# Intermetallic disilicides and titanium aluminides—a new class of structural high temperature materials under the aspect of their high temperature oxidation resistance

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*Abstract*: The light weight intermetallics TiAl and $TiSi_2$ are interesting materials for application in fast moving components like gas turbine blades etc. at high temperatures. Oxidation behavior is a major issue under these conditions and in the paper possibilities are discussed how to improve the oxidation resistance in air of these alloys in the temperature range 700-900°C for TiAl and 1000-1100°C for $TiSi_2$. In both cases a nitrogen effect exists for air oxidation by which protective oxide scale formation is impeded. Suppressing TiN-formation and stimulating the formation of continuous $Al_2O_3$ or $SiO_2$ barriers for TiAl or $TiSi_2$, respectively, by preoxidation in N-free atmospheres or by the chlorine effect are the keys to improved oxidation resistance.

## INTRODUCTION

In recent years several intermetallics have received increasing interest as structural materials for reasons of their high temperature properties which in many respects can be superior to those of the commercial metallic alloys presently used. In particular in aircraft industries and among the car manufacturers there is a need for advanced light weight high temperature materials which can increase the efficiency of jet and car engines when being used for fast moving parts like turbine blades, turbocharger rotors, exhaust and intake valves, rockers and rocker arms as well as push rods (ref. 1). Further positive aspects are reduced emissions and lower engine noise when replacing steel and the nickel base alloys presently used by advanced light weight materials. Even for stationary gas turbines in energy production there are plans to replace the blades in the last stage by light weight materials which would allow a significant increase in the blade size helping to increased efficiency of the turbine.

The most interesting materials under this respect are the intermetallic aluminides and silicides. In particular when aiming at technical applications it is the titanium aluminides and the titanium silicides which are preferred. Most of the work today focuses on γ-TiAl based and $\alpha_2$-$Ti_3Al$ based alloys with some research being conducted on $TiSi_2$ also. The temperature capability of γ-TiAl is estimated as 1000°C if the development potential of this group of materials is extensively used. Presently the limit is around 700°C but promising research on increasing oxidation resistance (e.g. by alloying and surface treatments) and mechanical high temperature strength (e.g. by dispersions) is going on. The potential of $\alpha_2$-$Ti_3Al$ seems to be slightly inferior to γ-TiAl in particular for its oxidation resistance. $TiSi_2$ offers a temperature capability of up to 1300°C. γ-TiAl and $TiSi_2$ have specific weights of about 3.9 and 4.4 g/cm³, respectively, which is about half the value of steel or nickel base alloys. The coefficients of thermal expansion lie around 10 to 13 · $10^{-6}K^{-1}$ which means excellent compatibility to conventional ferritic materials. As improving oxidation resistance is one of the key issues for leading these materials to application the present paper investigates these aspects for γ-TiAl and $TiSi_2$ in the temperature ranges 700 - 1000°C (TiAl) and 1000 - 1400°C ($TiSi_2$) in air and in argon/oxygen mixtures. The aim of these investigations was to understand the oxidation mechanisms and to use the understanding for improving the oxidation resistance.

## EXPERIMENTAL

The composition of the materials investigated is given in table 1. TiAl batches II to IV had been produced by the powder-metallurgical route while batch I was investment cast. The powder for batch II was very pure and had been fabricated by inert gas atomization. For batch III the powder was produced by

mechanical alloying which explains the relatively high amount of Fe (abrasive impurities from milling). Batch IV was reactively sintered from Ti-sponge powder and prealloyed AlMn powder. The materials TiAl (II), TiAl (IV) and TiSi₂ were prepared by hot-isostatic pressing, TiAl (III) by hot extrusion. It should be particularly mentioned that the alloys III and IV contained small amounts of chlorine, cf. table 1.

