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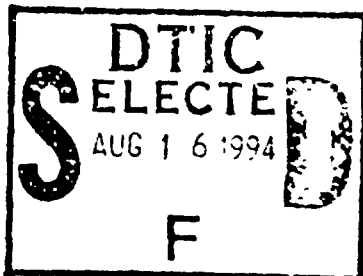
MARTIN MARIETTA

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Thin-Film Model Studies of Interfacial Reactions in Intermetallic Matrix Composites

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Final Report

June 1, 1991 - May 30, 1994

Submitted to:

**Office of Naval Research
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Arlington, VA 22217-5000**

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Submitted by:

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I. INTRODUCTION

The study of interfacial reactions in metal or intermetallic matrix composites goes back to the early sixties, when major programs funded by the US Air Force sought to develop high temperature composites. An excellent status summary on the subject was given by Metcalfe[1] in 1974. At that time, models of the interface[2] and its physical and chemical aspects[3], recognized the importance of the scale of the reaction, in particular the "under 10000Å zone", in determining composite properties. However, the methodology of studying interfacial reactions on this scale was largely restricted to electron microscopy (SEM and TEM) of specimens prepared from bulk composites, the main exception being studies of film-coated fibres[4,5]. The resolution in most cases was limited, and no special effort was made to define the reaction products on a scale smaller than a fraction of a micron. With the introduction of surface techniques (AES and XPS) and analytical electron microscopy(AEM), and developments in microelectronics processing which required detailed knowledge of metal/Si or metal/SiO₂ reactions, model studies in which a thin film of one material was deposited on a bulk substrate became popular. These studies provided a detailed picture of such processes as oxidation and diffusion on an atomic scale, but left largely unanswered the question of the link between them and real-life composite properties, a link which is still by-and-large missing. More recently, the interest in intermetallic based composites has added complexity to the study of nanometer-scale interfacial reactions, which have reverted to being carried out almost exclusively with TEM. The main drawback of standard TEM (which views an interface perpendicular to its normal) is that it provides great detail of a very minute part of the interface. This can be alleviated in part by using TEM (mainly in diffraction mode) on a layered thin-film model system with the beam parallel to the interface normal, thus acquiring data from a much larger area without significantly sacrificing resolution. Since the interface is now buried at a depth of a few hundred Å, it can be expected also to behave more like a real composite interface, in contrast with the situation present in most surface studies. It must be pointed out however that the layered film system differs in microstructure, possibly in chemistry and certainly in its formation history from a bulk composite. This, and the possible introduction of artifacts during thermal treatments used to induce nanometer interfacial reactions in the films, must be considered in evaluating thin-film model results.

The issue of interfacial reactions between matrix and reinforcement can be viewed in terms of chemical compatibility. As generally understood, "compatibility" implies chemical inertness and therefore a lack of reaction at the interface. However, although large scale reactions are clearly deleterious to composite properties, the existence of a nanoscale reaction may in fact be necessary for good bonding. The main IMC systems being currently evaluated for high temperature applications are based on nickel and titanium aluminides. The chemical compatibility of TiAl and NiAl matrices with various reinforcements has been calculated [6,7] using up-to-date thermodynamic data. These calculations can at best be relied upon to predict bulk behavior, i.e. "macroscopic" reactivity, and eliminate clearly incompatible systems, in which extensive reactions are highly likely to occur. Most "borderline" or compatible systems will still have to be tested experimentally. The purpose of this program was to obtain important information on the interfacial reactions in both (predicted) compatible and incompatible systems, by using a novel approach of modelling bulk IMC reactions experimentally with thin layered films.

In addition to being chemically compatible, reinforcements should be closely matched in their thermal expansion coefficient (TCE) with the matrix, and available commercially. Only a few materials fulfill all conditions vs TiAl and NiAl[6,7]. We will start with NiAl IMC's. Misra[6] indicates that of all chemically compatible reinforcements, only La_2O_3 , MgO, cubic ZrO_2 and CaZrO_3 are closely matched in TCE with NiAl at 827°C . The difference between the TCE of MgO ($15.2 \times 10^{-6} \text{ C}^{-1}$) and that of NiAl ($\sim 16 \times 10^{-6} \text{ C}^{-1}$) is about 5%. Interestingly, there are no reports in the literature on the NiAl-MgO composite system, possibly because it is expected to be unstable in dynamic environments, which are predicted to bring about the evaporation of Mg[6]. We therefore concentrated on Al_2O_3 , ZrO_2 and MgO for NiAl and Al_2O_3 and TiB_2 for TiAl. We also investigated the TiAl/TiC system, predicted to be incompatible. The following report basically summarizes the results published in four papers[8-11] as well as unpublished results.

II. BASIC PROCEDURE

A. General

The basic idea of modelling a reinforcement R (e.g fiber)/matrix M interface with layered thin-films is illustrated in Fig. 1. If one considers only the narrow region around the interface itself, the main objective is to be able to reproduce the reactions occurring during composite formation or use at elevated temperatures, and to investigate them with ease, preferably with high resolution. This can be done with self-supporting thin layered films which provide a very large area of interface sandwiched between materials identical to those in bulk composites. Reaction caused by thermal annealing can be observed and characterized with electron microscopy/diffraction, as well as with surface techniques such as x-ray photoelectron spectroscopy (XPS).

B. The Thin-Film Technique

The technique is illustrated in Fig. 2. Layered thin films are electron beam (E-beam) evaporated in a high vacuum system onto either Formvar- or carbon-coated molybdenum electron microscope grids. After deposition, the Formvar is removed and the grids are annealed under relatively well controlled time/temperature conditions in a rapid thermal annealing (RTA) system. The grids can be examined by TEM after annealings as short as 1-2 sec and as long as 5 min at temperatures between 200 and 1250°C. Repeating the annealing/examination sequence provides many data points, each including the microstructure, phases present (from diffraction patterns) and, in some cases, kinetics (from grain growth)[12]. "Sandwiches" of films simulating R/M/R interfaces with varying R/M ratios and incorporating thin diffusion barriers can be deposited without breaking the vacuum. A sequential deposition of e.g Ni/Al or Ti/Al with thickness ratios calculated to give a particular stoichiometry, followed by a low temperature reaction, forms an intermetallic M layer. The low temperature in this step prevents a reaction between the outer layer of M and the R layer from taking place. In each case, separate M and R specimens were also processed together with the R/M/R sandwich, and served as "baseline" specimens.

Specific experimental conditions regarding each M/R system studied can be found in references [8-11]. For example, TiAl/Al₂O₃ films were deposited by e-beam evaporation in an ultrahigh vacuum system with a base pressure of 5x10⁻⁸ torr. Pressures during evaporation were no higher than 2x10⁻⁷ torr for the Al and Ti films, and up to 10⁻⁶ torr for Al₂O₃. The latter was evaporated from polycrystalline chunks. The substrates were oxidized Si wafers and sapphire. The films-on-grid and on Si (deposited simultaneously and shown in Fig. 3a), were symmetrical, i.e., the Ti/Al layers were sandwiched between two 300Å- thick Al₂O₃ films with an Al thin layer adjacent to each Al₂O₃ film. The stacks on sapphire provided a nonsymmetrical structure, Fig. 3b, with an Al₂O₃ (film)/aluminide interface on one side and a sapphire/aluminide interface on the other. This arrangement allowed for a direct chemical comparison of Al₂O₃ films and sapphire, and for comparison of their respective reactions with the same aluminide. Other aluminide/R film stacks were prepared in a similar fashion. For example, the Ni/Al sequential deposition layer thicknesses are given in Table 1.

III. RESULTS

A. The NiAl/MgO System

1. Electron Microscopy

Figure 4 shows the SAD patterns of the as-deposited films. The MgO/Al/Ni film exhibits, as-expected, Al, Ni and MgO reflections. The standard Al/Ni specimen shows only Al and Ni reflections. In contrast with Al_2O_3 [8], room-temperature deposited MgO is crystalline and its pattern matches well the periclase (JCPDS #4-829) phase[13]. Figure 5 shows the patterns after RTA at 300°C for 100s. The MgO/Al/Ni film consists now of very fine grained (solid diffraction lines) aluminide. Using the internal MgO lines for calibration, the measured spacings of the additional solid lines (indicated by arrows) are 4.89, 3.48, 2.87, 2.01, 1.42 and 1.17Å, which match very well Al_3Ni_2 (JCPDS #14-648). This is a slightly more Al-rich phase than expected from the multilayer stoichiometry. Note that since the last four lines also match very well NiAl (JCPDS #2-1261 or 20-19), it is impossible to state unequivocally that the aluminide phase is not NiAl, and it may well be that both Al_3Ni_2 and NiAl coexist in the film. Nevertheless, because all lines are accounted for, it is clear that the aluminide forms at low temperature without a significant reaction between the individual layers (and particularly Al) and MgO. When the starting stoichiometry is changed to 55%Ni-45%Al, the 300°C SAD pattern shows clearly only NiAl and MgO, and after subsequent annealings the results are identical to those in 50% Al films.

The Al/Ni film shows Ni_3Al (JCPDS #9-97) and $\gamma\text{-Al}_2\text{O}_3$ (JCPDS #10-425) lines, while the MgO film is unchanged after the same RTA at 300°C. Although having an overall Al/Ni ratio identical to MgO/Al/Ni, oxidation of its external Al layers, possibly by residual oxygen in the RTA chamber, deprives the film of enough Al so that Ni_3Al forms instead of Al_3Ni_2 or NiAl (a simple calculation[8] shows that without the 100Å of the two external Al layers, the stack stoichiometry should be Ni_3Al). Formation of a metastable Al_2O_3 phase on NiAl in early oxidation stages is well established[14].

An additional RTA at 800°C for 300s yields the SAD patterns shown in Fig. 6, with their d-spacings listed in Table 2. Through comparison with the two standard films and the 300°C data, it is evident that a rather limited reaction took place. The arrows in the MgO/Al/Ni film point to the Al_3Ni_2 (NiAl) lines, still visible and quite strong.

