

## 利用表面改質以改善鈦鋁介金屬之高溫氧化抵抗

# OXIDATION RESISTANCE IMPROVEMENT OF TiAl INTERMETALLICS USING SURFACE MODIFICATION

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### 摘要

鈦鋁介金屬為最具應用潛力的高溫結構用材料，然而在 750°C 以上它的氧化抵抗能力變差，使它的很多工程應用受到了限制。本文就  $\gamma$ -鈦鋁介金屬在高溫下之氧化行為，氧化動力學及氧化機構等作一文獻的回顧及整理，同時也就  $\gamma$ -鈦鋁介金屬能有效改善其高溫耐氧化性的表面改質方法作一深入的文獻探討。

**關鍵詞：**鈦鋁介金屬、高溫氧化抵抗、表面改質。

### Abstract

TiAl intermetallics are one of the most promising structural alloys used at high temperature. However, the poor oxidation resistance at temperature above 750°C has hindered their practical engineering applications. In this paper, we review the oxidation behavior, kinetics and mechanism of TiAl alloys. The reported feasible surface modification methods to improve the high temperature oxidation resistance of TiAl alloys are also reviewed.

**Keywords:** TiAl intermetallics, high temperature oxidation resistance, surface modification.

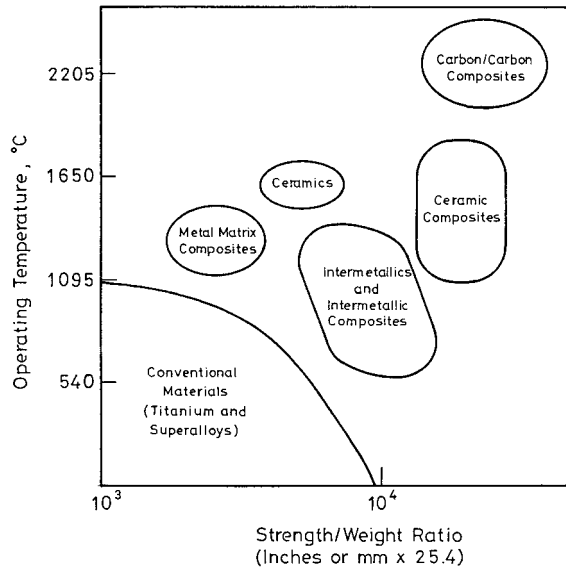
## 1. INTRODUCTION

The chemical bonding of ordered intermetallic compounds is tighter than that in the pure components of which they are formed, and hence they tend to have higher elastic stiffnesses and melting temperatures [1]. For intermetallics with low density, the beneficial structure-insensitive properties (high melting point and low density) imply that an intermetallic is a promising candidate for use in advanced structural applications, such as aircraft systems, or in any high-temperature moving parts, such as turbochargers for passenger vehicle diesel engines [2,3]. Figure 1 shows the operational temperature and specific strength of intermetallics among some states of the art materials [4].

As indicated in Fig. 1, intermetallic compounds exhibit more excellent properties than conventional alloys. Low density materials are particularly important since they are used in advanced aerofoil designs to reduce the structural weight of all other

engine components designed to support the load of a rotating blade set. The operation efficiency of gas turbine engines is strongly dependent on the operating temperature and even a small increase in temperature results in a significant increase in the overall efficiency. In addition, materials performed at higher temperatures may require less cooling air; this also serves to improve the efficiency [5].

Moreover, intermetallics often have higher thermal conductivities, which lead to higher cooling efficiency and lower thermal stresses (an often overlooked advantage) than ceramics and ceramic composites. Some intermetallic alloys (the titanium and nickel aluminides) can be processed using conventional metallurgical methods — a factor which is necessary for these materials to be economically competitive with the state of the art materials [5]. That is, the cost of facilities and personnel training will be lower than those for manufacturing and/or processing carbon-carbon or metal-matrix composites.

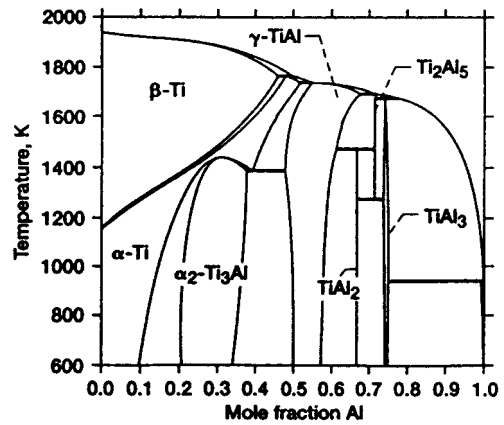


**Fig. 1 The specific strength and operation temperature of contemporary high-temperature materials [4]**

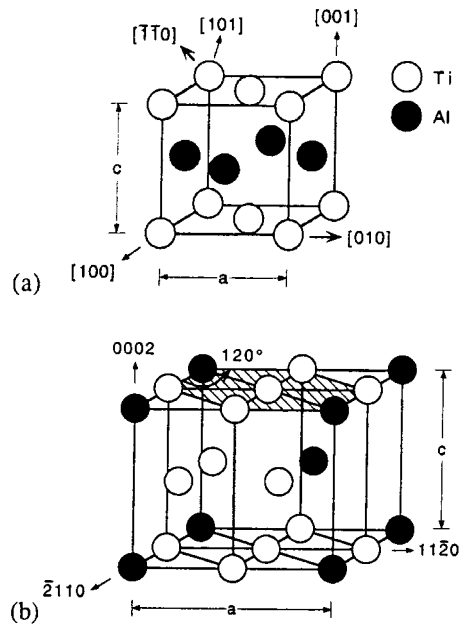
Among a wide variety of intermetallic compounds, most contemporary researches on high temperature structure materials have been focused on Ti-Al, Ni-Al, Fe-Al, silicide intermetallic, berillurumide, chromide intermetallic and other aluminide intermetallics [6-9]. Due to the early success of the experimental development of  $Ti_3Al$  [10], Ti-Al intermetallic always draws much attention. The new and widely accepted binary phase diagrams of the Ti-Al system is shown in Fig. 2 [11]. There are four binary intermetallic compounds of interest in the Ti-Al system:  $Ti_3Al(\alpha_2)$ ,  $TiAl(\gamma)$ ,  $TiAl_2$ , and  $TiAl_3$ . From the point of view of structural-insensitive property (the ratio of melting point to density),  $TiAl(\gamma)$ -based intermetallics are most promising among these titanium aluminides [1].

