>4</sub>	71 ( $Immm$ )	PBE	3.261	13.747	3.039	-0.937	0	stable	4x1x4
		Theo. [12]	3.259	13.737	3.039	-	-	-	-
		Exp. [57]	3.259	13.737	3.036	-	-	-	-
TiB	62 ( $Pnma$ )	PBE	6.113	3.052	4.567	-0.837	0	stable	2x2x3
		Theo. [12]	6.110	3.050	4.562	-	-	-	-
		Exp. [58]	6.12	3.06	4.56	-	-	-	-
TiB <sub>2</sub>	191 ( $P6/mmm$ )	PBE	3.032	-	3.224	-1.062	0	stable	4x4x4
		Theo. [12]	3.034	-	3.226	-	-	-	-
		Exp. [59]	3.029	-	3.228	-	-	-	-

## Appendix B

Table B.21: Summary of calculated phonon frequencies in Ti<sub>3</sub>Si, their corresponding symmetry mode and their respective activity.

Ti <sub>3</sub> Si (space group 86)								
Frequency (cm <sup>-1</sup> )	Symmetry mode	Activity	Frequency (cm <sup>-1</sup> )	Symmetry mode	Activity	Frequency (cm <sup>-1</sup> )	Symmetry mode	Activity
This work	"	"	"	"	"	"	"	"
76.60	E <sub>u</sub>	IR	183.85	B <sub>u</sub>	S	256.37	E <sub>g</sub>	R
80.74	B <sub>g</sub>	R	189.72	A <sub>u</sub>	IR	258.00	E <sub>u</sub>	IR
100.64	E <sub>g</sub>	R	190.02	B <sub>u</sub>	S	258.81	A <sub>g</sub>	R
113.16	B <sub>u</sub>	S	191.42	E <sub>u</sub>	IR	267.45	B <sub>g</sub>	R
114.19	A <sub>g</sub>	R	192.46	A <sub>g</sub>	R	269.26	B <sub>u</sub>	S
120.14	E <sub>g</sub>	R	195.26	B <sub>g</sub>	R	344.82	E <sub>g</sub>	R
123.84	A <sub>g</sub>	R	198.00	E <sub>g</sub>	R	347.12	A <sub>u</sub>	IR
128.89	B <sub>g</sub>	R	204.15	A <sub>u</sub>	IR	347.39	B <sub>u</sub>	S
133.69	B <sub>g</sub>	R	207.62	A <sub>g</sub>	R	348.52	B <sub>g</sub>	R
133.99	A <sub>u</sub>	IR	212.53	E <sub>u</sub>	IR	350.46	A <sub>g</sub>	R
136.30	E <sub>u</sub>	IR	213.50	B <sub>g</sub>	R	354.67	E <sub>u</sub>	IR
141.14	A <sub>u</sub>	IR	216.43	A <sub>u</sub>	IR	370.50	A <sub>g</sub>	R
145.68	E <sub>g</sub>	R	221.51	B <sub>u</sub>	S	370.76	B <sub>g</sub>	R
150.05	A <sub>g</sub>	R	227.32	B <sub>u</sub>	S	372.53	B <sub>u</sub>	S
152.12	B <sub>u</sub>	S	227.39	B <sub>g</sub>	R	373.57	B <sub>u</sub>	S
156.03	E <sub>g</sub>	R	227.99	A <sub>g</sub>	R	377.37	E <sub>u</sub>	IR
157.03	E <sub>u</sub>	IR	229.29	E <sub>g</sub>	R	377.37	E <sub>g</sub>	R
157.33	B <sub>g</sub>	R	231.29	A <sub>u</sub>	IR	378.84	A <sub>u</sub>	IR
164.11	A <sub>u</sub>	IR	235.77	B <sub>g</sub>	R	381.11	B <sub>g</sub>	R
171.19	B <sub>u</sub>	S	238.27	E <sub>g</sub>	R	385.32	E <sub>u</sub>	IR
171.49	E <sub>u</sub>	IR	238.71	E <sub>u</sub>	IR	389.33	E <sub>g</sub>	R
174.33	A <sub>g</sub>	R	245.78	A <sub>g</sub>	R	390.16	A <sub>g</sub>	R
181.01	E <sub>g</sub>	R	246.62	A <sub>u</sub>	IR	393.33	A <sub>u</sub>	IR

Table B.32: Summary of calculated phonon frequencies in  $\text{Ti}_5\text{Si}_3$ , their corresponding symmetry mode and their respective activity, compared with data available in literature.