**Table 1.** Composition of the materials investigated (at-%)

| Alloy | Ti | Al | Si | Cr | Fe | Mn | W | Cl |
|---|---|---|---|---|---|---|---|---|
| TiAl (I) | 48.1 | 51.0 | - | - | - | - | - | - |
| TiAl (II) | 50.5 | 47.0 | - | 2 | - | - | - | - |
| TiAl (III) | 47.0 | 45.0 | - | 1.5 | 3 | - | - | $\leq 0.01$ |
| TiAl (IV) | 47.0 | 48.0 | - | - | - | 1.8 | 0.3 | 0.02 |
| TiSi₂ | 32.4 | 0.02 | 67.8 | - | 0.06 | - | - | - |

From all materials coupon specimens were prepared by cutting and grinding up to grit 1000 (TiAl II to V), grit 4000 (TiAl I) and grit 1400 (TiSi₂). Most of the specimens were used for continuous weight gain recording in a thermobalance, some also for discontinuous weight gain measurements by exposing them in a furnace with weight determination before and after exposure. For TiAl in the present paper only the results obtained at 900°C in air and in 100 % oxygen will be discussed. For results measured at 800 and 1000°C it is referred to ref. 2. The temperature range for TiSi in this paper comprises 1000 to 1400°C. After the oxidation tests the specimens were examined in great detail concerning the structure and composition of the oxide scales formed. For TiAl (I) much emphasis was put on elucidating the details around the scale metal interface which required the use of the transmission electron microscope. For all alloys metallography and microprobe were employed. In the present paper for reasons of conciseness and clarity the results from the microstructural investigations are summarized in schematic representations.

## RESULTS AND DISCUSSION

### TiAl

#### *The nitrogen effect*

Figure 1 shows the kinetics of oxidation during the first 100 hrs for TiAl (I) in air and in pure oxygen. It turns out that in both cases there is a fast initial step before oxidation enters quasi-parabolic kinetics. Concerning the oxidation rate in the parabolic phase there is, however, a significant difference between air and pure oxygen. While in the latter case the rates are very close to alumina kinetics, it is the TiO₂-phase which dominates scale growth in air leading to much higher oxidation rates. This effect has been observed in the literature for several times (ref. 3) . It was very detailed TEM investigations in ref. 4 and by the present authors (ref. 5) which revealed that nitride formation at the scale/metal interface was responsible for the suppression of the formation of a continuous Al₂O₃-barrier layer in the inner part of the oxide scale. Rather a band of alternating TiN and a metastable Al₂O₃/AlON-phase is formed which does not offer protection. The metastable Al₂O₃/AlON-phase even becomes dissolved during subsequent oxidation while at the same time as a consequence of rising oxygen partial pressure due to inward scale growth TiN is converted into fast growing TiO₂. Al from the dissolved Al₂O₃/AlON-phase diffuses in outward direction in the scale where it reprecipitates as stable α-Al₂O₃ in a matrix of TiO₂. The consequence is that a porous inner TiO₂-layer remains while in outward direction a mixed TiO₂/α-Al₂O₃ is found. The most outer layer again is more or less pure TiO₂. Since the Al₂O₃-particles are embedded in a TiO₂-matrix no really protective situation can be established as the oxidation rates are controlled by rapid diffusion in TiO₂. Only after longer times a zone of α-Al₂O₃-enrichment at the outer boundary of the mixed TiO₂/α-Al₂O₃ zone links up to form a temporary barrier of a continuous α-Al₂O₃-layer. This barrier does, however, not have a long-term stability but becomes dissolved again after several hundred hours leading to a „breakaway" effect (ref. 6).