The  $\gamma$ -TiAl phase has the  $L1_0$  ordered face-centered tetragonal structure as shown in Fig. 3(a). The crystal structure of the hexagonal  $\alpha_2$ - $Ti_3Al$  is  $DO_{19}$ , as shown in Fig. 3(b). At the equiatomic TiAl composition, the  $c/a$  ratio is 1.02 and the tetragonality increases up to  $c/a = 1.03$  with increasing aluminum concentration [12]. The  $\gamma$ -TiAl phase remains ordered up to its melting point of about 1,450°C [13].

As is evident from Table 1 [5], TiAl alloys exhibit a significant density advantage over the currently used nickel and titanium based alloys and have a high potential for replacing some nickel based alloys at temperatures up to 900°C. Moreover, excellent high-temperature specific strength (Fig. 4(a)), high specific modulus retention (Fig 4(b)) [14-16], relatively high burn resistance (self-ignite) [17], high resistance to hydrogen absorption in the turbine-engine compressor



**Fig. 2 Ti-Al phase diagram [11]**

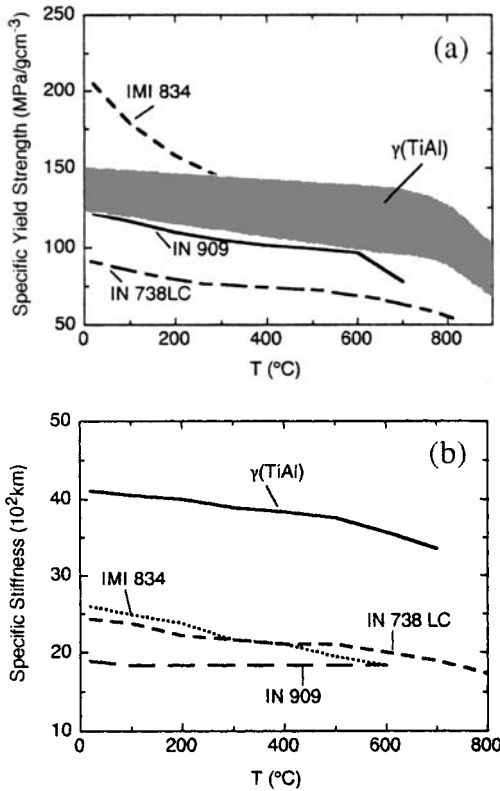


**Fig. 3 Atomic arrangement (a) in the ordered face-centered tetragonal (fct)  $L1_0$  structure of  $\gamma(TiAl)$  and (b) in the ordered hexagonal  $DO_{19}$  structure of  $\alpha_2-Ti_3Al$**

**Table 1 Selected properties of various conventional and intermetallic materials for turbine engine applications [5]**

	Density, $gcm^{-3}$	Elastic modulus, $GNm^{-2}$	Room temp. fracture toughness, $MNm^{-3/2}$	Tensile creep limit, °C	Oxidation limit, °C
Titanium base	4.5	110	35 ~ 60	600	600
Nickel base*	8.3	125	30 ~ 35	1100	> 1100
$\alpha_2-Ti_3Al$	4.3	145	25	800	650
$\gamma-TiAl$	3.8	176	25	650	900
NiAl eutectic	5.9	193	12 ~ 15	1100	-
MoSi <sub>2</sub>	6.5	379	4 ~ 5	-	> 1700
Nb-10 at% Si	7.5	145	25	-	~ 400

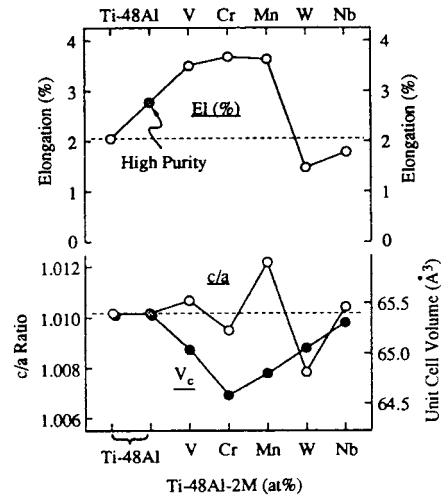
\*Single crystal alloy, <001> orientation.



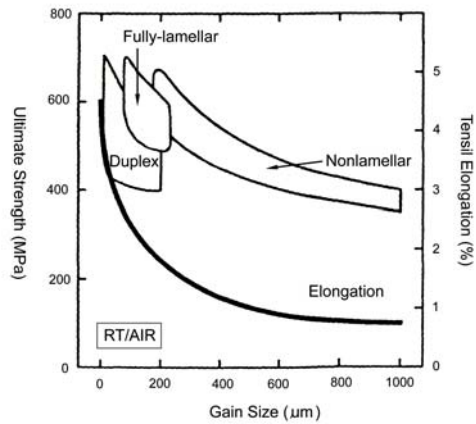
**Fig. 4** Variation of the specific yield strength (a), and the specific stiffness (b) with temperature of typical two-phase  $\gamma$  alloys in comparison with a low expansion iron based alloy (IN 909), a nickel based super alloy (IN 738 LC), and a conventional titanium alloy (IMI 834) [14]

application [16] (in contrast to Ti<sub>3</sub>Al) and excellent creep properties [18] make TiAl alloys a viable material for use in advanced structural applications, such as aircraft systems [19], high-temperature moving parts [20], and advanced transport systems such including planes and next generation engines [5].

However, the room temperature brittleness and poor oxidation resistance at temperature above 750°C have posed a bottleneck for its practical applications for years [5,18]. As a result of extensive research activity, several alloy designs based on Ti-(47-48) at.% Al (Fig. 5) and/or microstructural control through thermo-mechanical process (Fig. 6) can improve the strength and increase the tensile ductility at room temperature up to a desired level of about 3-4% [9,15,17,21~25]. Several possible factors or mechanisms have been suggested to explain the enhanced ductility of Ti-48at%Al: (a) the tetragonality decrease, (b) the decrease in twin energy, (c) the  $\alpha_2/\gamma$  lamellar structure, and (d) the scavenging (N or O) effect of  $\alpha_2$  phase, as summarized in Ref. [16].