New dotted rings indicate the presence of a minor new phase. As shown in Table 2, this phase is Ni₃Al. There is no evidence of Al₂O₃ being present. The presence of a weak line with d=4.68Å indicates that a minor amount of the spinel phase, MgAl₂O₃ (JCPDS #21-1152) has formed. Its presence at the interface between the aluminide and the top MgO layer is confirmed by XPS (see below). The standard Al/Ni film is practically unchanged from 300°C. The standard MgO film shows an unidentified secondary phase, with lines which do not match any known magnesium oxide phase. Note (below) that this phase becomes dominant at 1000°C. We conclude that the nickel aluminide/MgO system compares favourably with systems such as Al₂O₃/NiAl, and is more compatible at this temperature than other IMC's. Specifically, TiAl/MgO films annealed under identical conditions show no trace of TiAl, due to its total consumption in the reaction[15].

Further RTA at 1000°C for 100s yields the patterns and microstructures shown in Fig.7, and listed in Table 3. The MgO/Al/Ni film exhibits a number of clear semi-solid rings which match lines seen at 800°C. It is tempting to attribute these to the same phases (i.e. NiAl and MgO), in which case the conclusion is that the two are compatible even at 1000°C. On the other hand, all lines match quite well a spinel phase, either NiAl₂O₄ (JCPDS #10-339) or MgAl₂O₄. There is also extensive Ni agglomeration in the form of "globules" of material with diameters in the 0.2 - 1 µm range, in both MgO/Al/Ni and Al/Ni films. These globules also appear in Al₂O₃/Al/Ni and ZrO₂/Al/Ni but not in SiC/Al/Ni films [15], and are similar to the Ni globules in Ni/C reactions [12]. The Ni segregation implies that NiAl has broken up, freeing Ni. The presence of a spinel and free Ni points to a reaction such as



or



The molecular ratio of MgO/NiAl, taking a total of 600Å MgO and the thicknesses of the individual constituents of NiAl is roughly 1.77[8]. Given uncertainties in phase identification and in layer thicknesses, the above reactions can be reasonably considered balanced. Reaction (2) explains better the large amount of material in the Ni globules, and requires less free Mg to "disappear" from the film. The MgO film exhibits an excellent polycrystalline pattern which, however, does not match any standard Mg oxide file. The identity of this Mg(O_x) phase remains a mystery; it could

be a new Mg-deficient, high-temperature MgO phase, possibly induced by the evaporation of Mg from the film. The small grained phase also appears in a MgO/Al/Ni film annealed separately only at 1000°C for 100s. Its similar texture in the two films is an indication that the changes in the MgO are partially independent of the presence of the aluminide.

The Al/Ni film is completely oxidized, with an extremely strong (440) gamma-Al₂O₃ line plus minor amounts of unidentified phases (one of which may well be NiAl₂O₄, since a few lines seem to overlap the main lines in the MgO/Al/Ni film). The absence of the (440) gamma-Al₂O₃ line in MgO/Al/Ni films means that NiAl oxidation due to residual oxygen in the annealing chamber is a much slower process than the MgO/NiAl interfacial reaction. In other words, artifacts introduced by oxygen diffusion through the MgO film to the MgO/NiAl interface do not affect significantly our results.

2. XPS

XPS depth profiles are useful mainly at lower temperatures, where the interaction of MgO with the SiO₂/Si substrate is limited. Profiles of a 300°C annealed film, and the same film after 800°C and 1000°C annealings are shown in Fig. 8. After 300°C, Fig. 8a, one sees clearly the MgO/NiAl/MgO sandwich atop the SiO₂ layer. The bottom (closer to SiO₂) MgO/Al interface is very sharp, while the top one is much broader, due to partial Al oxidation during the evaporation of MgO. The apparent Ni segregation to the sides of the Al/Ni multilayer structure is puzzling, and may be due in part to some artifact of the sputtering process, as well as due to the Al oxidation at the top interface. Note however that the average Al/Ni layer stoichiometry is indeed close to equiatomic. The MgO stoichiometry, calculated after calibrations with MgO crystals, is also close to the expected 1:1.

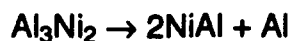
After exposure at 800°C, Fig. 8b, an interfacial reaction between MgO and NiAl is clearly visible. Limiting ourselves to the top interface in order to avoid artifacts introduced by the MgO/SiO₂ reaction, we see the formation of a wide Mg-O-Al region, which in accord with the SAD data is probably composed of the spinel MgAl₂O₄. The top MgO layer is still largely intact, but contains about 10% Al, which has diffused out of the aluminide. The outdiffusion of Ni is negligible, in marked contrast with the findings of Bobeth et al[16], who identified Ni as the major diffusant out of Ni₃Al in an early oxidation stage. We submit that this contradiction is due to the different aluminide stoichiometry, and possibly due to the different microstructures. It seems

clear though that with increased Al content and with polycrystalline aluminide, Al and not the noble component will in fact be the first major diffusing species at the aluminide-oxide interface, as seen also in TiAl/Al₂O₃ reactions[8], and in other studies[17]. This has obvious implications for the choice of a diffusion barrier, which, if required, should target Al and not the noble component. It is also worthwhile noting that oxygen diffusion into the aluminide occurs concurrently, as it does in TiAl/Al₂O₃ reactions[7].

The XPS profile of the 1000°C annealed film, Fig.8c, is not very instructive due to the extensive film-substrate reaction, which complicates tremendously the interpretation. This artifact can be eliminated of course by using MgO as a substrate, an experiment which has not been carried out. Nevertheless, some aspects of the MgO/NiAl reaction are clear: first, Mg has disappeared from the film, and this is not due to its diffusion into the substrate. Thus, the issue raised by Misra regarding Mg evaporation in a dynamic environment is confirmed. Second, the constant, low concentration of Ni, can best be explained by its existence in the form of globules distributed throughout the film, since once the distinct layer structure has broken up, phases coexisting side-by-side would give rise to a "smeared-out" depth profile. A direct comparison with the TEM results is of course impossible, but a certain conclusion is that the approximately 500Å thick aluminide layer has disintegrated.

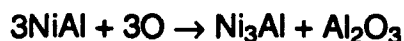
B. The NiAl/Al₂O₃ and NiAl/ZrO₂ Systems

The preparation of the thin-film specimens and the experimental procedure are detailed in ref. 9. After 300s at 300°C, an Ni-Al reaction forms an aluminide (either Al₃Ni₂ or NiAl) layer, about 400-500Å thick. The aluminide layer, sandwiched between 300Å-thick Al₂O₃ or ZrO₂ layers reacts with them at high temperatures. Figure 9 shows the 300, 800 and 1000°C SAD patterns of NiAl/Al₂O₃ films, and Table 4 lists their d-spacings. At 300°C, the pattern is clearly that of Al₃Ni₂(JCPDS card #14-648), with no Al₂O₃ lines visible, since the as-deposited Al₂O₃ film is amorphous[8]. Further RTA at 800°C for 5 minutes leads to the decomposition reaction

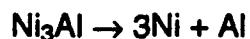


and the crystallization of the alumina layer to gamma-Al₂O₃. The NiAl lines (dotted) and the gamma-Al₂O₃ lines (solid) are seen clearly in the figure. It is quite possible that Al₃Ni₂ decomposes due to oxidation involving residual oxygen in the annealing chamber which diffuses to the interface through Al₂O₃. As shown in the NiAl/MgO study, this oxidation is also evident in Al/Ni baseline films which are not sandwiched between Al₂O₃ layers. These layers therefore play no role at 800°C, and we conclude that there is no interfacial reaction between Al₃Ni₂ and Al₂O₃, and that the interface is more stable than in NiAl/MgO thin films, where under identical conditions a reaction forms Ni₃Al and a spinel.

Upon additional RTA at 1000°C for 100s, the pattern changes drastically, and is identical to that of a 1000°C annealed baseline Al₂O₃ film. This means that NiAl has oxidised and decomposed into its constituents, probably through an intermediate reaction



leading to



The Ni agglomerates in globules, Fig. 10a, identical in size and shape to Ni agglomerates in a baseline Ni/Al film, Fig. 10b. The Al oxidises, or evaporates from the exposed surfaces. The transient oxidation of bulk NiAl at these temperatures is known to form gamma-Al₂O₃[14]. It is worth noting that the Al₂O₃ layer is continuous, with no voids of the type seen in the NiAl/ZrO₂ specimen (see below). The Al₂O₃ which forms in the baseline Ni/Al film is also continuous. These observations suggest that the oxidation is most likely due to residual O in the gas. Therefore, there is no true interfacial reaction between NiAl and Al₂O₃, and the two can be considered compatible, in agreement with bulk composite results reviewed in ref[18].

The SAD patterns of NiAl/ZrO₂ films after RTA at 300, 800 and 1000°C are shown in Fig. 11, and their d-spacings listed in Table 5. The microstructure at 1000°C is also shown. They can be compared with the patterns of a baseline 500Å-thick ZrO₂ film in Fig. 12. Both NiAl and tetragonal (t)-ZrO₂ (#34-1084) lines are evident in the 300°C films. NiAl may have formed instead of Al₃Ni₂ due to small differences in the Al/Ni ratio in the NiAl/ZrO₂ and NiAl/Al₂O₃ films.

The 800°C pattern contains all the lines seen at 300°C plus faint reflections of very small grained ZrO (#20-684) as well as reflections of very large grained Ni₃Al areas. This indicates a limited oxidation of NiAl, with some O probably coming from ZrO₂. Further annealing at 1000°C causes the disappearance of NiAl and Ni₃Al, the formation of Ni globules, and the transformation of t-ZrO₂ to monoclinic (m)-ZrO₂. In contrast with NiAl/Al₂O₃ and NiAl/MgO films, these films exhibit rather large voids in the ZrO₂ layers. The voids are not due to the t→m ZrO₂ transformation, which is known to be diffusionless[19] and do not appear in the baseline ZrO₂ film. Rather, they result from the decomposition of part of the ZrO₂ layer during reaction with Ni₃Al. **The NiAl/ZrO₂ system is therefore judged to be less stable than both NiAl/MgO and NiAl/Al₂O₃.** Note that as in NiAl/MgO, and unlike in NiAl/Al₂O₃, there is no trace of gamma-Al₂O₃ at 1000°C, as expected if the free Al has evaporated.