$\text{Ti}_5\text{Si}_3$ (space group 193)											
Frequency ( $\text{cm}^{-1}$ )		Symmetry mode		Activity		Frequency ( $\text{cm}^{-1}$ )		Symmetry mode		Activity	
This work	[1]	This work	[1]	This work	[1]	This work	[1]	This work	[1]	This work	[1]
104.08	96.00	$E_{1g}$	"	R	"	261.54	/	$E_{2u}$	/	S	/
160.84	/	$E_{2u}$	"	IR	"	285.35	/	$B_{2g}$	/	S	/
170.76	169.00	$E_{2g}$	"	R	"	297.04	/	$E_{2u}$	/	S	/
174.06	/	$B_{2g}$	/	S	/	301.11	305.00	$A_{2u}$	"	IR	"
182.71	/	$B_{1u}$	/	S	/	330.76	/	$B_{1u}$	/	S	/
198.27	193.00	$A_{1g}$	"	R	"	336.10	334.00	$A_{1g}$	"	R	"
200.77	197.00	$E_{2g}$	"	R	"	336.50	338.00	$E_{1g}$	"	R	"
205.21	202.00	$E_{1u}$	"	IR	"	343.85	/	$A_{2g}$	/	S	/
215.60	217.00	$A_{2u}$	"	IR	"	369.49	370.00	$E_{1u}$	"	IR	"
221.84	222.00	$E_{1g}$	"	R	"	370.66	/	$E_{2g}$	/	R	/
225.98	/	$B_{1g}$	/	S	/	386.86	/	$B_{1u}$	/	S	/
229.59	/	$A_{2g}$	/	S	/	390.60	392.00	$E_{2g}$	"	R	"
244.45	242.00	$E_{1u}$	"	IR	"	395.37	400.00	$E_{1u}$	"	IR	"
245.02	/	$B_{2u}$	/	S	/	397.91	/	$B_{2u}$	/	S	/
248.56	246.00	$E_{2g}$	"	R	"	438.18	/	$A_{2g}$	/	S	/

Table B.43: Summary of calculated phonon frequencies in  $\text{Ti}_5\text{Si}_4$ , their corresponding symmetry mode and their respective activity.