The situation is very much different for a pure oxygen environment, cf. fig. 1. In this case a very thin film of stable α-Al₂O₃ can be formed at the scale/metal interface which does not become dissolved during the oxidation period investigated in this paper. This film is not fully continuous but is locally interrupted by Al₂O₃/TiO₂ mixtures which lead to local more rapid oxide growth. Furthermore, parts of the layer consist of an amorphous Ti/Al-oxide, which also covers the outer parts of the scale. All in all the barrier formed by
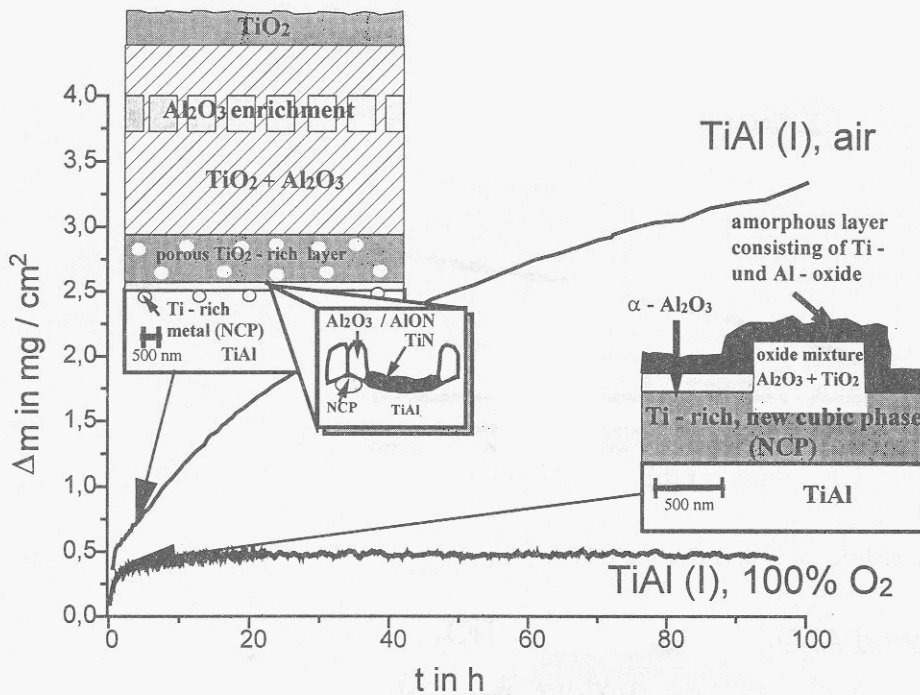
**Fig. 1** Mass gain curves and schematic illustrations of the oxide scales observed during oxidation of TiAl (I) at 900°C in air and 100% oxygen.

the inner film of $\alpha$-$Al_2O_3$ seems to be, however, efficient enough (despite of its incompleteness) to act in the sense of a significant reduction of the oxidation rates. It should, however, be mentioned that after longer times the situation becomes unstable and the growth of the local $Al_2O_3/TiO_2$ mixtures starts to dominate (ref. 3). The result is again a kind of „breakaway" effect indicating that even in pure oxygen environment no permanently protective situation based on a continuous $Al_2O_3$-barrier can be established.

### The chlorine effect

Figure 2 shows the thermogravimetric results of the TiAl alloys II, III and IV which had been produced by powder-metallurgical routes. As can be taken from table 1 the chlorine content of these alloys increases from the very pure alloy II (chlorine free) over alloy III (chlorine present but less than 100 ppm) to alloy IV (about 200 ppm of chlorine). Alloy II shows parabolic kinetics of a rate characteristic for the situation without protective alumina barrier formation. This is confirmed by the microstructural investigations which reveal that the oxide scale mostly consists of mixed $Al_2O_3/TiO_2$ in the inner part and an outer partial layer of pure $TiO_2$. For TiAl (III) there is a high oxidation rate at the beginning but after about 60 hrs, oxidation follows the kinetics of an $Al_2O_3$-barrier. In the microstructural investigations it can be seen that the scale at first glance is similar to that of TiAl (II) but of lower thickness. A detailed check of the oxide/metal interface reveals, however, that after more than 60 hrs of oxidation a continuous very thin $Al_2O_3$-barrier has become stable after this incubation period slowing down the oxidation rate dramatically (ref. 7). TiAl (IV) shows oxidation rates from the very beginning on which could be interpreted as alumina kinetics. Figure 3, however, indicates that this cannot be the full truth. In areas of the substrate where no homogeneous $\gamma$-phase was present but from production colonies of $TiAl/Ti_3Al$-lamellae were observed large porosity was found under a faster growing oxide mixture. These areas are presumed to be more chlorine-rich for reasons of the higher local Ti-content compared to $\gamma$-TiAl. The higher Ti-content is due to higher local amounts of Ti-sponge at the beginning of the production route with Ti-sponge carrying in chlorine from the Ti-production process. Volatile Ti- and Al-chlorides are formed at oxidation temperature evaporating from the material and leaving pores behind. At higher $pO_2$, i.e. in the outer part of the oxide scale the chlorides are converted into oxides leading to the observed oxide mixtures in these areas. In the regions above $\gamma$-TiAl a