**Fig. 5** The best elongatin reported to date, *cla* ratio, and unit cell volume (*Vc*) for Ti-48Al and Ti-48Al-M (M = V, Cr, Mn, W or Nb) alloys. The oxygen contents of all alloys range from 800 ~ 1000ppm; however, data for a very- high-purity (300ppm oxygen) Ti-48Al is shown for comparison [16]



**Fig.6** Relationships between RT tensile properties and microstructure/grain in gamma alloys [18]

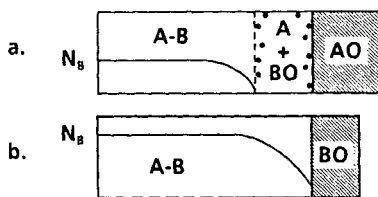
## 2. OXIDATION BEHAVIOR OF $\gamma$ -TiAl ALLOYS

Due to poor oxidation resistance, although the diffusivity of oxygen ( $4 \times 10^{-19}$  m<sup>2</sup>/s at 900°C) in TiAl is five orders of magnitude less than that in Ti [26], for making  $\gamma$ -TiAl alloys much more oxidation resistant than titanium alloys, the oxidation resistance is still a critical factor for  $\gamma$ -TiAl to be used at high temperatures (above 800°C) for a long time, especially under cyclic thermal conditions [27].

The development of oxidation resistance in alloys is based on the constitutive and/or additive elements which will oxidize selectively and produce a protective surface oxide. For a binary Ti-Al alloy, the products of oxidation of constitutive elements (Ti and Al) are rutile titania ( $\text{TiO}_2$ ) and  $\alpha$ -alumina ( $\text{Al}_2\text{O}_3$ ). Compared with alumina, titania has high diffusivity and poor protectiveness [28]. However, similar activities of Ti and Al result in the formation of titania and alumina simultaneously [29]. This results in inadequate oxidation resistance of the  $\gamma$ -TiAl alloy. Therefore the formation of an alumina scale or at least a continuous alumina layer in the scale is prerequisite for attaining sufficient oxidation resistance for  $\gamma$ -TiAl. The critical concentration for the transition from internal oxidation to external oxidation is needed for the formation of its oxide as a continuous external layer rather than as an internal precipitate, as schematically shown in Fig. 7 [30~33]. The critical solution concentration has been expressed by Wagner as [34]:

$$N_{\text{Al}}^* = \left( \frac{\pi g^* N_0 D_0 V_{\text{TiAl}}}{2 D_{\text{Al}} V_{\text{Al}_2\text{O}_3}} \right)^{1/2} \quad (1)$$

Here  $N_0 D_0$  is the oxygen permeability in TiAl,  $D_{\text{Al}}$  is the solute diffusivity,  $g^*$  is a factor determined by the volume fraction of oxide required for the transition (often near 0.3), and  $V_{\text{TiAl}}$  and  $V_{\text{Al}_2\text{O}_3}$  are the molar volumes of the alloys and oxide, respectively. For TiAl alloy, the Al content required for external scale formation seems to increase upon increasing the solubility and diffusivity of oxygen and decrease with an increase in the solute (Al) diffusivity in the alloy [31]. The critical Al concentration needed can also decrease or eliminate transient oxidation [35], which will result in the formation of undesired  $\text{TiO}_2$  crystal in the  $\gamma$ -TiAl alloy.



**Fig. 7 The effect of solute content on the transition from internal to external oxidation when the oxides of both elements can form. (a) Schematic diagram of the cross-section when  $N_B$  is less than the critical value showing internal oxidation of B under an external scale of AO. (b) Schematic diagram of the cross-section when  $N_B$  exceeds the critical value and results in the formation of external BO to the exclusion of AO [29]**

A higher concentration of Al is needed to achieve a protective alumina scale. Rahmel and Specer [29] showed by thermodynamical calculation that for titanium aluminides containing about 50 at% aluminium or less, titanium rather than aluminum oxide was the stable phase. Other studies [36~38] showed that approximately 60 ~ 70% of aluminum is needed for binary Ti-Al alloys to form a continuous  $\text{Al}_2\text{O}_3$  scale in air, while only about 47 ~ 49% of aluminum is needed in pure oxygen. However, the increase of aluminium concentration is technologically not desired for loss of ductility by the formation of brittle  $\text{TiAl}_3$  [39].

### 3. OXIDATION KINETICS OF $\gamma$ -TiAl ALLOY

In addition to the above thermodynamic consideration, the oxidation behavior of TiAl alloy is also governed by the kinetics. Since the oxide reaction product is generally retained on the metal surface, the rate of oxidation is usually measured and expressed as the weight gain per unit area. The various empirical rate laws sometimes observed during the oxidation of various metals under different conditions are illustrated in Fig. 8 [40], in which a plot of weight gain per unit area versus time is shown. The simplest empirical relationship is the linear one:

$$W = k_L \cdot t \quad (2)$$

where  $W$  is the weight gain per unit area,  $t$  is the time and  $k_L$  is the linear rate constant. Linear oxidation is the characteristic of metals for which a porous or cracked scale is formed so that the scale does not represent a diffusion barrier between the two reactants [40].

In 1933, Wagner showed that the ideal ionic diffusion-controlled oxidation of pure metals should follow a parabolic oxidation rate law,

$$(\Delta W)^2 = k_p \cdot t = k_0 \cdot e^{-Q_{\text{eff}}/RT} \cdot t \quad (3)$$

where  $\Delta W$  is the weight gain per unit initial surface area,  $k_p$  is the parabolic rate constant,  $t$  is the oxidation time,  $Q_{\text{eff}}$  is the activation energy,  $R$  is the gas constant, and  $T$  is the oxidation temperature in degree Kelvin.  $k_0$  is related to the pre-exponential factor of the effective diffusion coefficient and to the density of the scale [41].

In practical experiments, the oxidation mechanism is not unique and unchange during the course of oxidation. Sometimes, more than one factor or mechanism can simultaneously contribute to the oxidation kinetics, i.e., the rate-determining step of oxidation may shift with the passage of time toward a process involving larger activation energy [42].

For Ti-Al alloys, the dependence of the activation energy for oxidation on aluminum concentration (Fig. 9) shows a lack of protection by small aluminum concentrations when the concentration is increased above 25 atom percent [28]. For aluminum concentrations between zero and 25 atom percent the activation energy of oxidation falls below that of oxygen diffusion in titanium. This is consistent with the mass transport along fast diffusion paths and with the doping effect (the Wagner-Hauffe rule, or the valence-control rule [43]). At high aluminum concentrations (over 25 atom percent) the activation energy of oxidation is the intermediate between those of oxygen diffusion in rutile and alumina, and reflects the formation of a distinct alumina sublayer in the oxide scale.

