not only to analyze quantitatively the chemical composition of the γ'-free zone and the Al-rich phase by scanning transmission electron microscopy–energy dispersive X-ray analysis, but also to identify the crystal structure of Al-rich phase by X-ray diffraction. Furthermore, it is also necessary to evaluate quantitatively the decrease in the grain-boundary carbides and the increase in the Al-rich phases.

It is very important to emphasize that these microstructural changes at and near grain boundaries (a) + (b) + (c) are not observed in thermal-aged materials at 900 °C for 2214 hours. This suggests that stress plays an important role in Reactions [1] and [2]. As described previously, the changes in grain boundary microstructures can be favorable sites for fracture initiation. The Al-rich phase (for example, Al nitride) can be one of the most favorable sites of crack initiation, and also the γ'-free zone (grain-boundary γ matrix) can provide a preferential site for crack propagation. Therefore, in order to evaluate the creep damage accumulation in CM247LC, it is very important and can be critical to detect the microstructural changes including Al-rich phase.

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Nitridation of Ti-Al Alloys: A Thermodynamic Approach

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In the framework of the joint European action COST 507 (Development of a database for light alloys), an extensive thermodynamic assessment of the Ti-Al-N phase equilibria has been accomplished.[1] The purpose of this article is to demonstrate the application of that thermodynamic model to the nitridation of Ti-Al alloys. Figure 1 shows the calculated conventional ternary phase diagram and the corresponding stability diagram in terms of the nitrogen pressure, P_{N2}.

It is remarkable that TiAl$_3$, dissolving only very little N, can withstand the highest P_{N2} (1.58×10^{-14} bar) before transformation to the nitrides AlN + δ occurs, where $\delta =$ TiN$_{1-x}$. On the other hand, αTi, showing the highest nitrogen solubility of the metal phases in the ternary system, is getting nitrided at the lowest values of P_{N2}, either to the binary nitride ε-Ti$_2$N or to the ternary phase τ_1, depending on its Ti/Al ratio. The nitridation limit of the intermetallic phase γ(TiAl) depends strongly on its composition, being highest at 41.1 at pct Ti with $P_{N2} = 1.8 \times 10^{-15}$ bar and more than four orders of magnitude higher than that at the Ti-rich end 51.4 at pct Ti.

The formation of τ_1 is very sluggish at 1000 °C.[2] For real-time process applications, it is therefore useful to perform a metastable phase equilibrium calculation by suppressing the existence of τ_1. The result is shown in Figure 2. The metastable extension of those phase fields which previously had been saturated with τ_1 is most obvious for α and α_2, but also for γ at the Ti-rich end between 5.85×10^{-20} and 4.07×10^{-17} bar. Under these kinetically favorable conditions, virtually all compositions of γ are initially precipitating the ternary nitride τ_2. Further nitridation yields TiAl$_2$ + τ_2 and finally AlN + δ is obtained, as for all the other Ti-Al starting compositions.

The reactions observed during *in situ* processing of TiAl-''Ti$_2$AlN'' composites[3] are the first example of a quantitative application of our thermodynamic modeling. A powder mixture of Ti-Al (50 at. pct each) in a closed silica tube filled with nitrogen was inserted into a furnace at 1000 °C for 1 minute, where the combustion reaction produced γ(TiAl) + τ_2(Ti$_2$AlN$_{0.82}$) and a small amount of TiAl$_3$. The peak temperature was about 2000 °C, as opposed to the combustion in an evacuated tube (1500 °C), yielding γ with a small amount of TiAl$_3$ only.

These observations can be compared to the results from our thermodynamic calculations given in Table I. As starting material, a mixture of 1 mol Ti + 1 mol Al is selected, which is preheated to T_{start}. The two values of 700 °C and 800 °C cover the range observed as ignition temperatures.[3] In vacuum, the exothermic reaction under adiabatic conditions results in peak temperatures, T_{final}, of 1490 °C to 1500 °C. This narrow range, in spite of the 100 °C difference in T_{start}, is due to the two-phase $L + (\alpha$Ti$)$ reaction products and the varying amount of liquid, L. This is in excellent agreement with the observed[3] peak temperature of 1500 °C. After cooling to T_{start}, the equilibrium product is stoichiometric γ(TiAl).