$\text{Ti}_5\text{Si}_4$ (space group 92)								
Frequency ( $\text{cm}^{-1}$ )	Symmetry mode	Activity	Frequency ( $\text{cm}^{-1}$ )	Symmetry mode	Activity	Frequency ( $\text{cm}^{-1}$ )	Symmetry mode	Activity
This work	"	"	"	"	"	"	"	"
103.14	B <sub>1</sub>	R	229.02	B <sub>2</sub>	R	327.66	E	RI
106.88	A <sub>2</sub>	IR	232.39	E	RI	338.21	A <sub>2</sub>	IR
115.16	B <sub>2</sub>	R	236.97	A <sub>1</sub>	R	339.11	A <sub>1</sub>	R
127.82	A <sub>1</sub>	R	242.18	B <sub>1</sub>	R	340.74	A <sub>2</sub>	IR
147.25	A <sub>1</sub>	R	243.21	A <sub>2</sub>	IR	342.35	B <sub>1</sub>	R
158.14	E	RI	243.81	B <sub>2</sub>	R	343.85	B <sub>2</sub>	R
158.44	B <sub>2</sub>	R	244.51	E	RI	346.15	E	RI
158.87	B <sub>1</sub>	R	251.59	E	RI	367.36	A <sub>1</sub>	R
161.37	E	RI	254.13	A <sub>2</sub>	IR	367.62	E	RI
165.41	B <sub>2</sub>	R	259.31	A <sub>1</sub>	R	382.22	A <sub>2</sub>	IR
169.65	E	RI	260.14	E	RI	384.92	B <sub>2</sub>	R
173.86	A <sub>2</sub>	IR	265.05	E	RI	390.13	B <sub>1</sub>	R
174.4	E	RI	265.35	B <sub>1</sub>	R	390.46	E	RI
177.3	B <sub>1</sub>	R	268.52	B <sub>1</sub>	R	402.38	B <sub>2</sub>	R
181.21	E	RI	276.74	A <sub>1</sub>	R	408.29	A <sub>1</sub>	R
183.04	B <sub>1</sub>	R	278.91	A <sub>2</sub>	IR	411.26	E	RI
186.62	A <sub>2</sub>	IR	281.68	B <sub>2</sub>	R	416.11	B <sub>1</sub>	R
188.49	A <sub>1</sub>	R	295.3	B <sub>2</sub>	R	417.31	E	RI
190.39	E	RI	295.5	E	RI	421.15	A <sub>2</sub>	IR
194.9	E	RI	301.21	B <sub>1</sub>	R	431.7	A <sub>2</sub>	IR
198.5	A <sub>1</sub>	R	303.28	B <sub>1</sub>	R	434.67	E	RI
204.88	E	RI	303.72	E	RI	438.44	B <sub>1</sub>	R
210.59	B <sub>2</sub>	R	305.35	A <sub>2</sub>	IR	451.4	E	RI
214.23	B <sub>1</sub>	R	306.42	B <sub>2</sub>	R	452.47	B <sub>2</sub>	R
214.93	A <sub>1</sub>	R	306.85	A <sub>1</sub>	R	453.64	A <sub>1</sub>	R
223.81	A <sub>2</sub>	IR	314.57	E	RI			
227.62	E	RI	321.98	E	RI			

Table B.54: Summary of calculated phonon frequencies in TiSi, their corresponding symmetry mode and their respective activity.

TiSi (space group 62)		
Frequency (cm <sup>-1</sup> )	Symmetry mode	Activity
This work	"	"
181.44	A <sub>g</sub>	R
193.29	B <sub>1g</sub>	R
209.39	B <sub>2g</sub>	R
240.14	A <sub>u</sub>	IR
240.64	B <sub>3g</sub>	R
246.59	A <sub>g</sub>	R
252.06	B <sub>1u</sub>	IR
263.55	B <sub>2g</sub>	R
292	A <sub>u</sub>	IR
328.19	B <sub>1u</sub>	IR
334.6	B <sub>2g</sub>	R
336.74	B <sub>3u</sub>	IR
343.32	A <sub>g</sub>	R
367.76	B <sub>2u</sub>	IR
368.46	B <sub>1u</sub>	IR
389.23	B <sub>3u</sub>	IR
405.35	A <sub>g</sub>	R
408.49	B <sub>2g</sub>	R
427.79	B <sub>3g</sub>	R
449.16	B <sub>1g</sub>	R

Table B.65: Summary of calculated phonon frequencies in TiSi<sub>2</sub>, their corresponding symmetry mode and their respective activity, compared with data available in literature.

TiSi <sub>2</sub> (space group 70)					
Frequency (cm <sup>-1</sup> )		Symmetry mode		Activity	
This work	[1]	This work	[1]	This work	[1]
184.11	185.00	B <sub>3u</sub>	B <sub>2u</sub>	IR	"
192.43	194.00	B <sub>2g</sub>	B <sub>3g</sub>	R	"
206.65	208.00	B <sub>1g</sub>	"	R	"
230.96	230.00	B <sub>1u</sub>	B <sub>2u</sub>	IR	"
241.94	246.00	A <sub>g</sub>	"	R	"
254.47	253.00	B <sub>3g</sub>	B <sub>2g</sub>	R	"
256.77	259.00	B <sub>2g</sub>	B <sub>3g</sub>	R	"
276.24	277.00	B <sub>3g</sub>	B <sub>2g</sub>	R	"
292.86	283.00	B <sub>2u</sub>	B <sub>3u</sub>	IR	"
309.29	/	A <sub>u</sub>	/	IR	/
331.23	336.00	B <sub>1g</sub>	"	R	"
366.15	372.00	B <sub>3u</sub>	B <sub>2u</sub>	IR	R
378.51	384.00	B <sub>3g</sub>	B <sub>2g</sub>	R	"
401.05	411.00	B <sub>1u</sub>	"	IR	"
427.16	435.00	B <sub>1g</sub>	"	R	IR