very thin $Al_2O_3$-scale is found which is partially detached. This scale seems to offer good protection which is documented by the mass change kinetics in the experiments. Again volatile
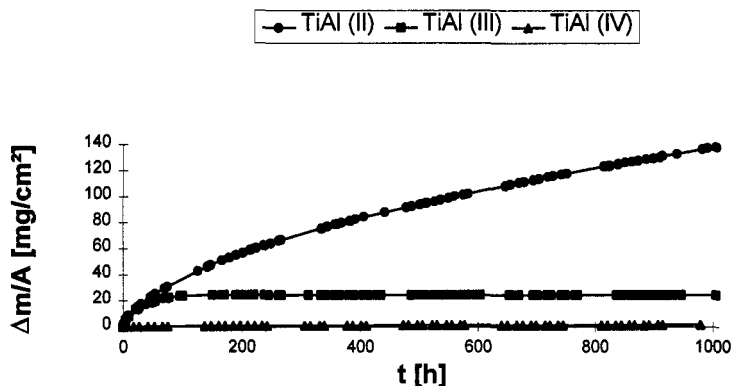


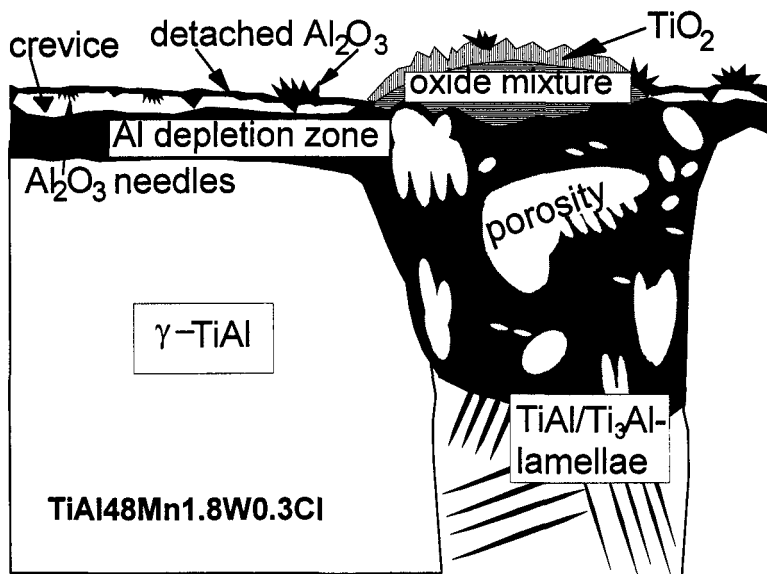**Fig. 2** Mass change by oxidation of P/M-TiAl at 900°C in air



