EFFECT OF OXYGEN PARTIAL PRESSURE ON OXIDATION BEHAVIOUR OF Ti-Al INTERMETALLICS AT HIGH TEMPERATURES

Ali A. Aljarany

Materials Science and Eng. Department,
7th of October University, Misurata, Libya
E-mail Ali.aljarany64@yahoo.com

الملخص

أجريت تجارب الأكسدة في درجات حرارة ثابتة على سبيكة Ti-46.7Al-1.9W-0.5Si في وسط خليط من غازي الارجون والأكسجين ($Ar-O_2$) و باختلاف المحتوي من غاز الأكسجين وفي درجات حرارة 750 و 850 و 950 درجة مئوية وضغوط أكسجينية 0.05، 0.2، 0.8 ضغط جوي وذلك لدراسة سلوك أكسدة السبيكة في أجواء مختلفة من الغازات المتفاعلة. تم الحصول على العديد من نتائج SEM/EDX عن طبقة الصدأ (صور وتركيب لطبقة الصدأ المتكونة) لسبيكة γ–TiAl عند درجات الحرارة 750 و 850 و 950 درجة مئوية على التوالي وزمن تعريض حتى 240 ساعة. طبقة الصدأ التي تكونت على السبيكة عند درجة حرارة 750 درجة مئوية وفي وسط $Ar-5\%O_2$ كانت مشابهه نسبيا لتلك الطبقة في وسط $Ar-80\%O_2$ عند نفس درجة الحرارة. تلك الطبقة كانت واضحة بصورة أكثر في الوسط $Ar-5\%O_2$ حيث لوحظ وجود شقوق في طبقة الصدأ في اتجاهات متعامدة على الحد الفاصل بين طبقة الصدأ وجسم السبيكة. نتائج أنماط XRD للعينات المتأكسدة في الوسطين المذكورين تعطي مؤشرا على وجود TiO_2 و Al_2O_3 ، كما أن نتائج EDX توضح وجود خليط متداخل من TiO_2 و Al_2O_3 عوضا عن كونها طبقات متعامدة من TiO_2 و Al_2O_3 في صورة منفردة. سمك طبقة الصدأ في الوسط $Ar-5\%O_2$ بقي أكبر منها في وسط $Ar-80\%O_2$ عند درجة حرارة 850 درجة مئوية. بعد 5 ساعات وعند درجة حرارة 850 درجة مئوية أظهرت نتائج EDX أن الصدأ المتكون على السبيكة يتكون من Al_2O_3 /TiO_2 ؛ وبزيادة زمن تعريض العينة عند هذه الدرجة إلي 72 ساعة بدأ ظهور نمط الطبقات المتعددة من TiO_2 و Al_2O_3 و بشكل واضح عند درجة حرارة 950 درجة مئوية. في وسط $Ar-5\%O_2$ ظهرت نسبة أكثر من TiO_2 في طبقة الصدأ المتكونة، بينما في وسط $Ar-80\%O_2$ تحول الصدأ إلي طبقة متماسكة من Al_2O_3 تحوي بعض من الدقائق الغير متصلة من طبقات TiO_2 حتى زمن تعريض 240 ساعة. عند تعريض العينة إلي درجة حرارة 950 درجة مئوية في كلا الوسطين $Ar-80\%O_2$ و $Ar-5\%O_2$ ظهرت العديد من الظواهر المثيرة في طبقة الصدأ نظرا لنضوب السبيكة من الألمونيوم ازدادت بزيادة الضغط الجزئي الأكسجيني، كما أن سمك المنطقة الناضبة تحت طبقة الصدأ بزيادة زمن تعريض السبيكة في كلا الوسطين حتى زمن قدره 240 ساعة في وسط $Ar-80\%O_2$ ، الطبقة المترسبة الداخلية تحولت في معظمها إلي طبقة من Al_2O_3 تتخللها طبقات قليلة و غير متصلة من TiO_2. من الظواهر الأخرى المهمة التي ظهرت في طبقة الصدأ المتكونة في الوسطين: $Ar-80\%O_2$ و $Ar-5\%O_2$ عند درجة حرارة 950 درجة مئوية وبعد زمن تعريض 240 ساعة هو وجود مسامات بداخل طبقة الصدأ في وسط $Ar-5\%O_2$ ووجود فجوات في المنطقة المتاخمة للحد الفاصل بين طبقة الصدأ وجسم السبيكة.