Another interesting aspect of this reaction is its apparent effect on the crystallization of ZrO₂. The as-deposited ZrO₂ is amorphous in both NiAl/ZrO₂ and ZrO₂ films. The baseline ZrO₂ film crystallizes in the monoclinic structure as expected[20]. However, in the NiAl/ZrO₂ film the structure up to 800°C is tetragonal, transforming to m-ZrO₂ at 1000°C. The existence of t-ZrO₂ at a temperature much lower than the m→t transformation temperature of ca. 1170C[20] indicates that ZrO₂ is "stabilized" by NiAl. Its nucleation pattern is "inverted", the phase sequence with increasing temperature being amorphous ZrO₂→t-ZrO₂→m-ZrO₂.

Some of the effects seen in these films are obviously exaggerated in comparison with bulk interfaces. For example, the agglomeration of Ni and the evaporation of Al, both involving fast diffusion paths, would probably be absent in bulk IMC's. However, when different thin-film model systems are compared with each other, we can still see a "stability ranking", one which we expect will extend to bulk composites. **As reinforcements in NiAl-based IMC's, Al₂O₃ would rank as most stable, followed by MgO. ZrO₂ rates as less stable than both.**

C. The TiAl/Al₂O₃ System

As mentioned in chapter I, among IMC's, the Ti aluminide (particularly gamma-TiAl) - Al₂O₃ system is quite promising for two reasons: excellent coefficient of thermal expansion (CTE) match and chemical compatibility between TiAl and Al₂O₃[7]. Bulk

studies show that aluminides with greater than or equal to 50% at. Al do not react with alumina[7,21,22], whereas for Al-poor (<50%) aluminides there is no consensus. For example, Misra[7] found that they do react; others[21,22] found that they do not. In thin films, the reports focus almost exclusively on Ti/alumina reactions; a good summary is given by Selverian et al[23]. The general view is that Ti film/bulk (crystalline) Al_2O_3 reactions form Ti_3Al and a Ti oxide[24], whereas thin film Ti/amorphous Al_2O_3 reactions form AlTi , TiO and Ti_2O [25]. Recent thermodynamic calculations of oxide stability in the Ti-Al-O system[26] indicate that at temperatures between 700°C-1100°C, Al_2O_3 would be unstable in alloys with compositions in the two-phase region $\text{Ti}_3\text{Al}/\text{TiAl}$. The scarcity of experimental data is one reason for the rather cloudy picture of Ti aluminide/alumina reactivity. Another is the poor resolution of most probing techniques with the exception of surface techniques [23,27] and high-resolution electron microscopy. The reactivity is thus defined by "macro" reactions (on a micron scale), while interfacial nanometer-scale reactions generally go undetected in supposedly "nonreactive" couples.

The experimental details of specimen preparation and annealings are given in ref. 8. Aluminide films with 30, 50 and 70% (atomic) Al were prepared and named Ti_{30}Al , Ti_{50}Al and Ti_{70}Al respectively (see Fig. 3). Unlike in the rest of this study, a special "sandwich" of sapphire/ $\text{TiAl}/\text{Al}_2\text{O}_3$ was also prepared, in order to follow both $\text{TiAl}/(\text{amorphous})\text{Al}_2\text{O}_3$ and $\text{TiAl}/\text{sapphire}$ reactions.

The diffraction patterns of all as-deposited films (see e.g. Ti_{50}Al in Fig. 13a) indicate the presence of polycrystalline Ti and Al, with ring intensities varying according to the relative amounts of the two materials. E-beam evaporated Al_2O_3 films are amorphous ($\alpha\text{-Al}_2\text{O}_3$). Figure 14 shows the XPS profile and the $\text{Al}2p$ and $\text{O}1s$ scans of the as-deposited Ti_{50}Al ($\alpha\text{-Al}_2\text{O}_3/\text{Ti}+\text{Al}/\text{sapphire}$). The atomic ratio O/Al in the Al_2O_3 film and in the sapphire is almost identical, as is the Al-O binding energy. Although reduction of both by the 4 kV Ar ion beam is evident, it is safe to assume that the evaporated film is nearly stoichiometric[28] and chemically almost identical to sapphire.

The microstructure and diffraction pattern of Ti_{50}Al after annealing at 700°C for 100s are seen in Fig. 13b as is the presence of a new aluminide phase, identified as TiAl . Table 6 gives its d-spacings and shows that they closely match those of standard TiAl (JCPDS file 5-678). The TiAl forms under conditions that keep the $\text{Al}_2\text{O}_3/\text{TiAl}$

interface stable: both TEM and XPS (not shown) indicate that there is no interfacial reaction at 700°C. We are thus able to form a 400 to 500Å-thick aluminide, sandwiched between two Al₂O₃ films or between Al₂O₃ and sapphire.

The diffraction patterns of Ti30Al and Ti70Al after the 700°C anneal are also listed in Table 6. The Ti-rich Ti30Al appears to consist of Ti₃Al (JCPDS file #9-98) and some retained Ti. Many lines almost overlap in these two phases, and since the observed intensities differ greatly from those of Ti₃Al, and XPS indicates the presence of metallic Ti, we conclude that some Ti remains unreacted.

The Al-rich Ti70Al d-spacings appear to match well the recently calculated values for TiAl₂[29]. In addition, in Ti70Al the d=1.99Å and 1.40Å sharp thin rings indicate the presence of extremely fine grained crystalline (c)-Al₂O₃. The crystallization of the a-Al₂O₃ film becomes evident in all specimens at 800°C. The a-Al₂O₃ to c-Al₂O₃ transformation occurs faster in the presence of Al-rich aluminides, which may provide excess Al to the Al₂O₃.

The diffraction pattern d-spacings of the three specimens after 100s at 800°C are listed in Table 7. Small changes in Ti30Al include the appearance of two c-Al₂O₃ lines.

The Ti50Al pattern, Fig. 13c, although basically similar to that at 700°C, shows additional lines. Two of these, at d=1.99 and 1.40Å belong to c-Al₂O₃. Others, at d=5.03, 2.52, 2.22 and 1.23Å, fit Ti₃Al (9-98) quite well, which would indicate a limited TiAl→Ti₃Al transformation and Al loss from the aluminide. However, the XPS profile (not shown) indicates that the Ti/Al ratio has not increased significantly, so the reaction at this temperature is quite limited.

The Ti70Al pattern remains unchanged from 700°C to 800°C, except that the c-Al₂O₃ lines are stronger at 800°C. In summary, at 800°C all three aluminides seem to be stable.

The d-spacings of polycrystalline phases in the three films after annealings at 900°C for 100s are given in Table 8, and are shown together with low magnification microstructures in Fig. 15 (Ti50Al is also shown in Fig. 13d). Changes from 800°C are seen in all three. In Ti30Al, the additional lines at d=2.57, 2.41, 2.27, 1.76, 1.48 and

1.37Å match Ti_2O (file #11-218) perfectly, and Ti_2O is a major phase in this specimen. $Ti_{30}Al$ also contains a few micron-size single crystals that appear to be either Ti_4O_7 or TiO_2 and that occupy 10-20% of the film area. These crystals sit in regions denuded of the former aluminide and probably represent the final product of the reaction.

The changes in the $Ti_{50}Al$ and $Ti_{70}Al$ patterns are interesting and difficult to explain at present. All lines in $Ti_{50}Al$ (except the Al_2O_3 reflections) fit the Ti_3Al pattern within ~1%. This would seem to continue the trend of a $TiAl \rightarrow Ti_3Al$ transformation, visible already at 800°C. Ti oxide single crystals appear only rarely in $Ti_{50}Al$. The Ti-enrichment of the aluminide is confirmed in the XPS profile, Fig. 16a. The profile indicates an outdiffusion of Al from the aluminide and an indiffusion of O from the Al_2O_3 layer. More puzzling, the aluminide/ Al_2O_3 interface, although wider than before, is still quite distinct, meaning that the "interfacial reaction" consists almost entirely of internal changes in the aluminide layer. A similar, and even more pronounced loss of Al and increase in O in the aluminide is evident in $Ti_{50}Al$, Fig. 16b. Note that here the Al/O ratio in both Al_2O_3 film and sapphire is practically identical to that in the unannealed specimen, Fig 14a. Since 4kV Ar ion sputtering is certain to induce stoichiometry changes it is impossible to tell from the XPS profile how much if any of the Al leaving the aluminide stays in the oxide.

In $Ti_{70}Al$, many lines match $TiAl$ (5-678) very well and the pattern is very similar to that of $Ti_{50}Al$ at 800°C, except for the "thin lines" with $d=2.29$, 1.20 and 1.15Å which remain unassigned. If confirmed, the apparent $TiAl_2 \rightarrow TiAl$ transformation in this sample implies, as in $Ti_{50}Al$, the breakup of the aluminide and loss of Al. Ti oxide single-crystals were not detected in $Ti_{70}Al$.

D. The $TiAl/TiB_2$ and $TiAl/TiC$ Systems

The experimental procedure here followed exactly that in $TiAl/Al_2O_3$ films, except that no sapphire substrates were used. Details are given in ref. 11. All the as-deposited films show SAD patterns consisting of only Ti and Al lines. All four reinforcements are amorphous as-deposited. Table 9 lists the d-spacings after a low-temperature reaction (660°C, 5 min.) to form the aluminide: a complete $AlTi$ (JCPDS file 5-678) pattern is seen in the $TiAl/Al_2O_3$ couple which was used for comparison. In addition, two strong lines with $d=1.98\text{Å}$ and 1.40Å show the presence of crystalline

gamma-Al₂O₃. The TiAl/TiB₂ (b) and TiAl/TiC (c) patterns are composed mainly of TiB₂ and TiC lines, respectively, with only the strongest AlTi line at d=2.31Å visible. It is clear that all three amorphous reinforcements start to crystallize below 660°C when in contact with TiAl. There is no evidence for any reaction occurring between TiAl and Al₂O₃ under these conditions. However, in view of the much weaker AlTi patterns in the two other couples, it appears that they have undergone a reaction.