Table B.76 : Summary of calculated phonon frequencies in  $\text{Ti}_6\text{Si}_2\text{B}$ , their corresponding symmetry mode and their respective activity, compared with data available in literature.

$\text{Ti}_6\text{Si}_2\text{B}$ (space group 189)					
Frequency ( $\text{cm}^{-1}$ )		Symmetry mode		Activity	
This work	[2]	This work	[2]	This work	[2]
188.02	188.55	E'	"	RI	"
207.15	201.59	A' <sub>1</sub>	"	RI	R
212.06	212.80	E''	"	RI	R
214.10	213.57	A'' <sub>2</sub>	"	IR	"
217.94	/	A' <sub>2</sub>	/	S	/
233.10	230.75	E'	"	RI	"
256.20	255.97	E''	"	RI	R
265.02	/	A' <sub>2</sub>	/	S	/
267.55	/	A'' <sub>1</sub>	/	S	/
279.64	278.52	E'	"	RI	"
314.00	318.45	A' <sub>1</sub>	"	RI	R
321.81	321.92	A'' <sub>2</sub>	"	IR	"
373.33	372.46	E'	"	RI	"
376.21	374.57	E'	"	RI	"
455.71	456.06	E'	"	RI	"
590.13	589.87	A'' <sub>2</sub>	"	IR	"

Table B.87 : Summary of calculated phonon frequencies in  $\text{TiB}$ , their corresponding symmetry mode and their respective activity, compared with data available in literature.

$\text{TiB}$ (space group 62)					
Frequency ( $\text{cm}^{-1}$ )		Symmetry mode		Activity	
This work	[3]	This work	[3]	This work	[3]
245.32	245.00	B <sub>1u</sub>	"	IR	"
261.61	255.00	A <sub>g</sub>	B <sub>3u</sub>	R	IR
262.31	259.00	B <sub>3u</sub>	A <sub>g</sub>	IR	R
273.16	272.00	B <sub>3g</sub>	"	R	"
282.45	280.00	A <sub>u</sub>	"	S	"
295.67	293.00	B <sub>2g</sub>	"	R	"
303.11	299.00	B <sub>1g</sub>	"	R	"
311.53	305.00	A <sub>g</sub>	"	R	"
342.11	347.00	B <sub>2g</sub>	"	R	"
452.50	453.00	A <sub>u</sub>	"	S	"
460.58	468.00	B <sub>3u</sub>	"	IR	"
488.36	494.00	B <sub>1u</sub>	"	IR	"
497.71	499.00	B <sub>2u</sub>	"	IR	"
534.01	542.00	B <sub>3u</sub>	"	IR	"
557.15	564.00	B <sub>1u</sub>	"	IR	"
565.23	570.00	A <sub>g</sub>	"	R	"
607.36	607.00	B <sub>2g</sub>	"	R	"
631.27	634.00	B <sub>2g</sub>	"	R	"
632.11	639.00	A <sub>g</sub>	"	R	"
752.44	760.00	B <sub>1g</sub>	"	R	"
770.67	780.00	B <sub>3g</sub>	"	R	"

Table B.98 : Summary of calculated phonon frequencies in  $Ti_3B_4$ , their corresponding symmetry mode and their respective activity, compared with data available in literature.