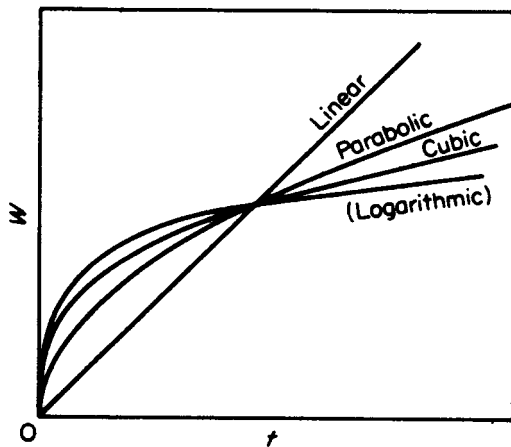


Fig. 8 Oxidation rate law [38]

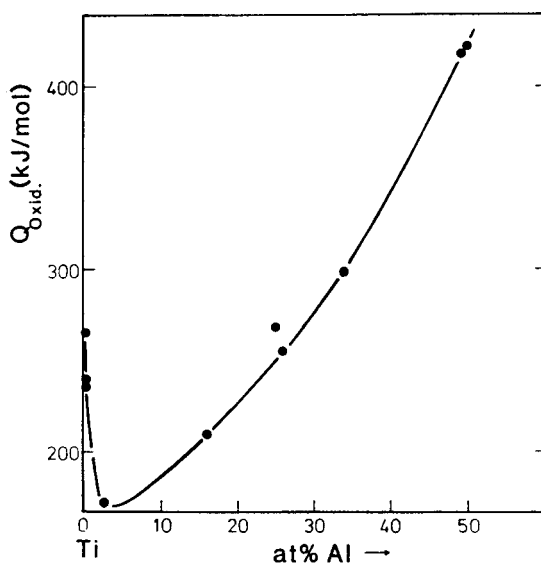


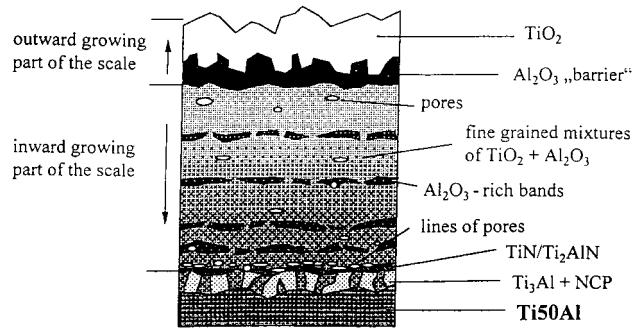
Fig. 9 Activation energies of oxidation of Ti-Al alloy [27]

#### 4. OXIDATION MECHANISM OF $\gamma$ -TiAl ALLOY

The initial step in the oxidation process is the dissociative chemisorption of oxygen molecule at the gas-solid interface to produce adsorbed atomic oxygen [44]. For  $\gamma$ -TiAl alloy, adsorption from the gas phase appears to occur through an adsorbed molecular state with dissociation occurring via the titanium surface atoms [45]. The initial oxide overlayer has an estimated thickness of 0.45–0.55nm. Neither metallic species nor any complete oxides, such as  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ , are detected in the overlayer [45]. However, the oxide scale contains oxides of both Ti and Al [46,47]. Further oxide growth that occurs during heating and the depletion of oxygen cause the local potentials of  $\text{O}_2$  and  $\text{N}_2$  to form TiN at the alloy/oxide interface and prevent the alumina from developing continuity. The presence of nitrogen when  $\gamma$ -TiAl is oxidized in air results in the formation of intermixed TiN and  $\text{Al}_2\text{O}_3$  on the alloy surface [48]. The presence of nitrides disrupts the continuity of the alumina and allows the development of an oxide morphology with continuous layer of  $\text{TiO}_2$  through which Ti, Al, and O are all rapidly transported [49]. The titanium nitrides ( $\text{TiN}$  and  $\text{Ti}_2\text{AlN}$ ) are oxidized essentially at the same rate as Ti [17,50,51] and, thus, do not alter the growth rate of the continuous Ti oxides. At the interface of TiAl matrix and oxide scale, an Al-depleted layer is formed. The microstructure of the Al-depleted layer, which consists of two phases ( $\alpha_2$  and new cubic phase) [52], will be elaborated and reviewed in the next section.

The preferential growth of rutile is responsible for the initial kinetics [52]. During the very initial stages of oxidation, the direction of oxidation is both inward and outward. With the progress of oxidation, however, the main growth direction becomes inward. The initial growth of rutile crystals almost follows the direction normal to the specimen surface followed by their subsequent lateral growth. Large voids are developed near the interface between the outer and inner oxide layers [53].

The main features of the oxide scales on Ti-50Al after longer oxidation time are shown in Fig. 10 [54]. The outermost partial layer is more or less pure  $\text{TiO}_2$ , followed by a band of  $\text{Al}_2\text{O}_3$ , and then by a layered structure with  $\text{Al}_2\text{O}_3$  enriched in a fine  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  mixture. Further down in the scales, the number of  $\text{Al}_2\text{O}_3$  phases dominates and exceeds the amount of  $\text{TiO}_2$ . However, with the exception of the rather thick outer  $\text{Al}_2\text{O}_3$  band, there is no continuous  $\text{Al}_2\text{O}_3$  partial layer in the inner part of the scales.



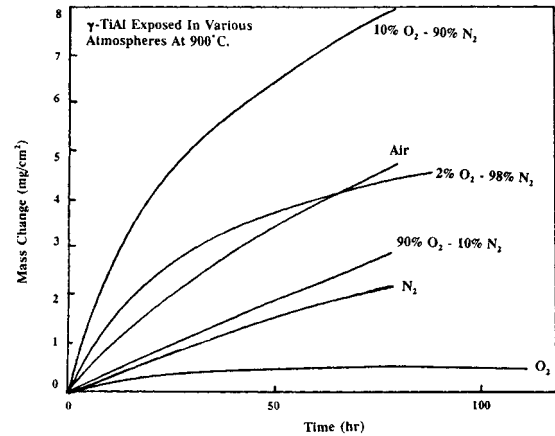
**Fig. 10 Schematic representation of the scale structure on Ti-50Al after oxidation in air at 900°C before breakaway [54]**

From the viewpoint of oxidation kinetics, three stages are generally recognized in the oxidation of an alloy: an incipient or “transient” stage characterized by the simultaneous formation of the oxides of every active component; a “steady state” stage coinciding with the development of a protective film and being governed by the continued growth of this continuous layer; and finally an ensuingly accelerated attack or “breakaway” stage [55].

The isothermal oxidation kinetics of  $Ti_{50}Al_{50}$  below 800°C follows the parabolic law [56] and the apparent activation energy is  $408 \text{ kJmol}^{-1}$ , which is between the value for oxygen diffusion in  $TiO_2$  and  $Al_2O_3$  [28]. For longer oxidation, a change in the oxidation kinetics occurs which is approximately parabolic in the beginning and becomes linear in the later stage (we would like to call this to be ‘breakaway’ as is often used in the Zr oxidation) [52,54,57]. The alumina band layer in the oxide scale is continuous before breakaway occurs and is interrupted afterwards [53,54,58].