In the presence of nitrogen, the reaction is much more exothermic, due to the formation of the ternary nitride τ_2. The total nitrogen amount (0.08 mol N$_2$) added to the same metal amount has been selected in order to reduce the amount of the intermetallic γ phase down to 70 pct (from 2.0 down to 1.41 mol of atoms), at the expense of the additionally formed τ_2 nitride. This selection complies with the actual samples in Reference 3, where 70 ± 10 pct γ phase was formed. Under these conditions, the calculated peak temperature is 1872 °C to 1949 °C. This is in reasonable agreement with the about 2000 °C observed with an ignition temperature of about 800 °C.[3]

It is interesting to note in Table I that at peak temperature, only L + (βTi) but no nitride is formed under nitrogen. Virtually all the nitrogen is dissolved ($\sim$10 at. pct N) in (βTi). After cooling to 700 °C to 800 °C, the two-phase equilibrium structure $\gamma + \tau_2$ is obtained, where the excess aluminum is dissolved in γ phase (57 at. pct Al + 43 at.

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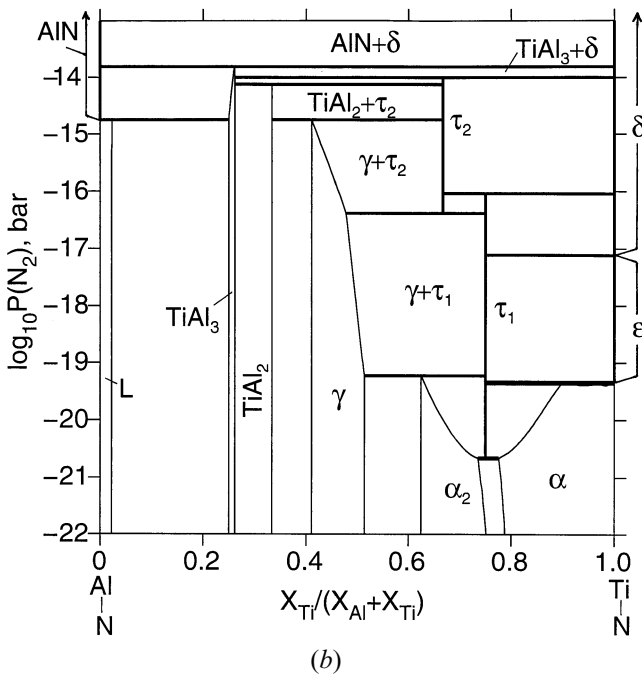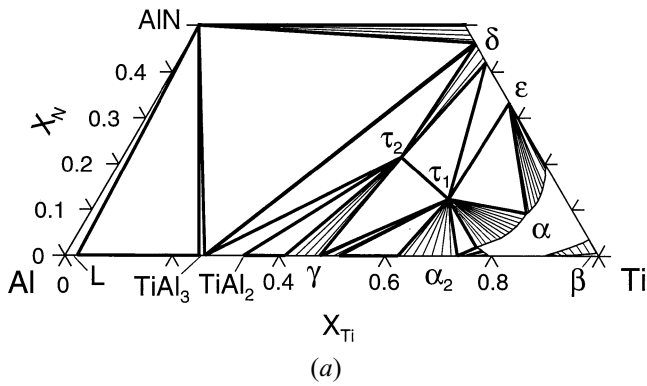Manuscript received April 25, 1997.