**Fig. 3** Oxide scale on TiAl (IV) after oxidation at 900°C in air

chlorides are assumed to play the key role. When looking at a „stability" diagram with $pCl_2$ and $pO_2$ as the axes it turns out that AlCl is the most volatile metal chloride that can be formed from TiAl and that the vapor pressure pAlCl decreases with increasing $pO_2$, fig. 4. Three fields can be distinguished in fig. 4. In field A the vapor pressure of the potential metal chlorides like AlCl and $TiCl_3$ is below $10^{-5}$ bar which is taken as the limit of considerable transport of species via the gas phase (ref. 8), i.e. no mentionable transport of Al or Ti via the gas phase is possible. In field B the pAlCl is above $10^{-5}$ bar while the $pTiCl_3$ is below $10^{-5}$ bar, i.e. Al can be transported via the formation of volatile chloride to a considerable extent while Ti cannot. When AlCl moves in outward direction in pores, crevices or other types of channels of the oxide scale it will very soon become converted into $Al_2O_3$, cf. steep slopes for the pAlCl lines in fig. 4. The result is an $Al_2O_3$ enrichment close to the oxide/metal interface ending up in a continuous alumina barrier. Field C represents the situation where the vapor pressures of both chlorides (titanium and aluminum chloride) are above $10^{-5}$ bar. Al and Ti are transported in outward direction via the gas phase and
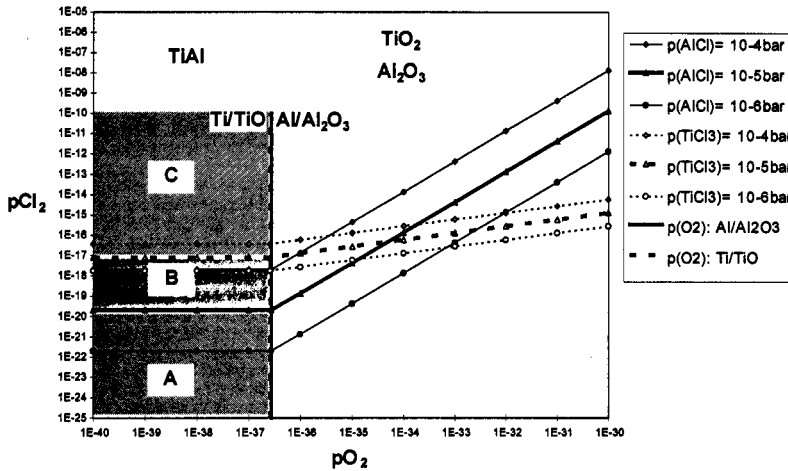
**Fig 4** Vapor pressures of AlCl and TiCl₃ as a function of oxygen and chlorine partial pressure

converted into oxides at higher $pO_2$ ending up in a mixed oxide scale of faster growth and without barrier. Situation A stands for all TiAl-alloys produced by the melting route where chlorine escapes during melting. In this case conventional oxidation without the interference of Cl occurs. B stands for low Cl-contents in e.g. alloys produced by the P/M-route where the alloy components (in particular the Ti-sponge) are not molten in any production stage. Examples for this behavior are TiAl (III) and TiAl (IV), the latter in the γ-TiAl areas. High chlorine contents lead to type C behavior. This situation is observed in the $\alpha_2$-Ti₃Al/γ-TiAl colonies of alloy TiAl (IV).

## TiSi₂

### *The nitrogen effect*

Similarly as for TiAl alloys there is a nitrogen effect for TiSi₂. Oxidation in pure oxygen leads to much lower rates than oxidation in air, cf. fig. 5. Another striking feature of fig. 5 is that oxidation rates decrease from 1100 to 1200°C and even further when moving to 1400°C. The development of the oxide scales
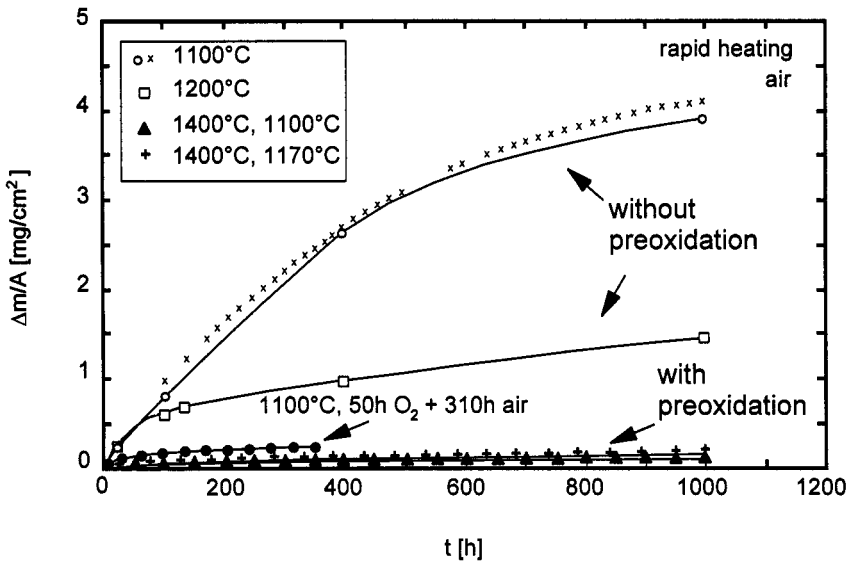