After the “breakaway”, the intermixed, rather than layered nature of the reaction product implies poor protection against the diffusion of oxidizing species. The oxidation of TiAl alloy can be alleviated by changing the atmosphere from air to Ar/O<sub>2</sub> [59]. It reveals that a continuous supply of nitrogen from the atmosphere is required to maintain the accelerated kinetics, and mixed oxide layers are permeable to nitrogen. Moreover, the same conclusion can also be made from the fact that the amount of nitrogen detected at the metal-scale interface increased with the oxidation time [51].

Presence of nitrogen in the atmosphere is also found to significantly decrease the “incubation period” until the breakaway of the initially formed alumina scale and enhance the growth rate of the mixed  $TiO_2/Al_2O_3$ -scale [57,59]. The rate of oxidation increases continuously upon increasing the amounts of nitrogen in pure oxygen, as illustrated in Fig. 11 [60]. In addition to the detrimental nitrogen effect, the presence of



**Fig. 11 Oxidation rates for  $\gamma$ -TiAl at 900°C in various O<sub>2</sub>-N<sub>2</sub> atmospheres [59]**

sodium chloride on TiAl also accelerates the oxidation of TiAl [61]. However, a contradictory result has also been reported, in which the cover of halogen compounds, including NaCl, MnCl<sub>2</sub> and ZnF<sub>2</sub> on TiAl alleviated the oxidation in air [62].

## 5. Z-PHASE

Due to a net Al-consumption during the oxidation of titanium aluminide in oxygen or air, the Al-depleted layer beneath the oxide scale can be found. For the  $\gamma$ -TiAl, the Al-depleted layer beneath the oxide scale is formed during oxidation in oxygen or air. Dowling *et al.* found a new phase with a Ti:Al ratio of 2:1 in the Al-depleted layer, which results in the loss of tensile ductility at room temperature [63]. Beye *et al.* claimed that there are two phases in the Al-depleted layer, identified as  $Ti_{10}Al_6O$  and  $Ti_{10}Al_6O_2$  [64]. Their subsequent study indicated a new phase with composition  $Ti_3Al_2O_3$  in this layer [65]. However, recent studies favored that there are two phases in the Al-depleted layer, one is an oxygen-interstitial solid solution of  $\alpha_2$ -Ti<sub>3</sub>Al(O) and the other is a new cubic phase (Z-phase) of  $Ti_5Al_3O_2$  [52,59,66~68] with the space group of P432 or P4<sub>3</sub>2 [51,59,69,70]. A very recent study of Copland *et al.* reported that the Z-phase has a very limited composition range [71], indicating that Z-phase is prone to be stoichiometric. However, Dettenwanger *et al.* found the oxygen content of Z-phase seemingly increased by increasing the oxygen concentration in oxidizing atmosphere [72]. Moreover, Abe *et al.* considered the Z-phase as a solid solution of oxygen in the Z-like phase in the Ti-Al system according to the observation of metastable Z-like phase during the early stage of crystallization of magnetron-sputtered Ti-48Al amorphous film [73]. Hence, the characteristic of the Z-phase is still controversial.

## 6. SURFACE FINISH EFFECT

In addition to the above-mentioned variables such as composition, microstructure, oxidizing temperature and oxidizing atmosphere, the surface finish will also influence the oxidation behavior of binary  $\gamma$ -titanium aluminate. Choudhury *et al.* studied the oxidation of Ti-50Al in air and oxygen at temperatures between 1073 and 1473K [60]. They found that the oxidation of cast TiAl in oxygen depended on surface preparation. Polished specimens (1 $\mu$  diamond paste) exhibited much faster kinetics compared to ground specimens (600-grit SiC paper), which formed continuous alumina scales. The alumina-forming kinetics for the rougher surface finish was believed to be due to homogenization of the alloy surface region [60]. Recent studies advocate that the ground surface of metals or alloys suffers heavy strain on it. The subsequent high temperature exposure will lead to recrystallization. Due to the higher amount of defects, an increase in diffusivity via short-circuit diffusion paths can be expected in the subsurface region of the alloy [51,74]. Increasing the diffusivity of Al in the alloy favors the development and maintenance of a continuous alumina film as opposed to simultaneous oxidation of both Ti and Al. However, since the recrystallized layer forms within five minutes, dislocations in the strained layer would only play a role in the earliest stage of oxidation before they are eliminated by recrystallization [74]. An additional factor may be that surface roughness promotes Al<sub>2</sub>O<sub>3</sub> nucleation, thus making it easier to establish a continuous Al<sub>2</sub>O<sub>3</sub>-scale layer [67]. Surface finish will not only influence the oxide scale but also the microstructure in the Al-depleted zone. The Z-phase is formed as a continuous zone during the initial stages of oxidation of the  $\gamma$ -alloy with 600-grit surface finish. The continuous Z layer in the  $\gamma$  alloy with a 600-grit finish will eventually breakdown into a mixture of  $\alpha_2(O)+Z$  upon prolonged oxidation [71]. This "surface-finish effect" was not observed for specimens oxidized in air, which showed rapid kinetics independent of surface preparation [60]. This may be attributed to the fact that the rapid oxidation in air effectively masks the surface finish effect.

## 7. CURRENT METHODS TO IMPROVE THE HIGH TEMPERATURE OXIDATION

The oxidation resistance becomes a critical factor for  $\gamma$ -TiAl alloys to be used at high temperatures, especially under cyclic thermal and/or load conditions.

There are two major ways to achieve this, viz., to improve the bulk oxidation resistance of TiAl by alloying and to enhance the protection against oxidation by surface modification. In general, the protection is accomplished by the formation of an external oxide scale on the coating surface, which becomes a diffusion barrier and, in turn, significantly lowers the oxidation kinetics. The development to date will be reviewed in the following.

### 7.1 Alloying

A number of investigations have been carried out to improve the oxidation resistance of TiAl alloy by adding ternary and quaternary elements [75].

#### Nb

Nb is a well-known element to improve the mechanical properties (especially for ductility and toughness) of  $\alpha_2$ - and/or  $\gamma$ -titanium aluminides [76]. It is reported that 2 to 30 mass% Nb is also effective in decreasing the oxidation rate [3,17,77~81]. The adherence of oxide scale to the matrix is improved by the addition of Nb in TiAl intermetallic for thermal cyclic oxidation at 900°C in air [77]. Nb in TiAl matrix can also favor the formation of alumina on the surface in the initial stage of oxidation to suppress further oxidation of the alloy [42,82]. That is, niobium can accelerate the formation of Al<sub>2</sub>O<sub>3</sub> and change the structure of the diffusion barrier against oxidation during this oxidation stage. The niobium addition to the TiAl alloy can also enhance the erosion resistance substantially when used in turbochargers [3].