ABSTRACT

Isothermal oxidation experiments were carried out on Ti-46.7Al-1.9W-0.5Si (wt%) alloy in Ar-O_2 with various oxygen contents at a temperatures of 750, 850 and 950°C and oxygen partial pressures of 0.05, 0.2 and 0.8 atm in order to study the oxidation behavior of the alloy under investigation. The oxidation results of the alloy in different reactive atmospheres show several interesting findings. Typical SEM / EDX scale morphologies and composition of γ-TiAl at 750, 850 and 950°C for up to 240h exposure were carried out. The scale formed in Ar-5% O_2 at 750°C was relatively similar to that in Ar-80% O_2. Very thin layer of internal oxidation in both atmospheres at 750°C, but it is more obvious in Ar-5%O_2 where the scale showed micro-transverse cracks perpendicular to the scale/alloy interface. The XRD pattern of the oxidised samples in the two atmospheres indicated the presence of both TiO_2 and Al_2O_3. EDX results revealed inter-mixed scale of TiO_2 and Al_2O_3 rather than single multi-layers scale. The scale in Ar-5% O_2 remains thicker than that in Ar-80% O_2 at 850°C. After 5h exposure, EDX analysis revealed that the scale is consisting of TiO_2/Al_2O_3 in Ar-5% O_2 and Al_2O_3/TiO_2 in Ar-80%O_2. However, the scale in Ar-80%O_2 after the same exposure time is a mixture of Al_2O_3/TiO_2. Further increase of the exposure time to 72h the alternating fashion of Al_2O_3 and TiO_2 and the scale becomes more noticeable.

At 950°C, the scale in Ar-5%O_2 showed substantially more TiO_2 content. However, the scale is virtually converted to almost ‘dense’ alumina (Al_2O_3) containing very thin and discontinuous layers of rutile (TiO_2) in Ar-80%O_2 even with the increase of exposure time up to 240h. However, more interesting features of the cross-sectioned scales were observed at 950°C in both atmospheres. The depletion of aluminum is increased as the oxygen partial pressure increased, also the thickness of the depleted layer increases as the exposure time increased. Further increase in the exposure time for 240h in Ar-80% O_2, the internally precipitated layer was converted into Al_2O_3 oxide layer with trace amounts of discontinuous TiO_2 layers. Another important feature of the scale formed in Ar-5% O_2 and Ar-80% O_2 at 950° C after 240h is the existence of porosities within the scale in Ar-5% O_2 and voids at the scale/alloy interface in Ar-80% O_2.

KEYWORDS: High temperature; Isothermal; Oxidation; TiAl; Intermetallics; Scale morphology; Scale kinetics

INTRODUCTION

The performance of metals and alloys in high temperature corrosive environments is dependent upon their ability to promote and maintain a protective oxide (scales) such as Cr_2O_3 and Al_2O_3. These scales limit the degradation of the base metal or alloy to be employed at high temperatures and for long periods of time. Thus improving efficiency (for example in power generation) and decreasing maintenance costs [1]. Improved corrosion resistance also reduces the number of the spalled fragments (especially in cyclic temperature conditions), which, in certain applications such as gas turbines, can cause abrasive damage. Under the conditions of high temperatures where the oxygen activity is high, a protective, mechanically stable external oxide scale is produced on the exposed alloy surface, which normally reduces the subsequent corrosion to acceptable design levels [2]. However, under the influence of a second oxidant e.g. sulphur, severe corrosion may occur; sulphidation (in high P_{S2}) may take place, commonly as a form of internal degradation [3].