$Ti_3B_4$ (space group 71)					
Frequency ( $cm^{-1}$ )		Symmetry mode		Activity	
This work	[3]	This work	[3]	This work	[3]
262.28	249.00	$B_{2g}$	$B_{3g}$	R	"
263.78	263.00	$B_{3g}$	$B_{1g}$	R	"
277.54	277.00	$B_{3u}$	$B_{1u}$	IR	"
286.09	287.00	$B_{2u}$	$B_{3u}$	IR	"
313.03	313.00	$A_g$	$B_{2u}$	R	IR
314.43	323.00	$B_{1u}$	$A_g$	IR	R
475.31	483.00	$B_{1u}$	$B_{2u}$	IR	"
485.36	488.00	$B_{3u}$	$B_{1u}$	IR	"
499.45	499.00	$B_{2g}$	$B_{3g}$	R	"
522.62	504.00	$B_{3g}$	$B_{1g}$	R	"
524.29	528.00	$B_{2u}$	$B_{3u}$	IR	"
547.23	550.00	$A_g$	"	R	"
551.5	556.00	$B_{2u}$	$B_{3u}$	IR	"
571.1	574.00	$B_{3g}$	$B_{1g}$	R	"
712.84	715.00	$B_{1u}$	$B_{2u}$	IR	"
798.62	804.00	$B_{3u}$	$B_{1u}$	IR	"
824.13	829.00	$B_{2g}$	$B_{3g}$	R	"
827.7	835.00	$A_g$	"	R	"

Table B.109 : Summary of calculated phonon frequencies in  $TiB_2$ , their corresponding symmetry mode and their respective activity, compared with data available in literature.

$TiB_2$ (space group 191)					
Frequency ( $cm^{-1}$ )		Symmetry mode		Activity	
This work	[3]	This work	[3]	This work	[3]
509.20	515.10	$E_{1u}$	"	IR	"
514.51	521.50	$A_{2u}$	"	IR	"
551.90	557.90	$B_{1g}$	"	S	"
880.36	883.10	$E_{2g}$	"	R	"

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## Figure captions

**Figure 1:** Optical micrographs of uncoated (a) and glass coated (b) Ti-6Al-4V samples, oxidized in an electric furnace 8 h at 1150 °C in air, after Kroll chemical etching.

**Figure 2:** Forescatter electron (FSD) micrograph and EDS maps of Ti, Al, V, O, Si and B of the glass|alloy interfacial region. The rectangle highlighted in the FSD image indicates the region subsequently analysed with Raman spectroscopy, see below. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 3:** (a) Raman spectra of the main Ti oxides. (b) Raman spectra of Ti borides, along with the computed frequencies (vertical bars beneath spectra). (c) Raman spectrum of  $Ti_5Si_3$ , along with the computed frequencies (vertical bars beneath spectrum). The group of thin lines below ca  $150\text{ cm}^{-1}$  are the rotational Raman lines of  $O_2$  and  $N_2$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 4:** Characteristic Raman spectra extracted after a first visual inspection of the interfacial region of the sample considered in this work (blue traces), and Raman spectra recorded for the standards (red traces). Concerning  $Ti_6Si_2B_2$ , the experimental spectrum (blue trace) is confronted to the computed frequencies (red bars). One can see that the agreement is satisfying. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 5:** Top: FSD image. The analyzed area ( $85 \times 48\ \mu\text{m}^2$ ) is highlighted by the white rectangle. Bottom: Raman images. Left: PCA analysis of the image data file. Only 5 from the 10 images that were used to reconstruct the data set are given. The intensity scale is the score of the corresponding principal component. Middle: MCR analysis of the image data file. 5 of the 8 corresponding images are given. The intensity scale is the relative contribution of each component. The MCR1, 5, 6 and 7 images correspond to the spatial distribution of  $Ti_2O_3$ ,  $Ti_5Si_3$  and TiB respectively. Right: linear combination of the model spectra given in Figure 3. The intensity scale is the relative contribution of each component. The spatial distribution of  $Ti_2O_3$ ,  $Ti_5Si_3$ , TiB and  $Ti_6Si_2B$  are given. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 6:** Red traces: reference spectra used in the multivariate, supervised approach. Blue traces: the four Raman “signatures” retrieved using the MCR algorithm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 7:** EBSD band contrast (a) and phase map (with colour code corresponding to Raman maps) (b) of the glass/alloy interfacial region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 8:** Left: Optical image. The analyzed area ( $85 \times 48\ \mu\text{m}^2$ ) is highlighted by the white rectangle. Right: linear combination of the model spectra given in Figure 3. The intensity scale is the relative contribution of each component. The spatial distribution of  $Ti_2O_3$ ,  $Ti_5Si_3$ , TiB and  $Ti_6Si_2B$  are given, along with images constructed from two slightly different signals recorded in the metallic part of the sample, tentatively assigned to  $\alpha$ - and  $\beta$ -Ti phases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