Table 10 lists the d-spacings of films annealed at 800°C for 5 minutes. Annealings at 900°C for 100s lead to the same results. The TiAl phase disappears in each case: in TiAl/Al₂O₃ couples, the reaction products are Ti₃Al (file 9-98) and gamma-Al₂O₃. After internal calibration using the gamma-Al₂O₃ lines, the Ti₃Al spacings are within less than 1% of the file data. Reaction at 1000°C (unpublished) induces the formation of a small amount of Ti₂O (file 11-218).

In TiAl/TiB₂, the products appear to be a mixture of borides, possibly TiB + TiB₂. In TiAl/TiC, the main lines are those of TiC, with two very weak lines at d = 2.64 and 2.29Å indicating a minor Ti₂AlC (file 29-95) phase. There are no lines that can be attributed to TiAl in any of the films. **We thus see that on a nanometer scale TiAl is chemically incompatible with all three reinforcements at 1000°C, or even at a lower temperature if the times are long enough.**

IV. SUMMARY AND CONCLUSIONS

A. NiAl/MgO

We have found that NiAl will react with MgO at predicted operation temperatures. Even taking into consideration the possible differences between thin polycrystalline film and bulk reactivities, it is still likely that a limited interfacial reaction will occur in bulk composites, following roughly the same steps, and leading to the formation of a spinel and Ni₃Al. A limited nanoscale interfacial reaction, as pointed out, is not necessarily detrimental, as it may lead to strong bonding and therefore good mechanical strength. On a RELATIVE basis, when compared with other systems such as NiAl/ZrO₂, NiAl/Y₂O₃, NiAl/SiC, TiAl/Al₂O₃ and TiAl/MgO, investigated by the same method [8,15], the MgO/NiAl reaction at 800°C is more limited, indicating that it is indeed one of the more stable aluminide-based IMC's.

B. NiAl/Al₂O₃ and NiAl/ZrO₂

The changes observed in NiAl/ZrO₂ films cannot be solely attributed to NiAl oxidation by external oxygen, and therefore indicate a NiAl-ZrO₂ interfacial reaction, while those seen in NiAl/Al₂O₃ films are fully consistent with "external" oxidation. As reinforcements in NiAl-based IMC's, Al₂O₃ would rank as most stable, followed by MgO. ZrO₂ rates as less stable than both. Although bulk results with ZrO₂ are few and ambiguous[18], they also seem to indicate that it is a less stable reinforcement than Al₂O₃. The agreement in the stability rankings between thin-film and bulk couples is therefore quite good.

C. TiAl/Al₂O₃

The XPS comparison of the e-beam-evaporated α -Al₂O₃ film and sapphire before and after annealing, as well as other studies [28], indicate that the two are similar enough to consider α -Al₂O₃/intermetallic reactions as substantially equivalent to bulk c -Al₂O₃/intermetallic reactions. Moreover, layered Ti/Al films "sandwiched" between α -Al₂O₃ films form a Ti aluminide at 700°C, where the reaction with the

alumina film is negligible. The Ti/Al film reaction is probably similar to the exothermic reaction between Ti and Al powders at between 640 and 700°C reported recently[30]. Also, the formation of aluminides from thin Ti and Al films in the temperature range 350-700°C is well documented[31]. Thus we submit that the observations reported here can be considered as quite relevant to nanoscale interfacial reactions in real IMC's.

Regarding the nanoscale reactivity of Ti aluminides containing 30 to 70% (at.) Al we find that regardless of stoichiometry, all aluminides react with Al_2O_3 . As expected, the reaction is faster (starts at lower temperature) for Ti-rich aluminides, in which it forms Ti oxides. At all compositions, it involves the indiffusion of O into the aluminide and its breakup, and the outdiffusion of Al. If the amount of material is finite (as in our films), one gets formation of more Ti-rich aluminides (i.e. $TiAl_2 \rightarrow TiAl$ and $TiAl \rightarrow Ti_3Al$ transformations), which, in the presence of increased O levels eventually decompose to form Ti oxides and partially oxidized Al. In our films, the Al that leaves the aluminide may diffuse through the oxide and reach the surface where it can be carried away by the Ar stream, a phenomenon observed also in bulk couples[7]. We emphasize that the interfacial reaction described here may be quite limited spatially. Nevertheless, in the context of its possible influence on the IMC properties it could be important.

While keeping in mind the difference between thin, finite reaction couples and infinite bulk couples, we find that for contents of less than the gamma (50%) composition, our results are in agreement with some bulk results[7] but contradict others[21,22]. Specifically, Misra [7] demonstrates that bulk Ti-54%Al/ Al_2O_3 couples do not react even at 1300°C after 66 hours. Decock et al.[21] find similar stability of gamma-Ti/ Al_2O_3 couples at 1100°C after 192 hours. For Al-rich aluminides our results basically disagree with all published experimental data [e.g 7,22,32] as well as with predictions of recent Ti-Al-O phase diagrams[21,33]. We conclude that on a nanometer scale, Ti aluminides and Al_2O_3 are not chemically compatible, and that aluminides with 30-70% Al lose their Al and transform first into more Ti-rich aluminides and eventually into Ti oxides.

D. TIA/TIB₂ and TIA/TIC

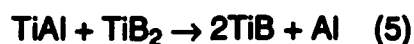
Our study is showing extensive nanoscale reactivity in these couples. To understand these results, one has to look at the possible reactions as well as the mechanisms by which such reactions may occur. Regarding the predicted unstable TiAl/TiC system, the following reaction



is favored thermodynamically[34,35]. The very weak Ti_2AlC reflections indicate that it does indeed occur. The strong TiC lines at 900°C are due to excess TiC. The relative amount of TiAl and reinforcement "molecules" in each specimen can be calculated approximately using the film thicknesses, bulk density values and atomic or molecular weights. The molecular ratio is found from the formula:

$$\frac{\text{Layer \#1 thickness} \times \text{density} / \text{molecular weight}}{\text{Layer \#2 thickness} \times \text{density} / \text{molecular weight}}$$

Assume that volume changes during formation of TiAl from Ti and Al are accommodated fully by changing only the thickness; therefore, 252Å Al + 265Å Ti will form a 480Å TiAl layer. By using bulk densities (in g/cm³) and molecular weights of 3.9 and 74.88 for TiAl, 3.9 and 101.96 for Al₂O₃, 4.5 and 69.54 for TiB₂, and 4.9 and 59.91 for TiC, respectively, we find the following molecular ratios: a) TiAl/Al₂O₃ = 25/23; b) TiAl/TiB₂ = 25/39; and c) TiAl/TiC = 25/32; thus it is clear that excess TiC will exist after the entire TiAl layer is consumed in reaction 1. Regarding the other two systems, possible reactions are:



The lack of thermodynamic data on Ti₂O precludes a definitive check on the validity of reaction (4). In accordance with the molecular ratios calculated above, excess Al₂O₃ as well as excess Al should be seen in the TiAl/Al₂O₃ couple. The strong gamma-Al₂O₃ lines provide evidence of Al₂O₃ existence, but Al lines are never seen. However, we mentioned above that X-ray photoelectron spectroscopy (XPS) profiles of TiAl/Al₂O₃ couples show that Al from the aluminide layer diffuses out, crosses the thin Al₂O₃ layer and evaporates, being swept from the specimen surface by the flowing

argon[7], thus explaining the missing pattern. As an interesting aside, the observed reactivity of TiAl with Al_2O_3 may explain its oxidation behavior. When a lamellar TiAl/Ti₃Al structure is oxidized[36], Al_2O_3 "paths" initiate from the TiAl area, suggesting that aluminum to form Al_2O_3 is mainly supplied to the lamellar boundaries from the Al-rich TiAl phase. Such outdiffusion of Al from TiAl matches our observations exactly[8].

Regarding reaction (5), calculated phase equilibria for the system Ti-Al-B at 1100°C[21] indicate that it should be favored thermodynamically: a tie line exists between gamma-TiAl and TiB but not between gamma-TiAl and TiB₂. The molecular ratios clearly show that excess TiB₂ should be present after total consumption of the TiAl layer. Missing Al lines may again be attributed to its outdiffusion.

In summary, this study strongly suggests that the likelihood of nanoscale interfacial reactions in "stable" systems is greater than anticipated. This finding appears to contradict existing evidence of BULK non-reactivity in most of these systems (except TiAl/TiC). There may be a number of reasons for this apparent contradiction between bulk and thin-film results. For example, the resolution of the techniques used in bulk studies may be too poor to detect nanometer-scale reaction products; the reactions may be self limiting, with the product phase becoming an efficient diffusion barrier preventing further layer growth. Thin-films may differ chemically from bulk, affecting the reactivity, although comparisons of TiAl (film) reactions with thin Al_2O_3 films and with sapphire show that if anything, the sapphire is more reactive [8]. We suggest however that the existence of nanoscale reactions at supposedly "stable" interfaces should be considered the norm, rather than the exception, particularly at the high temperatures of IMC preparation or use.