In environments of low oxygen and high sulphur activities (sulphidation/ oxidation), sulphides formed on certain alloys may offer a moderate measure of protection [3], in fact analogous to a protective oxide film, but in general, sulphide scales are much more friable and more subject to exfoliation than oxide scales on most high temperature (HT) alloys due to larger Pilling-Bedworth ratios. Furthermore, oxide scales formed on the alloys usually melt at relatively high temperatures, above the melting point of the alloys, whereas sulphides have comparatively low melting points and frequently form low melting point eutectics [3]. In addition, the diffusion coefficients of cations in sulphide scales are relatively high because of the greater degree of non-stoichiometry of sulphide structures. The improvement of corrosion resistance was generally attributed to the formation of a dense protective external scale instead of the loose of adhesion and non-protectiveness to the alloy [4].

The development of oxidation resistance alloys where the solubility of additional elements is limited depends on the addition of an element, which will oxidise selectively so that it will produce a more protective surface oxide [5]. If alloying elements are added in sufficient quantities, a continuous external oxide layer may be formed by the outward diffusion of solute. In this context, aluminium is the principal element in common HT alloys designed to provide adequate degrees of corrosion resistance to iron-nickel-cobalt and titanium-based alloys in the presence of oxygen even at low activity (that is, at activities generally lower than those required to allow formation of oxides of Fe, Ni, Co or Ti) to permit the formation of protective alumina on the alloy surface [6].

Among the various types of intermetallics, Fe_3Al and γ-TiAl are considered as candidate structural and coating materials for industrial and aero-gas turbines respectively. However, these materials have low fracture toughness (K_{Ic}) and relatively poor high temperature corrosion resistance. Recently γ-TiAl- and Fe_3Al-based intermetallics alloys in particular are receiving significant attention. Low density (3.8 g/cm^3) γ-TiAl intermetallics with their high specific strength at elevated temperatures are being studied extensively with a view to application e.g. engine valves, turbine blades, aircraft and automotive engines [7]. Of major concern for structural applications is the low oxidation resistance at high temperatures. The poor high temperature oxidation resistance of Ti-Al intermetallics alloys is due to the fact that they do not form long-lasting protective alumina scales at high temperature in air. Even if they contain high aluminium concentration closes to 50 at%. After longer exposure times, the scales initially rich in alumina, deteriorate and scales with a high amount of Titania predominate with similar high growth rates as pure Titania. According to previous studies, a higher concentration of aluminium is needed to achieve a protective alumina scale [8]. However, the increase of the aluminium concentration is technologically not desired for loss of ductility by the formation of brittle $TiAl_3$ compound.

A great deal of research effort has been directed towards improving the corrosion resistance of Ti-Al by adding ternary and quaternary alloying elements [9]. Addition of small amounts of a ternary or quaternary element can be performed by either alloying or ion implantation. The later technique offers the advantage of adding one or more elements to the alloy in a near-surface layer in a well-controlled and reproducible manner. This technique has already been proved to be powerful to modify the subsurface layer of metals and alloys in order to be employed as a fast "screening" test for modifying or developing new materials [10]. While various alloy systems form Al_2O_3 scales, the attention here is on the formation of compact, dense scales at high temperatures. This excludes systems such as Ti-Al where, the thermodynamic stability of TiO_2, a mixed TiO_2/Al_2O_3 scale was formed.

There are several important aspects of the high temperature corrosion behaviour of Ti-aluminides intermetallics that need further attention: the occurrence of multi-layered scales (TiO_2/Al_2O_3), the transition kinetics of γ-TiAl, and the effect of nitrogen and partial pressure of oxygen on the scaling behaviour of γ-TiAl. All of these aspects need to be critically examined and investigated in a wide range of temperatures and exposure time. Studies of these important aspects form the basis of the current research paper.

Based on such a background, the present paper has been undertaken with two main objectives: (1) to provide new experimental HT corrosion data essential for alloy design purposes and (2) to provide new fundamental information concerning the mode of degradation of γ-TiAl.