**Figure 9:** Ti-TiB<sub>2</sub>-TiSi<sub>2</sub> domain of the Ti-Si-B ternary system, computed at 1150 °C using the TCTI4 thermodynamic database from Thermo-Calc.

**Figure 10:** Modified version of the computed Ti-TiB<sub>2</sub>-TiSi<sub>2</sub> domain presented in Figure 9 allowing to reproduce the experimental diffusion path.

## Tables

*Table 1: Composition of the present Ti-6Al-4V alloy.*

Element	Ti	Al	V	Fe	C	H	N	O
Content (wt. %)	Bal.	6.33	3.89	0.17	0.0052	0.0033	0.003	0.171

*Table 2: Possible compounds that may compose the interfacial layers.*

Binary and ternary systems	Possible compounds
Ti-O	TiO <sub>2</sub> (rutile and/or anatase) Ti <sub>2</sub> O <sub>3</sub>
Ti-B	TiB <sub>2</sub> Ti <sub>3</sub> B <sub>4</sub> TiB
Ti-Si	TiSi <sub>2</sub> TiSi Ti <sub>5</sub> Si <sub>4</sub> Ti <sub>5</sub> Si <sub>3</sub> Ti <sub>3</sub> Si
Ti-Si-B	Ti <sub>6</sub> Si <sub>2</sub> B



Table 3: Group symmetry, lattice parameters ( $a, b, c$  in Å) and size of the supercell used to compute IFC.

System	Compound	Space group	Ref/Method	Lattice parameters (Å)			Supercell size
				a	b	c	
Ti-Si	Ti <sub>3</sub> Si	$P 4_2/n$ (86)	PBE	10.156	-	5.071	1x1x2
			[50]	10.196	-	5.162	
	Ti <sub>5</sub> Si <sub>3</sub>	$P 6_3/mmc$ (193)	PBE	7.468	-	5.131	2x2x2
			[51,52]	7.461	-	5.1508	
	Ti <sub>5</sub> Si <sub>4</sub>	$P 4_1 2_1 2$ (92)	PBE	6.708	-	12.195	2x2x1
			[53]	6.713	-	12.19	
TiSi	$Pnma$ (62)	PBE	3.646	5.010	6.536	3x2x2	
		[55]	3.63	4.99	6.54		
TiSi <sub>2</sub>	$Fddd$ (70)	PBE	4.805	8.263	8.565	2x1x1	
		[54]	4.800	8.267	8.55		
Ti-Si-B	Ti <sub>6</sub> Si <sub>2</sub> B	$P\bar{6}2m$ (189)	PBE	6.787	-	3.316	2x2x3
			[15,52,56]	6.801	-	3.338	
Ti-B	TiB	$Pnma$ (62)	PBE	6.113	3.052	4.567	2x2x3
			[58]	6.12	3.06	4.56	
	Ti <sub>3</sub> B <sub>4</sub>	$Immm$ (71)	PBE	3.261	13.747	3.039	4x1x4
			[57]	3.259	13.737	3.036	
	TiB <sub>2</sub>	$P 6/mmm$ (191)	PBE	3.032	-	3.224	4x4x4
			[59]	3.029	-	3.228	