#### W

The addition of W element can significantly reduce the oxygen solubility in the TiAl alloys. Owing to this effect, the internal oxidation is inhibited in the alloy [83]. W is the most effective ternary additive for improving the high temperature oxidation resistance of TiAl alloy. The TiAl alloy containing 2 wt.% W exhibits a protective oxidation even after long-term oxidation up to 1000hr at 1173K [80].

#### Mo

Mo is a beneficial element for room-temperature ductility and also for high temperature oxidation resistance [77,80,84]. Molybdenum is thought to increase the aluminum content in the oxide scale because molybdenum itself remains on the metal side of the scale/metal interface and causes reductions on the oxygen solubility there, thus increasing the amount of aluminum which is available to diffuse into the oxide scale [20]. Mo-modified TiAl can improve the oxidation resistance by prohibiting the Al<sub>2</sub>O<sub>3</sub> internal oxide formation. The internal Al<sub>2</sub>O<sub>3</sub> oxide, which will

disturb the continuity of Al<sub>2</sub>O<sub>3</sub>-rich layer, will penetrate from the internal scale layer into the inner scale and would not play any protective role. The decrease of the oxygen in solid solubility might be the cause for the preferential Al<sub>2</sub>O<sub>3</sub> external oxide formation in the Mo-modified TiAl [84].

Si

Instead of favoring the formation of continuous Al<sub>2</sub>O<sub>3</sub>, silicon formed crystalline and/or amorphous SiO<sub>2</sub> in the oxide scale, which acted as a barrier against the oxidation together with the Al<sub>2</sub>O<sub>3</sub> layer in the oxide scale [42]. The combination of silicon and niobium resulted in much better oxidation resistance than the addition of individual elements [42].

Zr

The addition of 0.2 mass% Zr to TiAl specimens resulted in a significant decrease in the overall oxidation rate at 1200 and 1300K by forming thin and very protective alumina scales [85].

Cr

Cr can significantly enhance the plasticity of Al-lean duplex alloys which contain grains of both single-phase  $\gamma$  and lamellar  $\gamma/\alpha_2$  [86]. However, it was found that chromium at low concentrations (< 4 at.%) has a detrimental effect on the oxidation resistance of TiAl intermetallics and that at high concentrations (> 10 at.%) has a beneficial effect [87]. For Ti-50Al-10Cr, at lower temperatures (800 ~ 900°C), Cr increases the oxidation rates upon doping it in the scale. However, at higher temperatures (1000 ~ 1100°C), especially at 1100°C, Cr reduces the oxidation rates significantly as a result of the formation of a continuous Al<sub>2</sub>O<sub>3</sub> film on the surface [88].

Sb

A recent study shows that the room temperature bending deflection and fracture strength can be enhanced significantly upon adding 0.15 Sb in the TiAl alloy due to the refinement of microstructure [89]. Additionally, the high-temperature oxidation resistance can also be substantially increased in the presence of 0.15Sb, being higher than those for Ti-48Al and Ti-48Al-2Cr-2Nb [89]. Although the preliminary result is encouraging, further investigations are required.

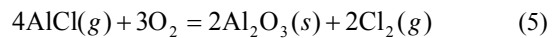
Among these beneficial elements (except Sb), the relative effectiveness is in the order W, Mo, Nb, Si (the former, the better) at 1173K [83]. Other elements, such as Cu, Y, V and Mn, are detrimental for the oxidation resistance of TiAl alloys and V is particularly harmful and the ternary additives of Sn, Zr, Hf, Ta, Ni and Co in TiAl alloys play little influence on the properties of oxidation [90].

Although some achievements have been made, the addition of large amount of Nb or W is harmful.

Hence, some microalloying (only a few hundred ppm or even less of the added element) has been attempted. Surface treatment (elaborated in next section) is also thought to be more attractive for further improvement in oxidation resistance of TiAl alloy.

Cl

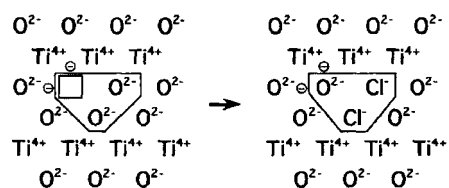
Very small amount (~ 200ppm) of halogenides can dramatically improve the oxidation behavior. Chlorine is found to have the strongest effect and can improve the oxidation resistance by two orders of magnitude compared to unalloyed TiAl [62,91]. The positive Cl effect on TiAl oxidation resistance happens only in a narrow range of Cl concentration [92,93]. The Cl positive effect on the oxidation resistance of TiAl is initially attributable to the decrease in oxygen ion vacancies in titanium oxide due to the substitution of Cl ion for oxygen ion, as shown in Fig. 12 [62]. However, recent studies reported that the Cl effect is due to the formation of volatile metal chloride species [92]. For TiAl with optimal amount of Cl doping, i.e, region B of Fig. 13, only AlCl can develop a vapor pressure. Thus AlCl vapors move into pores and fissures at the scale/substrate interface where the oxygen pressure increases and AlCl becomes converted into Al<sub>2</sub>O<sub>3</sub> as



The catalytic effect of Cl<sub>2</sub> can operate continuously to transport Al selectively into the most inner parts of the scale generating an alumina barrier. Hence, the optimal range of Cl concentration for improving the oxidation of TiAl is narrow. Moreover, a number of pores were observed when Cl is over-dosed. This can be explained by the simultaneous evaporation of both TiCl<sub>3</sub> and AlCl, as shown in region C of Fig. 13.