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INVESTIGATION OF BULK INTERFACIAL REACTIONS WITH THIN-FILM MODELS

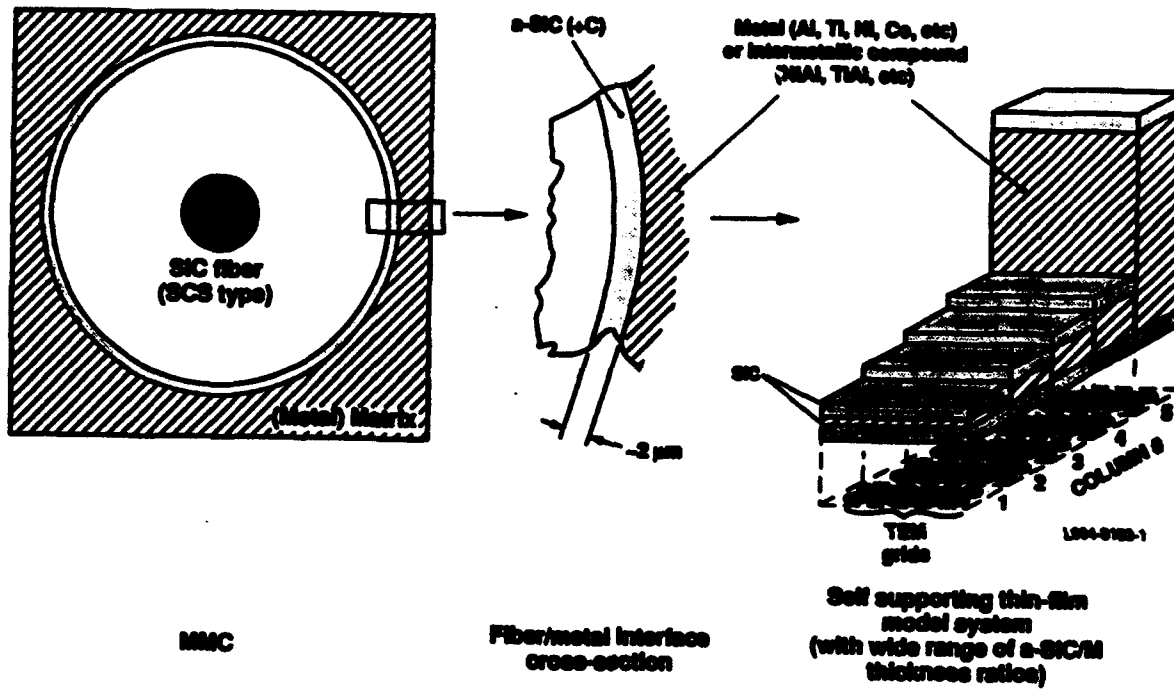
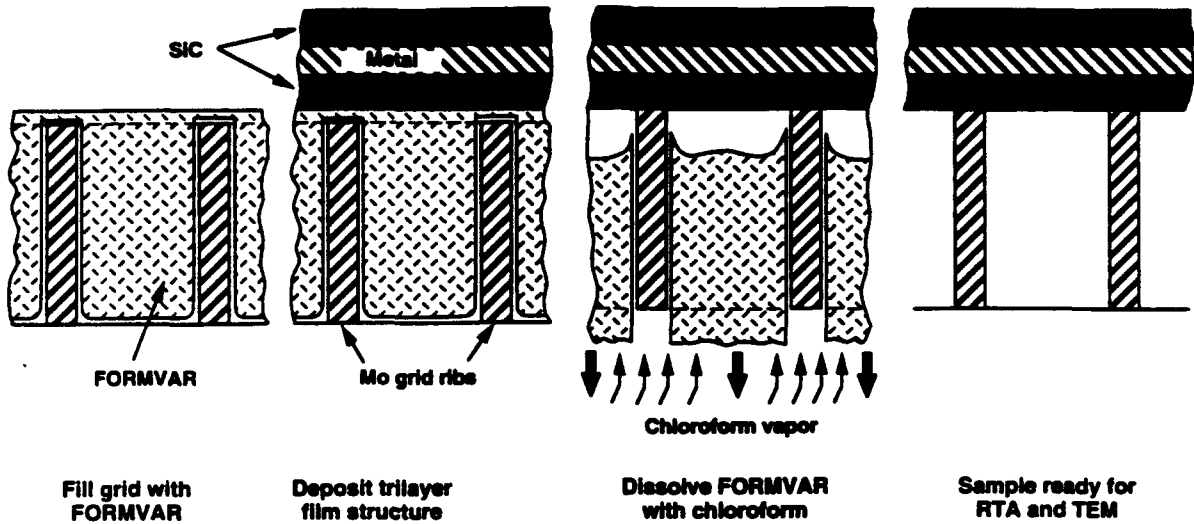
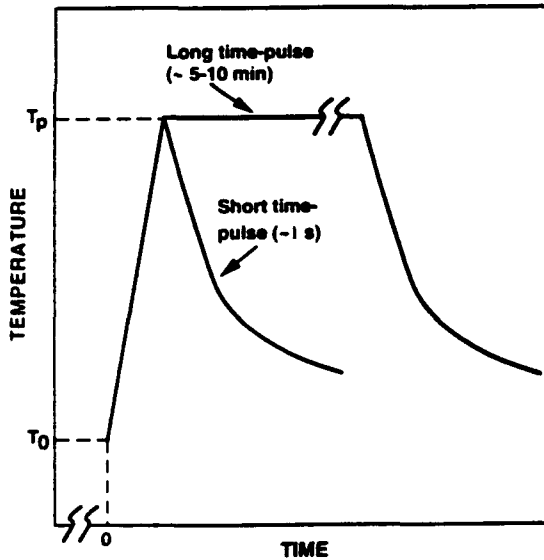


Figure 1. Investigation of bulk interfacial reactions with thin-film models. Although the specific drawing describes a SiC fiber/matrix system, it can of course be considered general.

PROCESS TO PRODUCE FREE-LYING LAYERED FILMS ON TEM GRIDS IS STRAIGHTFORWARD AND FLEXIBLE



RAPID THERMAL ANNEALING (RTA) ALLOWS CLOSE CONTROL OF TEMPERATURE AND ANNEALING TIME



WITH RTA 2-10 GRIDS CAN BE TREATED SIMULTANEOUSLY

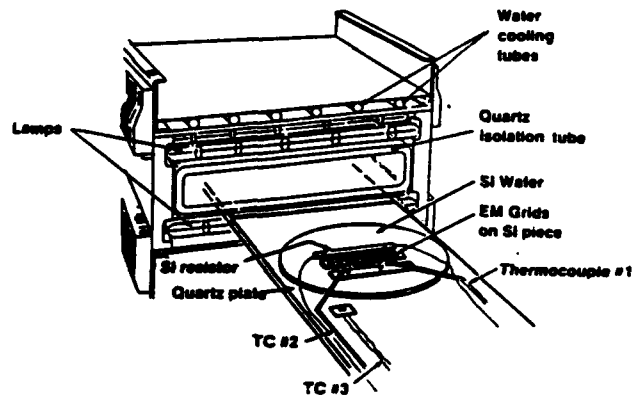


Figure 2. Schematic description of the steps in the preparation of layered films-on-grid, typical rapid thermal annealing T-t curves, and the annealing procedure.

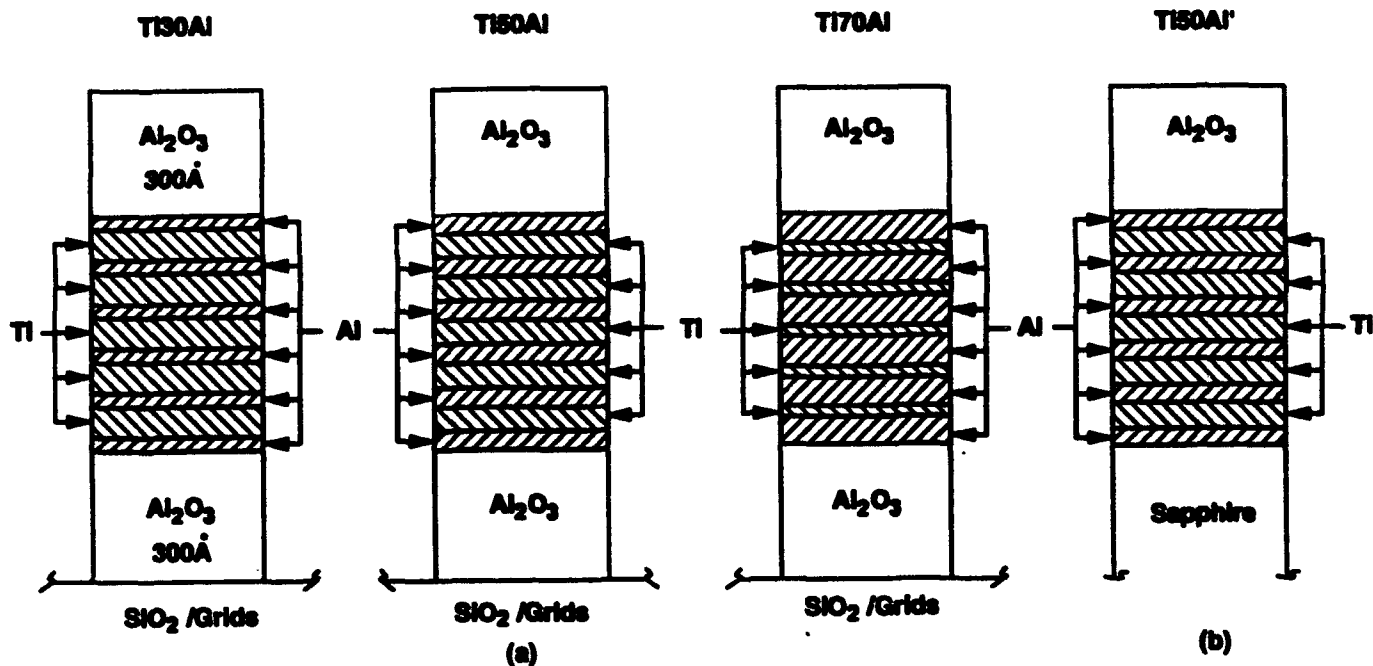


Figure 3. Schematic description of the layered films used in this study: (a) Al_2O_3 /Ti aluminide/ Al_2O_3 structures with three different Ti/Al ratios in the aluminide; (b) Al_2O_3 /Ti50Al/sapphire structure. Al/Ti/Al layer thicknesses:

Ti30Al - 30/74/23/74/23/74/23/74/23/74/30Å;
 Ti50Al and Ti50Al' - 42/53/42/53/42/53/42/53/42/53/42Å;
 Ti70Al - 58/32/58/32/58/32/58/32/58/32/58Å.