**Fig. 5** Mass change by oxidation of TiSi₂ at 1100, 1170 and 1200°C in air without and with preoxidation in oxygen at 1100°C and with preoxidation in air at 1400°C
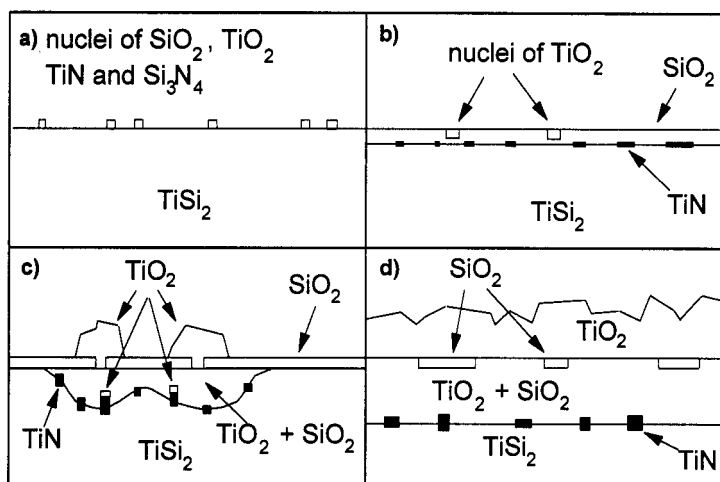
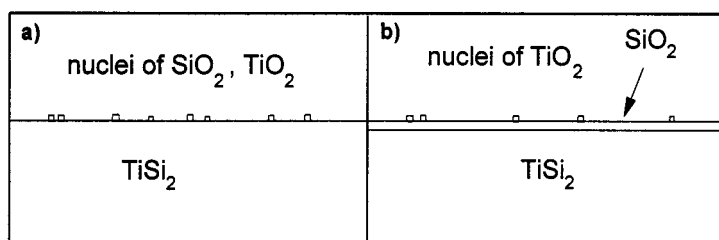**Fig. 6** Development of the oxide scale on TiSi$_2$ at 1000-1100°C in air



**Fig. 7** Development of the oxide scale on TiSi$_2$ at 1000-1100°C in nitrogen-free atmospheres

during oxidation at 1000 - 1100°C is schematically shown in fig. 6 (ref. 9). After the formation of the different nuclei (a) a layer of SiO$_2$ is formed (b) which is, however, interrupted by TiO$_2$ nuclei which grow through the layer. Beneath the scale titanium nitrides are present which again stimulate the formation of a TiO$_2$/SiO$_2$ mixture (c) by a comparable mechanism as for the TiO$_2$/Al$_2$O$_3$ mixture with TiAl destroying the potentially protective effect of the slow growing SiO$_2$. In the end a complex scale comes out (d) consisting of a fast growing TiO$_2$ matrix with embedded particles of SiO$_2$. If nitrogen is not present in the atmosphere nitride formation is suppressed and, thus, the formation of a continuous SiO$_2$ scale becomes possible, fig. 7b, following the formation of the different nuclei, fig. 7a.