P

Microalloying of phosphorus in TiAl will alleviate the high temperature oxidation [94]. Retallick *et al.* have painted phosphoric acid onto the aluminide, and the subsequent calcination substantially improved the oxidation resistance at 800°C [95,96]. The oxidation rate of titanium aluminide is lowered by two orders of



**Fig. 12 Disappearance of oxygen ion vacancies in TiO<sub>2</sub> by the existence of chlorine [62]**



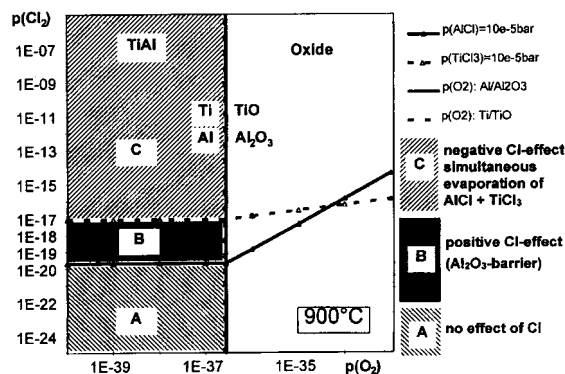


Fig. 13 “Quasi” stability diagram for the system for Al-Ti-O-Cl at 900°C [89]

magnitude if phosphoric acid surface treatment is applied. Although the process has the merits of good conformal coverage, low facility cost and easy operation, time-consuming work and poor appearance after treatment need further improvement.

## 7.2 Diffusion-Barrier Coatings (Overlay Coatings)

The coating materials against oxidation should have excellent hydrogen and oxygen diffusion barrier properties, good thermal stability, high thermal emittance, low catalytic efficiency, and low density [97]. The coefficients of thermal expansion (CTEs) of the coating material and the substrate should be compatible to reduce the residual thermal stress [87,97]. Coatings of uniform thicknesses on substrates with complex geometry (e.g., engine components) are also desirable [97].

The promising candidates for barrier coatings on TiAl alloys against high temperature oxidation include the  $\text{Al}_3\text{Ti}$  layer by pack-cementation aluminizing [98~100] or reduced pressure metal-organic chemical vapor deposition [2], air-plasma-sprayed  $\text{ZrO}_2\text{-Ni-4.5wt\%Al}$  coatings [101],  $\text{Si}_3\text{N}_4$  coatings by ion-beam-enhanced deposition (IBED) [102~104], Al+Y codeposition using EB-PVD [105], and a mixture of M-CrAlY and/or  $\text{Al}_2\text{O}_3$  by plasma spray methods [56, 106], aluminosilicate glass coatings from a mixture of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  [107,108], and  $\text{CaTiO}_3$  coating prepared at 473K in  $\text{Ca(OH)}_2$  solutions by hydrothermal and the hydrothermal-electrochemical treatments [109]. However, the improvement against cyclic oxidation resistance of TiAl is limited.

Aluminizing and MCrAlY (M = Ni, Fe, Co) overlay coatings are widely used for the protection of Ni-base superalloys. Nevertheless, these two methods are not successful for the improvement of high temperature oxidation resistance of TiAl due to the formation of brittle phases, such as  $\text{Al}_3\text{Ti}$ , at the interface [98,110,111]. The oxidation resistance of  $\text{Al}_3\text{Ti}$  is

much better than that of Ti-50 at%Al [39] due to higher aluminum content, which favors the formation of external protective  $\text{Al}_2\text{O}_3$  scale. However, the  $\text{Al}_3\text{Ti}$  layer usually contains a number of microcracks. It has been found to be difficult to form  $\text{Al}_3\text{Ti}$  layers without these microcracks, which may cause the direct oxidation of the TiAl substrate [98]. For the ion-beam-enhanced deposition (IBED) and plasma spray technique, in addition to the poor conformal coverage, the expensive facilities cause a higher initial cost. Relatively higher personnel training cost due to its complexity and the requirement of more sophisticated processing equipment have also limited its application commercially.

Other methods, such as electrolytical chromium plating [56], CVD  $\text{Al}_2\text{O}_3$  films of about  $3\mu\text{m}$  thickness [112] or  $\text{Al}_2\text{O}_3$  coatings deposited by reactive sputtering technology [108,110] as well as boronising by pack-sintering with  $\text{B}_4\text{C}$  and/or  $\text{Na}_2\text{B}_4\text{O}_7$  powder in the temperature range between  $1150^\circ\text{C}$  and  $1250^\circ\text{C}$  [113], were claimed to be useful to the improvement of oxidation resistance of TiAl. Although these can enhance the isothermal oxidation resistance, the improvement is still limited for cyclic oxidation resistance. The Ti-Al-Cr coating [110,114,115] or 0.1% Y-doped Al-Ti-Cr coatings [116] prepared with magnetron sputtering technology yields better results among the overlay coating technology. However, the sputtering technology requires high facility cost and the conformal coverage is poor.

## 7.3 Ion Implantation

Ion implantation has two principal advantages. First, it has a shallow depth, typically 500-1000Å, of implantation of ions into the metal surface. The other unique feature is the ability to introduce controlled concentrations of most element ions into the surface layer. Hence implantation of an element affects high temperature oxidation in a comparable manner [117] and offers the advantage of adding an element to the alloy in a surface layer in a well-controlled and reproducible manner. It can be a very efficient technique in the screening tests for evaluating the effect of possible alloying addition in materials and serves as a research tool to study the influence of various elements on the corrosion behavior of materials [117~120]. Moreover, a certain enrichment of the element with high atomic weight, such as Nb [78], is possible without any significant increase in the specific mass of the specimen and a considerable amount of the element can be saved in comparison with the case of alloying addition.

In addition to the successful attempts of ion implantation of the beneficial element, such as Mo [121,122], Y [121], Mn [121], Pt [121], Al [118,122], Si

[118,122-124] and Nb [78,118-121,125], the implanted chromium [122,126] and/or yttrium [126], can also lead to a decrease in the oxidation rate due to the formation of an alumina scale on the implanted materials in the early stages of oxidation. However, as the oxidation time increased, the difference in oxidation behavior between the implanted and non-implanted alloy gradually disappeared.

Although ion-nitriding can improve the corrosion resistance of TiAl in acid corrosive solution [127],  $N^+$  ion implantation is detrimental to the high temperature oxidation resistance (1300K) of TiAl [103], due to the notorious nitrogen effect (see section 4).

U.S. Pat. No. 5,695,827 (date of patent: Dec. 9, 1997) disclosed the application of ion implantation to the titanium aluminides for high-temperature oxidation resistance [128]. The ion beam includes elemental species, capable of promoting alumina ( $Al_2O_3$ ) formation, such as P, Ar, B, N and O, which are often classified as minor alloying elements. Among them, the preferred elemental species is phosphorous ion. Implantation of phosphorous ions exhibit the best result and can satisfactorily improve the oxidation resistance of TiAl alloy. Some reports show that the moderate dose of implantation of another beneficial element, Cl, also enhances the protection of TiAl alloy by two orders of magnitude compared to unalloyed TiAl [123,128].

However, ion implantation requires higher degree of sophistication and a higher initial cost. The conformal coverage is also an intrinsic drawback for workpieces with complex shapes.