Figure 4. SAD patterns of as-deposited films.



Figure 5. SAD patterns of films after annealing at 300°C for 100s.

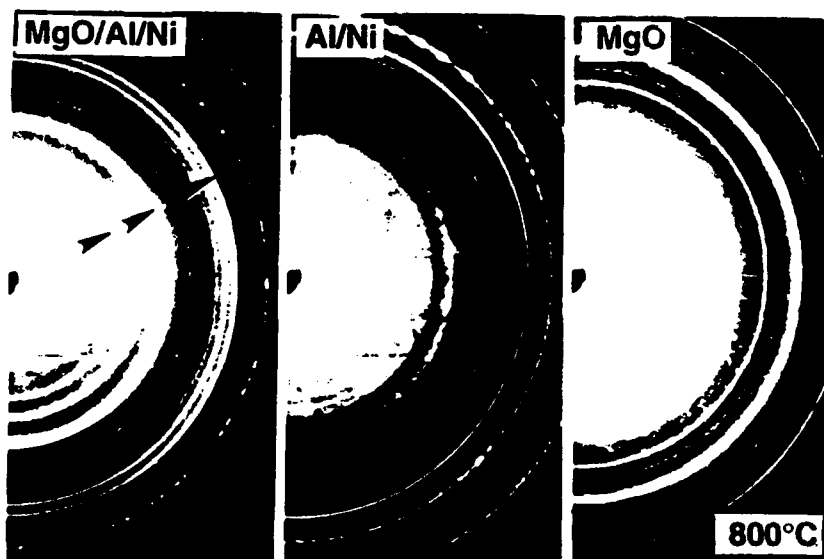


Figure 6. SAD patterns of films after additional annealing at 800°C for 5 minutes.

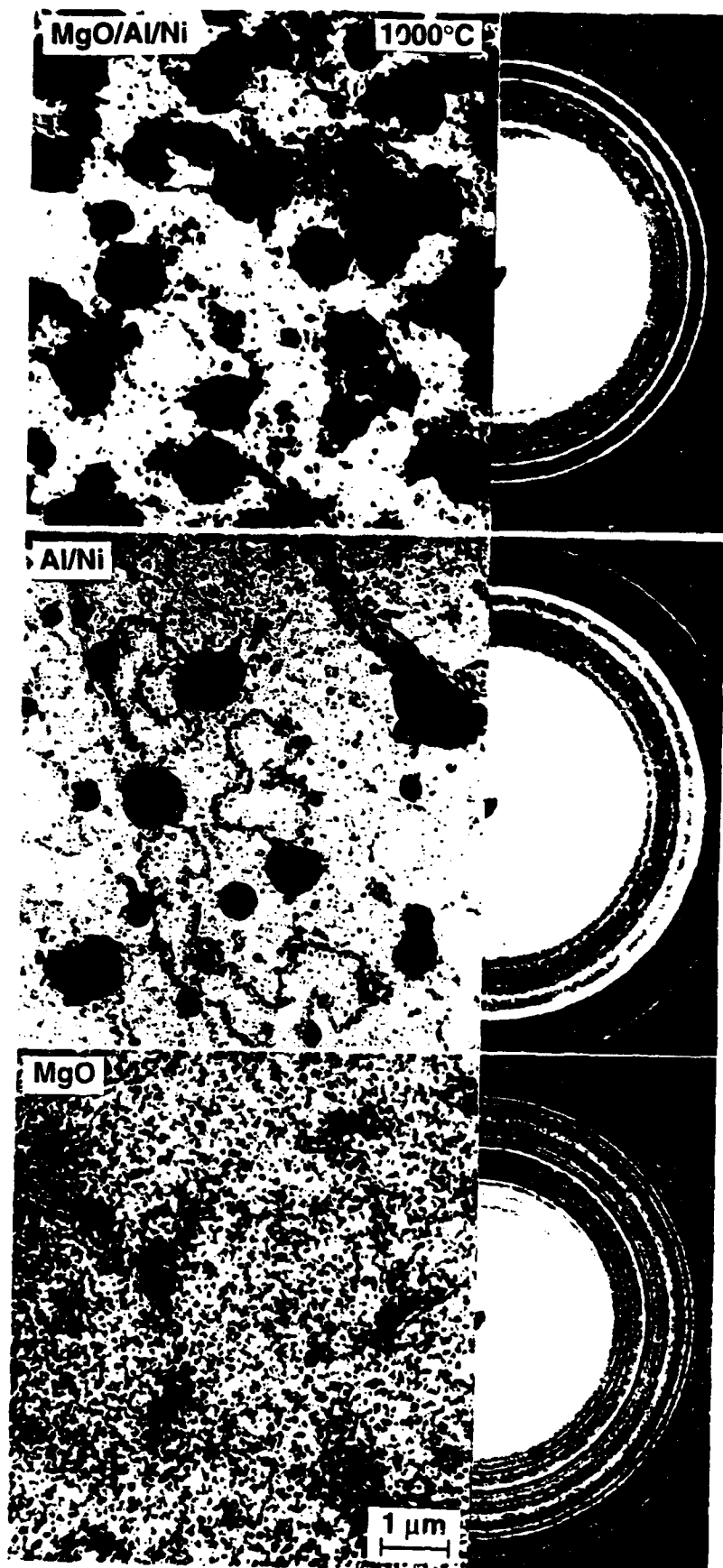


Figure 7. SAD patterns of films after additional annealing at 1000°C for 100s.

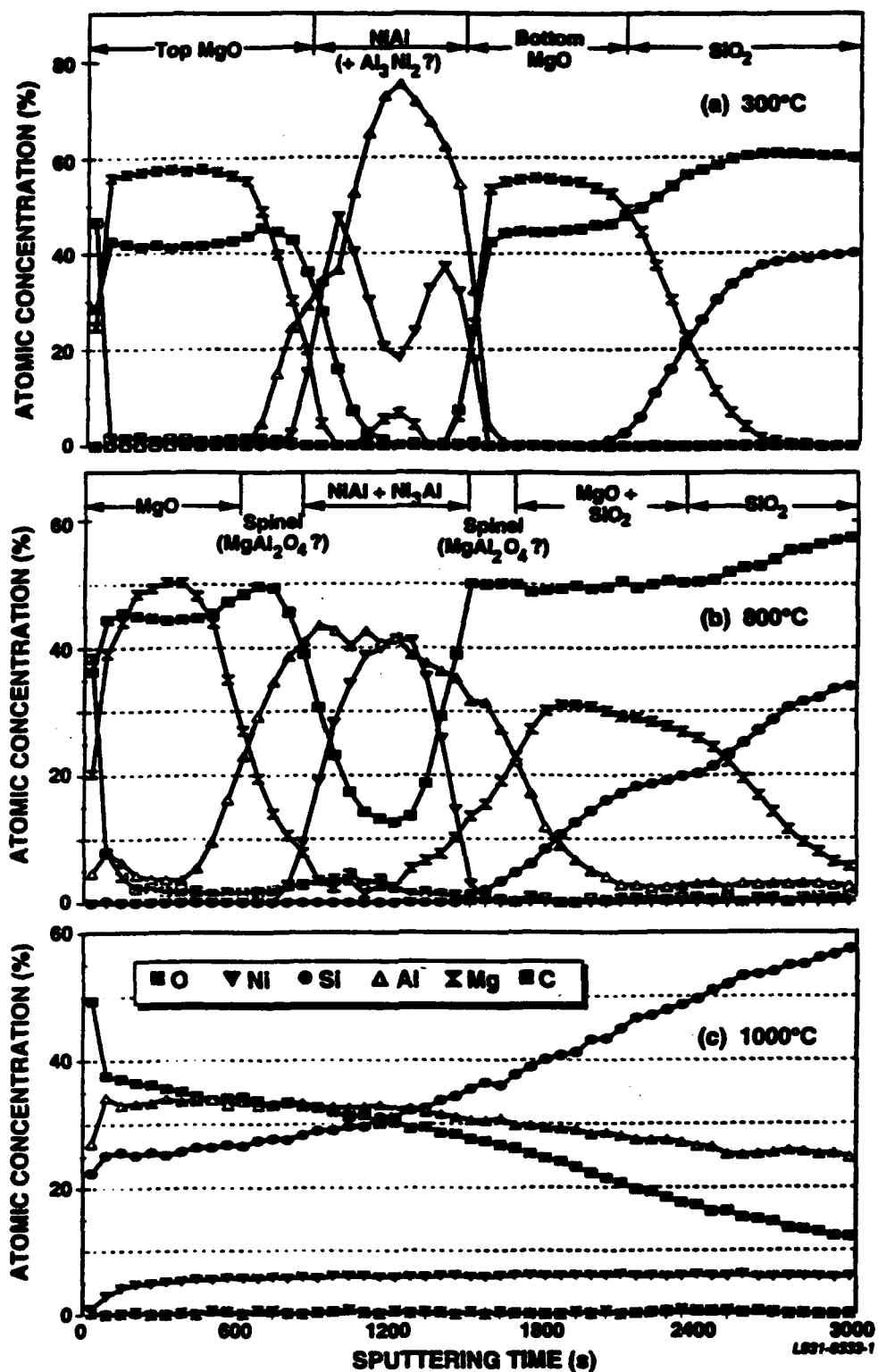


Figure 8. XPS depth profiles of films on oxidised Si substrates: a) after 300°C annealing; b) after additional 800°C annealing; c) after additional 1000°C annealing. The atom percentages have errors on the order of 5-10% due to uncertain sensitivity factors and overlapping peaks. "Negative" going signals caused by the signal processing method (and obviously artifacts) have also been eliminated.