Isothermal oxidation (at 750-950°C) study of γ-TiAl is intended to understand the effect of partial pressure of oxygen on their oxidation behaviour. Generally the oxidation studies of the selected materials are to adopt an integrated approach involving assessment of weight gain data, scaling kinetics and examination of scale formation and development.

HIGH TEMPERATURE CORROSION BEHAVIOUR OF TITANIUM-ALUMINIDES

Corrosion behaviour of titanium and Ti-Al alloys has been studied by many researchers. The nature of oxide scale on titanium aluminides is more complex than that of pure titanium. The scale on Ti-Al is a mixture of fast-growing TiO_2 and potentially protective slow growing Al_2O_3 [11]. Even though Ti-Al alloys contain about 50 at% Al, this is not sufficient to form a long-lasting protective alumina layer at high temperatures (> 700°C) in air. Poor oxidation resistance of Ti-Al systems in air at high temperatures initially results from the formation of Al_2O_3, TiO_2 (rutile), Ti_2AlN and TiN [12], with the latter two near the scale/substrate interface. After longer exposure times, the mixed corrosion scale was overgrown by relatively fast growing TiO_2 [13]. However, since Al_2O_3 does not form a continuous barrier in TiO_2/Al_2O_3 mixtures, generally the scale is non-protective. For long-term oxidation resistance, the formation of an α-AI_2O_3 barrier in the metal/oxide interface zone is necessary.

Corrosion by gaseous environments containing sulphur is a serious problem in various technical high temperature processes, since sulphidation can significantly reduce the service life of metallic components. Whereas in strongly oxidizing conditions adequate corrosion resistance can be achieved, this is more difficult in environments characterized by a low oxygen and high sulphur activity. In these atmospheres the simultaneous nucleation of sulphides as well as oxides was observed [14]. A great deal of research work has been undertaken to improve the corrosion behavior of Ti-Al alloys by adding ternary and quaternary elements [15]. From these studies, both beneficial and detrimental results have been reported and even apparently contradicting conclusions were obtained. This might be partly caused by differences in alloy purity, since several alloying elements have been demonstrated to possess a significant effect on the corrosion properties, even if they are present in small quantities. Also differences in alloy conditions and reactive gas composition can affect the corrosion behavior of the materials under investigation.

Mechanism and Corrosion Rates of Titanium-aluminides

The oxidation resistance of γ-TiAl-based alloys becomes poor at temperatures near or about 700°C [16]. According to Jiang [17], that is because of the following reasons: (i) the little difference in free energy of the oxidation between aluminum and titanium; (ii) the larger oxidation rate of titanium than that of aluminium; (iii) the high solution content of oxygen in TiAl; (iv) the small diffusion rate of aluminium in TiAl, and (v) the internal oxidation tendency of aluminum in TiAl. Therefore, improving the oxidation resistance of this alloy is key to its practical application. The research activities in this field including surface treatment and alloying addition were extensively carried out, but the achievement of adequate oxidation resistance is still a matter of concern.

It seems likely that the reduction in oxygen diffusion into Ti-Al alloys is a consequence of the improved barrier properties of their oxide scale and the subsequence inhibition of oxygen diffusion through this scale. If aluminum is substituted into the rutile lattice, according to the Wagner-Hauffe theory, the trivalent (Al^{3+}) cations will cause an increase in the number of anion vacancies and consequently enhance their rate of diffusion. Accelerated oxidation is not observed, which might suggest that aluminum takes up interstitial positions in the rutile.

A modification of the flux of oxygen across the scale may arise from a reduction in the rate of ionic charge in the presence of alumina, which has a lower rate of ionic conductivity than rutile. In addition to the electronic effects, which inhibit the diffusion of oxygen through the scale, alumina-containing scales are more protective because they are less porous and have improved adhesion. The multi-layering of oxide scales is less distinct in the mixed scales and the oxide layers are thinner. Hence scales become denser as the aluminum content increases and oxygen has more limited access to the metal/oxide interface.