#### 7.4 Preoxidation

It is well-known that the insufficient oxidation resistance of TiAl results from the formation of titania layer instead of the protective  $Al_2O_3$  layer. The equilibrium dissociation pressures for  $Al_2O_3$  and  $TiO_2$  at 1000°C are about  $10^{-30}$ Pa and  $10^{-23}$ Pa, respectively [129]. Therefore,  $Al_2O_3$  is more stable than  $TiO_2$  and Al has a tendency to be oxidized preferentially during the treatment and forms a tight film on the specimen surface [130]. Heat treatment under a low partial pressure oxygen atmosphere ( $10^{-3}$ Pa) is very effective in improving the resistance for the cyclic oxidation of TiAl at 900°C [130]. The best condition for the heat treatment under a low partial pressure oxygen atmosphere is found to be: pressure,  $6.7 \times 10^{-3}$ Pa; temperature, 1373K; and time, 7.2ks (2h) or more [131].

The preoxidation under a low-oxygen pressure can also be performed by heating the specimens buried in the oxide powder, such as silica [132], titania [133], a mixture of chromia and metal chromium powders [134], or under an atmosphere with low partial pressure of

oxygen. This low pressure may be near the dissociation pressure of silica and much lower than that attained by modern vacuum pumps. The resistance of TiAl coupons to cyclic oxidation at 1300K in a flow of purified oxygen under atmospheric pressure has been significantly improved by preoxidation. The successful employment of titania powder has excluded the possibility of alloying effect due to the reduced metallic element in the oxide. Moreover, the oxidation resistance of preoxidized TiAl tested in  $O_2$  increases as the oxygen partial pressure decreases [135]. This verifies that the improvement of oxidation resistance is mainly attributable to the preferential formation of alumina in low oxygen partial pressure. However, without the degassing of rutile powder, the preoxidation in packed rutile powder results in poorly protective scale [130]. This implies that the purity of oxygen will be another crucial factor to form a protective  $Al_2O_3$  layer on the TiAl.

#### 7.5 Anodization

The anodizing technique is a well-established method to improve the corrosion resistance of aluminum alloy [136]. The anodic oxide coating, when properly produced, has excellent resistance to marine and general atmospheric corrosion. Through extensive efforts, the commercial application of this technique has been extended to the field of corrosion-resistance coatings, undercoat for organic coatings, colored anodizing coatings, anti-marking applications, lighting equipment, heat reflection and radiation, wear resistance and lubrication and electrical insulation [137]. However, there is no report related to the application of anodizing to the improvement of high temperature oxidation resistance of TiAl so far.

The progress in the formation of anodic coating depends on the chemical composition of the anodizing electrolyte and the chosen conditions of electrolysis (such as the bath temperature, the duration, the current density or applied voltage and the mode of power supply.) In general, the films produced under strong solutions tend to be more porous, softer and more flexible than those produced in weak ones. The films produced in cold electrolytes are harder and less absorbent than those produced in warm electrolytes. The process is known as the "hard anodizing" (using refrigerated electrolytes). The current density and the rate at which the film is dissolved by the solution alter markedly with temperature. Local overheating increases current density (or reduces the applied voltage if the current density is kept constant) resulting in uneven films with uncontrolled quality.

Some anodizing electrolytes have little or no

solvent action on the oxide coating so that the process soon ceases, leaving a thin film usually referred to as a barrier-layer-type coating, the thickness of which is solely governed by the applied voltage. This type of coating is typically produced in solutions of weak acid, e.g., borates, boric acid or tartrates for the anodization of aluminum alloy. The non-solvent electrolytes provide thin and impervious barrier layers with electrical properties suitable for using in capacitors.

If the electrolyte has some solvent action, then a porous film is formed and the oxidation process can continue leading to the production of relatively thick films, for example, sulphuric acid while anodizing the aluminum. Eventually the rate of film formation is balanced by the rate of solvent attack, but this stage of the process is avoided in commercial practice. The diameter of the pores and the thickness of the barrier layer for any given electrolyte and temperature are proportional to the applied voltage.

For aluminum, compared with the sulphuric acid film, the practical total thickness for the phosphoric acid film (up to 6 $\mu$ m) is less. This is due to the greater solubility of aluminum oxide in phosphoric acid anodizing solution. The anodic films produced in phosphoric acid have larger pore diameters than those in conventional sulphuric acid. The greater diameter provides a better conducting path and it is for this reason that phosphoric acid films have been used as one of the methods for pretreating aluminum prior to electroplating. The phosphoric acid process is rarely used as a finish in its own right due to the existence of other more convenient process [137].

For the passivation of the anodized titanium alloy, acid electrolytes, in general, give by far the best results among acid, base and salt electrolytic solutions. However, a very strong acid such as HF or HClO<sub>4</sub> has strong tendencies toward dissolving the films produced. Thus, the anodic films in these cases are essentially nonadherent. Very weak acids, such as the usual organic acids, produce very adherent but thick and translucent films. Acid, such as sulfuric acid, tends to yield heavy, opaque and amorphous films which could be formed by high voltages, but there is also a tendency toward dissolution of the films. Films thus formed have a tendency to retain a rather porous structure. Among the acidic electrolytes that have been tried, the phosphate-based materials give by far the best results [138].

In addition to the fact that phosphorus is a beneficial element to oxidation resistance for TiAl [94~96], the satisfactory performance of titanium and aluminium alloys anodized in phosphoric acid arises the expectation that anodizing TiAl in phosphoric acid solution seems to be feasible and deserves to be investigated.

## 8. SUMMARY

TiAl intermetallics are one of the most promising structural alloys used in the high temperature due to their significantly low density, excellent high-temperature specific strength, as well as high modulus retention. However, the poor oxidation resistance at temperatures above 750°C has posed a bottleneck for their practical engineering applications for years. In this paper, we review the oxidation behavior, oxidation kinetics and oxidation mechanism of TiAl alloys. We also review the methods of surface modification to improve their high temperature oxidation resistance, such as the effects of surface finish and the reported feasible methods which have been developed. In the past decade, several promising methods of surface modification for TiAl alloys have been conducted in our research group, such as spraying or sputtering coatings of pure Al on TiAl alloys [99,139], pre-oxidation for different duration of TiAl alloys in high pressure oxygen [67] and anodic coatings of TiAl alloys in phosphoric acid solution [140,141]. All of these studies show a significant improvement of high temperature oxidation resistance of TiAl intermetallics, including  $\alpha_2$ -Ti<sub>3</sub>Al,  $\gamma$ -TiAl and ( $\alpha_2$ + $\gamma$ )-TiAl alloys. Other novel methods of surface modification are still under investigation in this research group.

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