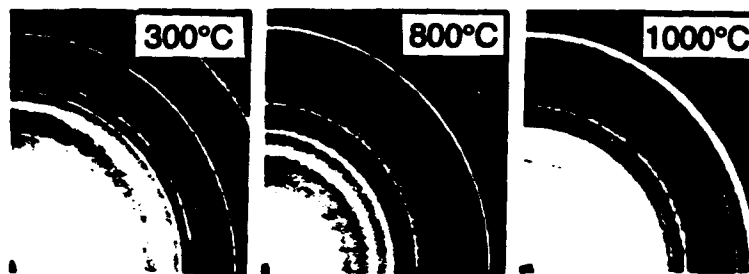


Figure 9. Electron diffraction patterns of NiAl/Al₂O₃ films annealed at 300°C for 5 minutes, then reannealed at 800°C for 5 minutes and 1000°C for 100s.



Figure 10. Microstructures after annealing at 1000°C: a) NiAl/Al₂O₃; b) NiAl film. Arrows in both point to Ni globules. The background is Al₂O₃.

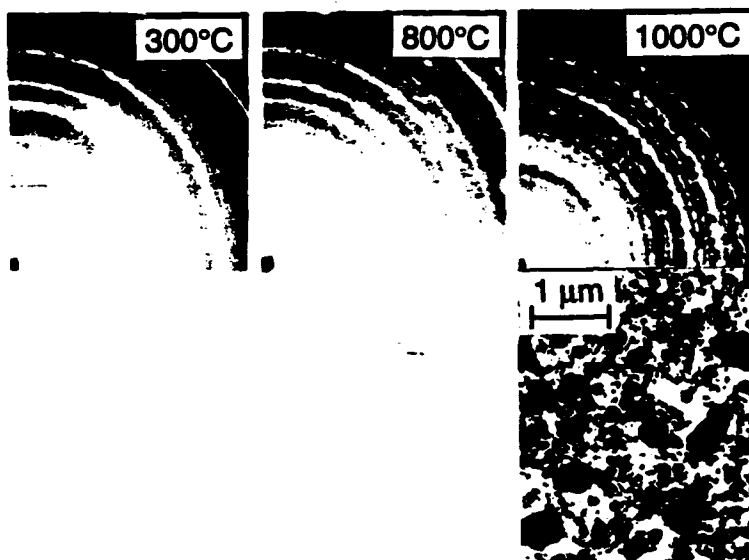


Figure 11. Electron diffraction patterns of NiAl/ZrO₂ films annealed at 300°C for 5 minutes, then reannealed at 800°C for 5 minutes and 1000°C for 100s. The microstructure at 1000°C exhibits voids (white areas) as well as Ni globules.



Figure 12. Electron diffraction patterns of a baseline 500A-thick ZrO₂ film, annealed simultaneously with the NiAl/ZrO₂ film. The structure is monoclinic at both 800 and 1000°C.

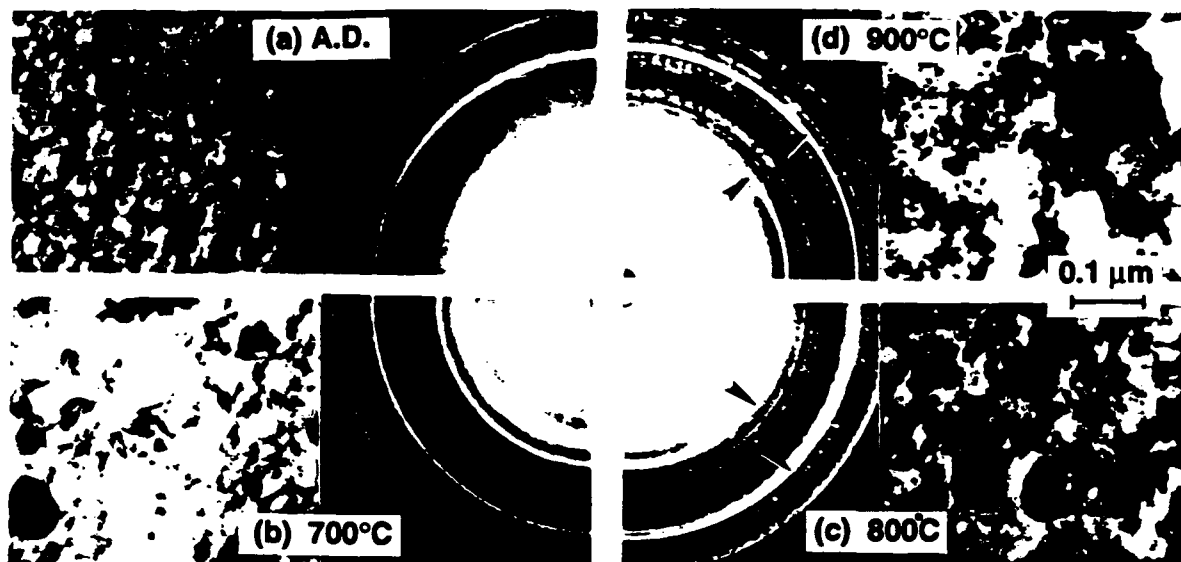


Figure 13. High magnification microstructures and diffraction patterns of Ti50Al: (a) as-deposited; and (b),(c),(d) - after 100s anneals at 700, 800 and 900°C respectively. Arrows in the diffraction patterns indicate c-Al₂O₃ reflections.

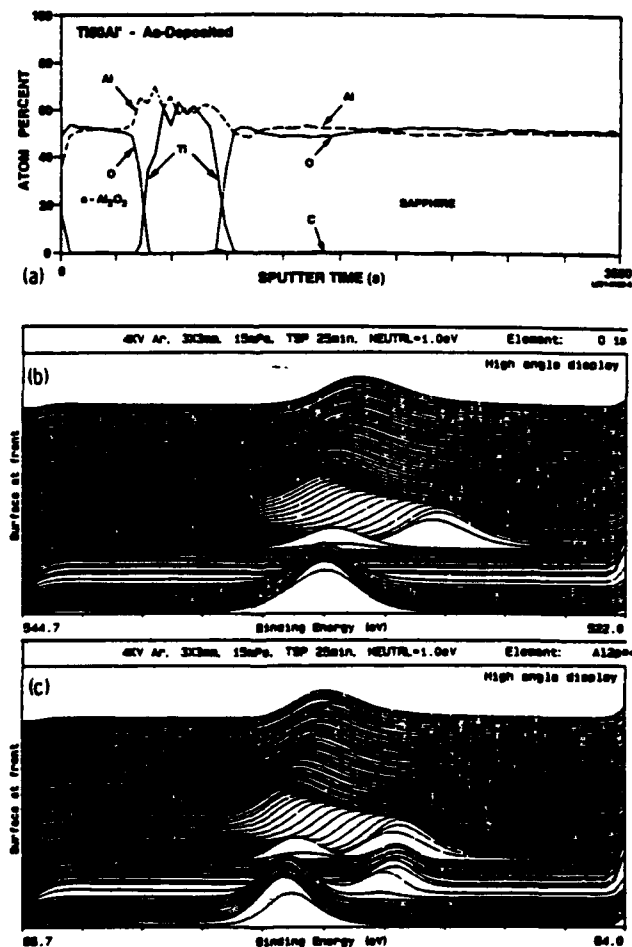


Figure 14. (a) XPS profile, (b) O1s scans and (c) Al2p scans of the as deposited a-Al₂O₃/Ti50Al/sapphire structure. Note the almost identical O/Al ratio in the a-Al₂O₃ film and the sapphire substrate. The energy shifts in the sapphire are artifacts due to the sputtering process, as is the apparent oxide substoichiometry.



Figure 15. Low magnification microstructures and diffraction patterns of the three specimens after 100s anneals at 900°C. A single crystal Ti oxide region in Ti30Al is indicated by an arrow.

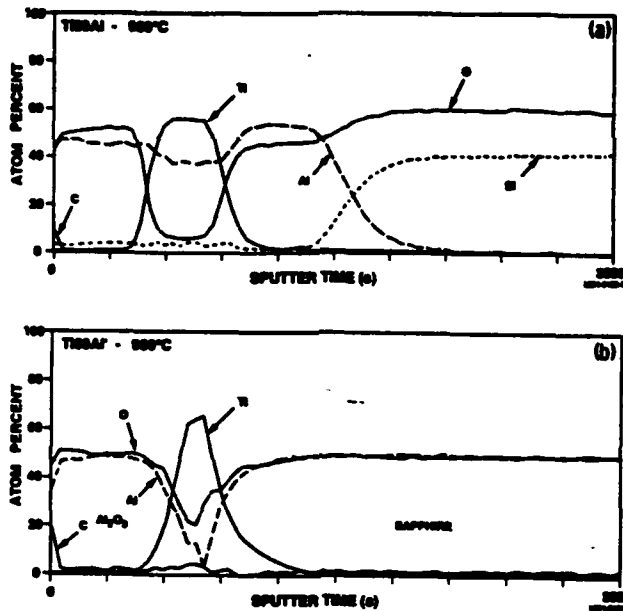


Figure 16. XPS profiles of 900°C annealed films: (a) Ti50Al; (b) Ti50Al'. The loss of Al from the aluminide layer is clear, particularly in Ti50Al'. Also evident is the diffusion of O into the aluminide. Due to sputtering effects and background correction uncertainties the exact stoichiometry in each layer is unknown. However, the error in the aluminide is not likely to be greater than a few percent.

TABLE 1. Al/Ni layer thicknesses (in Angstroms) for the NiAl/MgO study. Top and bottom layers are 300A-thick MgO. The thicknesses yield an equiatomic NiAl compound.

MgO	Al	Ni	Al	Ni	Al	Ni	Al	Ni	Al	Ni	Al	MgO
300	50	40	50	40	50	40	50	40	50	40	50	300

TABLE 2. Interplanar spacings of films annealed at 300°C for 100s + 800°C for 300s. Intensity notations: s- strong, m - medium, w - weak, v - very. * - possible NiO reflections.