Fig. 1—Calculated Ti-Al-N (*a*) phase diagram and (*b*) stability diagram with stable equilibria at 1000 °C; $\tau_1 = Ti_3AlN_{0.56}$, and $\tau_2 = Ti_2AlN_{0.82}$.
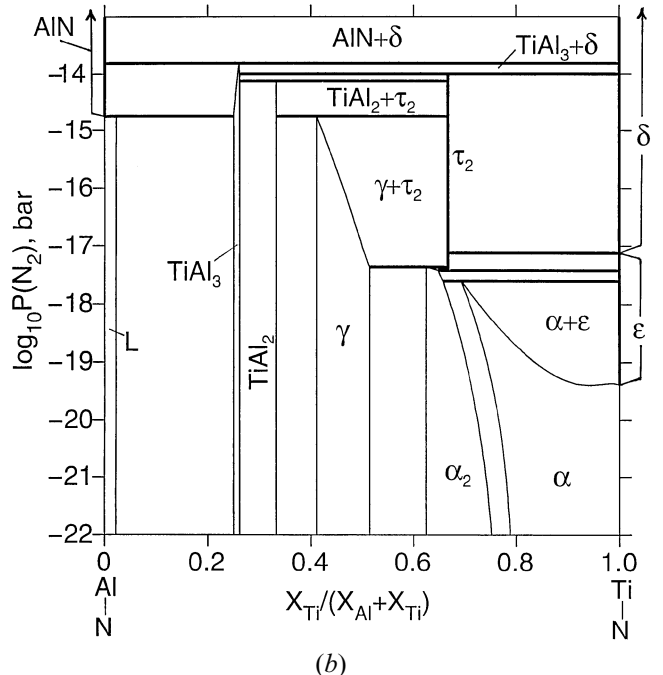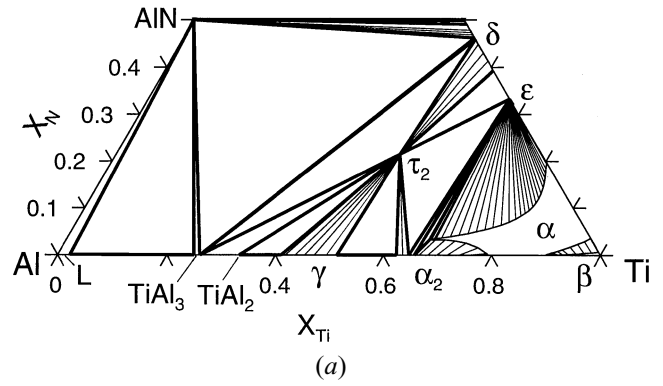
Fig. 2—Calculated Ti-Al-N (*a*) metastable phase diagram and (*b*) stability diagram at 1000 °C with τ_1 suspended in calculation.

pct Ti). This example demonstrates that a detailed understanding of the complex reaction processes is gained based on the thermodynamic calculation, covering the phase formation and the heat balance.

Further processing by arc melting of the as-reacted samples under argon did not change the phase assembly,[3] which is consistent with the solidification path that can be calculated for such an alloy using our thermodynamic model. It is also consistent with the fact that the samples must have been already partly molten at peak temperature. After homogenization of these as-cast samples for 2 days at 1150 °C in vacuum, the TiAl$_3$ phase vanished, leaving finely distributed τ_2 precipitates in a TiAl matrix. It is evident from Figure 2(b) that the majority phase mixture $\gamma + \tau_2$ in the sample defined its own P_{N2} value in the range from 1.73×10^{-15} to 4.39×10^{-18} bar at 1000 °C. At 1150 °C, the P_{N2} values are shifted to somewhat higher values. The minority (nonequilibrium) phase TiAl$_3$ is not forming any nitride in that environment. This results in a very simple dissolution path, involving only the intermetallic phases TiAl$_3$, TiAl$_2$, and γ-TiAl (at 1150 °C, there is an additional phase Ti$_2$Al$_5$). After complete dissolution, the composite $\gamma + \tau_2$ is formed, as observed by Mabuchi *et al.*[3] If this

process were performed by external control of P_{N2}, the limits given in Figure 2 could be observed.

The next example is given by the nitridation of the powdered intermetallic compound TiAl$_3$ at 600 °C and 1200 °C in flowing nitrogen or NH$_3$. This results initially in some nitrogen uptake, without observation of new phases,[4] possibly due to some solubility. Eventually, the nitrides TiN (first) and AlN (second) are formed. No other nitrides could be detected, and this direct phase transformation from TiAl$_3$ to (δ-TiN + AlN) is in perfect agreement with both Figures 1 and 2.

Mixed coatings of TiAl$_3$ + TiN on titanium were prepared to improve both the oxidation resistance (with TiAl$_3$) and the hardness (with TiN).[5,6] Two different processing routes were studied, nitridation after aluminization and *vice versa*. One set of Ti samples (labeled "Ti-Al-N") was first treated by fluoride activated pack aluminization at 850 °C for 5 hours, resulting in a 30-μm-thick TiAl$_3$ layer on titanium. Upon subsequent nitridation in N$_2$ at 850 °C for 5 hours, some 10 mol pct TiN were formed in the outer layer of TiAl$_3$, about 5-μm deep. Traces of AlN were only found after nitriding at 900 °C. A second set of Ti samples ("Ti-N-Al") was first nitrided at 850 °C for 5 hours resulting in a 2-μm TiN layer and a gradient of dissolved nitrogen in

Table I. Thermodynamic Modeling Results (Stable Equilibria) of Isothermal or Adiabatic Reactions of (1 Mol Ti + 1 Mol Al), in Vacuum and under Nitrogen