## *The effect of temperature*

While at 1000 - 1100°C a scale is formed where TiO$_2$ dominates oxide growth, cf. fig. 6, at higher temperatures an SiO$_2$ matrix builds up in which TiO$_2$ particles are embedded, cf. fig. 8. The result is a dramatic drop in the oxidation rates, cf. fig. 5, due to the excellent protective effect of silica. This effect can be used by preoxidising the materials at 1400°C and then using them at 1000 - 1200°C (ref. 9).

## CONCLUSIONS

• A nitrogen effect exists for TiAl alloys as well as for TiSi$_2$. This effect impedes the formation of protective oxide scales by preventing continuous Al$_2$O$_3$ or SiO$_2$ barriers, respectively .

• For TiAl alloys the negative nitrogen effect can be overcome by using the positive aspects of the chlorine effect. In this case a very low, optimum amount of chlorine must be present at the scale metal interface.

• Preoxidation in pure oxygen does not seem to be a long-term solution for improving the oxidation resistance of TiAl-alloys.

• For TiSi$_2$ preoxidation at 1100°C in pure oxygen or at 1400°C in air can very much help to a better oxidation resistance in the temperature range from 1000 to 1200°C by suppressing the nitrogen effect.
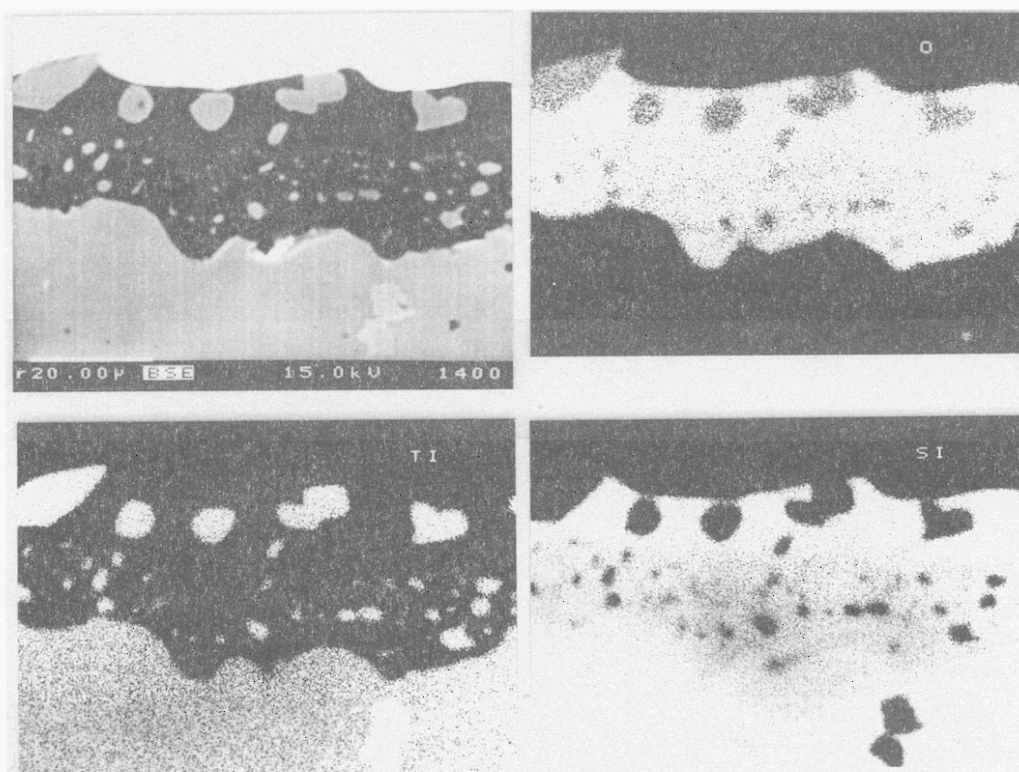
**Fig. 8** Element distribution maps from microprobe investigations of the oxide scale on $TiSi_2$ formed at 1400°C in air

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