Al/Ni	MgO	MgO/Al/Ni	Comments
dotted rings	solid rings	solid rings	
2.54ms	5.12vw	4.68vww	spinel?
2.07vs	3.92m	3.94vww	MgO
1.78vww	3.75vw	2.84w	Al Ni or NiAl
1.60mw	3.49w	2.44s	MgO
1.47mw*	3.01m	2.11s	MgO
1.27vs	2.52m	2.01s	Al Ni or NiAl
1.20w*	2.45s		
1.08vs	2.27w	1.49s	MgO
	2.11vs	1.42s	Al Ni or NiAl
	1.75m	1.23w	MgO
	1.68vww		
solid rings	1.64vw	dotted rings (trace)	
	1.49vs		
2.76vw	1.40vw	2.05vww	Ni Al
2.41vw	1.35w	1.78vw	"
1.98vw	1.32vww	1.26s	"
1.40vs	1.22m	1.07m	"
	0.94s	0.81m	"

TABLE 3. Interplanar spacings of the films in Table 2, further annealed at 1000°C for 100s. Same notations as in Table 2.

Ni/Al*	MgO	MgO/Al/Ni
solid ring	dotted rings	semi-solid rings
1.40vs	5.11m	4.68w
	4.33vw	2.88m
	3.90s	2.44s
	3.73m	2.02s
	3.49s	1.66vw
		1.55m
	3.02m	1.43s
	2.79s	
	2.52s	dotted rings (trace)
	2.48m	
	2.27m	5.13w
	2.17s	3.92m
	2.03vw	3.49m
	1.95vw	2.78m
	1.89vw	2.52m
	1.75vs	2.32m
		2.18w
		1.75s

* Due to the fuzziness of the lines, accurate spacings are unavailable and the phases cannot be identified.

TABLE 4. Interplanar spacings of NiAl/Al₂O₃ films annealed at various temperatures. Same notations as in Table 2.

300°C, 5 min	Comments	+800°C, 5 min	Comments	+1000°C, 100s	Comments
<u>dotted lines</u>		<u>dotted lines</u>			
4.85s	Al ₃ Ni ₂	2.88m	NiAl	6.56w	Lines identical to those is a 500Å Al ₂ O ₃ film
3.48s	"	2.04s	"	4.50w	
2.85s	"	1.66w	"	4.03w	
2.44w		1.44m	"	3.28m	
2.00vs	"	1.29vw	"	3.02vw	
1.87s	"	1.18vs	"	2.78s	
1.74s				2.73s	
1.64w		<u>solid lines</u>		2.60m	
1.48w				2.45vs	
1.42s	"	4.50vww	γ-Al ₂ O ₃	2.28s	
1.33vw		2.40m	"	1.98s	
1.27vw		2.28m	"	1.97s	
1.16s	"	1.99m	"	1.62w	
1.15s	"	1.52vw	"	1.50w	
		1.39vs	"	1.41vvs	
		1.14m	"	1.40vvs	

TABLE 5. Interplanar spacings of NiAl/ZrO₂ films annealed at various temperatures. Same notations as in Table 2.

300°C, 5 min Comments		+800°C, 5 min Comments		+1000°C, 100s Comments
<u>solid (*) + dotted lines</u>		<u>dotted lines</u>		
2.91s	t-ZrO ₂	2.90s	t-ZrO ₂	Combination of t and m-ZrO ₂ lines, with no evidence of either aluminides or Al ₂ O ₃ . Many lines overlap those of a 500Å ZrO ₂ film.
2.88w	NiAl	2.55m	"	
2.56mw	ZrO ₂	2.50m	"	
2.53mw	"	2.06vw	"	
2.08vw	"	2.01vvw	"	
2.02s*	NiAl	1.17s	"	
1.80s	ZrO ₂	1.53m	"	
1.65vvw	NiAl	1.51m	"	
1.55m	ZrO ₂	1.45vvw	"	
1.52m	"			
1.17s*	"	<u>solid lines</u>		
		2.69vvw	ZrO	
		2.33vvw	"	
		1.66vvw	"	
		1.40vvw	"	
		<u>dots</u>		
		2.07	Ni ₃ Al	
		1.27	"	

TABLE 6. Experimental d-spacings of films-on-grid after 700°C, 100s RTA; standard patterns with the closest match are listed for comparison.

Ti30Al	AlTi ₃ file 9-98	Comments	Ti50Al	AlTi file 5-678	Ti70Al	TiAl ₂ (ref. 11)	Comments
5.05ms	5.010 ₁₀		4.06w 2.84m	4.070 ₂₀ 2.810 ₂₀	3.96w 2.74vww	3.916 _{7,4} 2.733 _{2,9}	
2.90vww	2.880 ₅	Ti?	2.32vs	2.310 ₁₀₀	2.32vs	2.305 ₁₀₀	
2.53vs	2.500 ₅₀	Ti?	2.01s	1.990 ₈₀	2.01m 1.99m,d 1.99m,c	2.026 _{14,1} 1.984 _{33,5}	Al ₂ O ₃
2.35w	2.320 ₇₀	Ti?	1.81w 1.66w	1.790 ₁₀ 1.650 ₁₀	1.78w	1.770 _{1,1}	
2.23m	2.205 ₁₀₀	Ti?	1.43s 1.41w	1.424 ₈₀ 1.407 ₂₀	1.42s 1.41s,c	1.418 _{16,0}	Al ₂ O ₃
1.91vw	1.886 ₅	?	1.21w 1.16m	1.203 ₈₀ 1.159 ₂₀	1.22s 1.21s	1.217 _{7,3} 1.200 _{21,6}	

Experimental intensity notations: s strong, m medium, w weak, v very, d dotted, c continuous.

TABLE 7. Experimental d-spacings of films-on-grid after 800°C, 100s RTA.

Ti30Al	Comments	Ti50Al	Comments	Ti70Al	Comments
5.05ms		5.03vww 4.06w 2.84m		2.74vww	
2.90vww		2.52vw 2.33vs		2.32vs	
2.52vs		2.22mw 2.05m			
2.22m		1.99m 1.98m,c	Al ₂ O ₃	1.99m 1.98s	Al ₂ O ₃
1.98m.c	Al ₂ O ₃	1.81vww 1.67vww		1.78w	
1.91vw		1.43m		1.43s 1.41s,d 1.41s,c	
1.46m		1.40s,c	Al ₂ O ₃	1.22s 1.21s	Al ₂ O ₃
1.40s.c	Al ₂ O ₃	1.23m 1.21m			
1.26w					
1.24w					
1.22m					

TABLE 8. Experimental d-spacings of polycrystalline phases in films after 900°C, 100s RTA; single-crystal reflections in Ti30Al are not listed.

Ti30Al	Comments	Ti50Al	Comments	Ti70Al	Comments
5.05w		5.05vww		4.09w	
		3.44m		3.44vww	
				2.84m	
2.57s		2.52s			
2.53s		2.40w,c	Al ₂ O ₃	2.40m,c	Al ₂ O ₃
2.41vw					
2.38vw		2.33s		2.33s	
				2.29w,c	Very thin line
2.27s		2.23m		2.23m	
2.23m		1.98c	Al ₂ O ₃	1.99c	Al ₂ O ₃
1.99c	Al ₂ O ₃	1.91vw			
		1.83vw		1.80vww	
1.76m		1.76vww			
		1.73m		1.72vww	
				1.66vw	
1.48s		1.49vww			
1.46m		1.46w		1.44m	
1.40c	Al ₂ O ₃	1.40c	Al ₂ O ₃	1.41c	Al ₂ O ₃
1.37vw		1.34m		1.34w	
1.26w		1.26m			
1.24w		1.24m		1.23m	
1.22m		1.22m		1.22s	
				1.20w,c	Very thin line
				1.15m,c	Very thin line

TABLE 9. Interplanar spacings of films annealed at 660°C for 5 min.

TiAl/Al ₂ O ₃ d (nm)	TiAl/TiB ₂ d (nm)	TiAl/TiC d (nm)
0.409 m ^a	0.323 ^b vww	0.281 vww
0.283 m	0.282 vw	0.259 vww?
0.232 vs	0.249 vw	0.249 ^b s,c
0.205 w	0.231 vs	0.231 s
0.201 w	0.215 vw?	0.227 w
0.198 ^b m,c	0.198 m	0.215 ^b s,c
0.179 w	0.168 vww	0.200 vw
0.166 vw	0.150 ^b w	0.153 ^b s,c
0.143 s	0.141 m	0.143 w
0.139 ^b s,c	0.138 ^b vww	0.139 w
0.134 vww	0.120 ^b w	
0.127 vww		
0.122 m		
0.121 ms		
0.116 w		

^as, Strong; m, medium; w, weak; v, very; c, continuous; ?, unidentified. ^bReinforcement reflection.

TABLE 10. Interplanar spacings of films annealed at 800°C for 5 min.

TiAl/Al ₂ O ₃ <i>d</i> (nm)	TiAl/TiB ₂ <i>d</i> (nm)	TiAl/TiC <i>d</i> (nm)
0.505 vw ^a	0.263 m	0.264 vvw
0.343 m	0.250 s	0.250 vs
0.290 vvw	0.216 s	0.229 vvw
0.274 w,c?	0.204 m,d	0.215 s
0.251 s	0.153 vs	0.153 vs
0.239 ^b m,c	0.140 w	0.131 m
0.236 s	0.131 vw	0.125 mw
0.227 m,c?	0.125 vw	0.099 mw
0.222 s	0.122 vw,d	0.097 m
0.198 ^b s,c	0.104 vw	
0.190 vvw	0.096 w	
0.182 vw		
0.175 vvw		
0.171 s		
0.148 w		
0.145 m		
0.140 ^b vs,c		
0.136 vw		
0.132 s		
0.125 m		
0.123 m		

^aNotation as in Table II except d, diffuse and ^bγ-Al₂O₃.