T_{start} (°C)/Atmosphere	$\Delta_{rxn}H$ at T_{start} (kJ)	Equilibrium Phases at T_{start} (Mol Atoms)	T_{final} (Adiabatic) (°C)	Equilibrium Phases at T_{final} (Mol Atoms)
700 / vacuum	−89	2.0 γ	1490	1.16 L + 0.84 (αTi)
800 / vacuum	−88	2.0 γ	1500	1.53 L + 0.47 (αTi)
700 / +0.08 mol N_2	−144	1.41 γ + 0.75τ_2	1872	0.61 L + 1.55 (βTi)
800 / +0.08 mol N_2	−143	1.41 γ + 0.75τ_2	1949	0.68 L + 1.48 (βTi)

the Ti-base metal. Upon subsequent aluminization at 800 °C for 5 hours, the outer layer was converted to TiN + AlN + TiAl₃, with the TiAl₃ extending to a depth of some 20 μm.

The results of Kabbaj et al.[5,6] can be very clearly understood based on the present ternary phase equilibrium and stability diagrams. When nitriding the ''Ti-Al-N'' samples, we start with a saturated (Ti-rich) TiAl₃ layer and—upon increasing P_{N2}—enter first the narrow TiAl₃ + δ phase field in Figure 2(b). This results in the observed δ(TiN$_{1-x}$) precipitation; the released aluminum can easily diffuse toward the Ti base in view of the very high diffusivity of Al in TiAl₃.[7] Eventually, the conditions of the AlN + δ + TiAl₃ three-phase field in Figure 2(b) may be locally obtained in the outer layer, producing the observed AlN traces at higher temperature. It should be noted that we have quantitatively calculated the respective diagrams at all relevant temperatures (not shown here) but refer in this discussion to the qualitatively similar 1000 °C section.

In the second set of samples (''Ti-N-Al''), we start with a δ(TiN$_{1-x}$) layer and—upon addition of Al—clearly enter the three-phase field AlN + δ + TiAl₃ in Figure 2(a). Any nitrogen ''released'' by this reaction will be directly converted to AlN. Eventually, aluminum will shortcut diffuse through the TiAl₃ in this three-phase mixture to form more TiAl₃ directly with the Ti-base metal. This results exactly in the observed microstructure.

These coatings are not thermodynamically stable because of the nonequilibrium TiAl₃/Ti interface. In fact, TiAl₃ completely disappeared after annealing at 900 °C for 30 hours due to the reaction with Ti, and beyond this point, the oxidation resistance is distinctly reduced.[6] Already after 8 hours at 900 °C, the TiN and AlN phases were consumed, in association with the formation of ''Ti₂AlN'' (τ_2).[6] The underlying reactions can be clearly interpreted using Figure 2. The reaction of TiAl₃ with Ti results in the formation of the subaluminides TiAl₂, γ, and α_2, and all three of them are in equilibrium with the ternary nitride τ_2 (metastable equilibrium for α_2). Following this cascade from TiAl₃(+AlN + δ) toward the broad αTi field, the first phase to vanish is AlN when the TiAl₃ + δ equilibrium is locally established at the outer layer. Second, δ(TiN$_{1-x}$) will be consumed in the three-phase reaction TiAl₃ + δ → τ_2, leaving TiAl₃ + τ_2 in the outer layer, just as observed. Eventually, the TiAl₃ layer would be entirely consumed. The relatively small amounts of Al and N introduced in the initial coatings can be easily accommodated in solid solution in αTi in a final stage (refer to Figure 2 or 1).

In summary, it should be emphasized that once the thermodynamically calculated phase and stability diagrams are established, all the complex ternary interactions are much simpler and more accurately understood compared to a treatment using a collection of single chemical reaction equations. This is because the inter-relation of all possible chemical reactions and also the solubilities have already been taken care of in the process of thermodynamic modeling and phase diagram calculation. Suitable conditions for local equilibria can be easily identified in a wide temperature, composition, and activity range using thermodynamic modeling of stable and metastable equilibria. This could be of practical interest for optimizing the processing of these promising materials.

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Wear Behavior of As-Cast ZnAl27/SiC Particulate Metal-Matrix Composites under Lubricated Sliding Condition

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Metal matrix composites (MMCs) have attracted considerable attention recently because of their potential advantages over monolithic alloys. The MMCs are commonly

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