From the above background self-diffusion data on Ti and Al in Ti-aluminides are necessary to understand the corrosion mechanism of Ti-Al systems and also for the interpretation of the Ti-Al high temperature corrosion phenomena. Unfortunately, experimental studies of diffusion in the Ti-AI system are hampered primarily by the non-availability and expensive radioactive isotopes of Ti and Al. ^{44}Ti is the only suitable radiotracer for Ti [18], but it is produced by a nuclear reaction at a cyclotron and is very expensive. The only suitable isotope for Al, ^{26}Al [18], which is also a cyclotron product; it is even more expensive than ^{44}Ti and, in addition, has very low specific activity.

Leyens et al [19] launched a broad programmed of extensive experimental investigations of diffusion in the Ti-Al systems. Such investigations included lattice diffusion in different phases of the system and grain boundary diffusion and diffusion along γ/α_2 interfaces. To date, their efforts have resulted in accurate measurements of lattice self-diffusion and Al impurity diffusion in pure α-Ti [18], and Ti self-diffusion and single-phase inter-diffusion in bcc Ti-Al alloys [19] and in the Ti_3Al aluminide [20]. However, Sprengel et al. [21] could not make any reasonable evaluation of Al diffusivity in TiAl by combining their inter-diffusion coefficients with the data of Kroll et al. [22].

Recently, the work of Leyens et al. [19] led to accurate measurements of ^{44}Ti self-diffusion coefficients in γ-TiAl over a wide temperature range Table (1). They also studied diffusion in three different Ti-Al materials with near-stoichiometric compositions. One of the materials used was the same material as that studied by Kroll et al. [22]. They [19] evaluated Al self-diffusion coefficients in TiAl by using their new Ti self-diffusion data and the inter-diffusion coefficients obtained by Strafford et al. [23].

Table 1: The thermodynamic factors and chemical diffusion coefficients of TiAl (D_{TiAl}), titanium and aluminium

T (ºC)	Φ	D_{TiAl} (m^2/s)	D_{Ti} (m^2/s)	D_{Al} (m^2/s)
900	3.596	2.07×10^{-17}	1.18×10^{-17}	2.40×10^{-18}
1000	3.088	2.23×10^{-16}	8.87×10^{-17}	3.52×10^{-17}
1100	2.885	6.40×10^{-16}	2.17×10^{-16}	1.69×10^{-16}

The calculations of Leyens et al. [19] suggest that, in the compositions studied experimentally, Ti diffusion at low temperatures is dominated by the vacancy mechanism. At higher temperatures the anti-structural bridge mechanism can essentially contribute to the overall diffusivity, which can explain the experimentally observed non-Arrhenius behavior of Ti diffusivity. Al diffusion occurs predominantly by the vacancy mechanism, but 3-jump cycles and especially anti-structural bridges can also play an important role. These results were in agreement with their experimental data and their calculations predict that Al diffuses with higher activation energy than Ti. These findings are very useful for the interpretation of our oxidation results of γ-TiAl as presented and discussed in section five of this work.

Effect of Environmental Gas Composition on the Corrosion Behaviour of Ti-Al Alloys

The reaction of gaseous species (exclusively oxygen) with titanium and titanium-aluminides at different temperatures has been studied in numerous investigations [23, 24]. A comparison of the different studies however, shows large disagreement and discrepancies in both the mechanism and rates of their corrosion. The reasons for this lie in the complexity of processes involved in the reaction, the different temperatures and pressures of the reacting species. Also the corrosion reaction is influenced by the alloy composition and surface conditions. Several studies by various researchers have dealt with the influence of various alloy composition and surface conditions. Both improved and decreased environmental resistance of Ti-Al were reported [22-25]. However, the studies regarding the influence of gaseous species on their corrosion behavior have been relatively few. The influence of nitrogen in oxidizing gases has been reported and discussed by Aljarany [26].

Effects of oxygen partial pressure on corrosion behavior of Ti-Al alloys

Taniguch et al. [27] used commercial gases (O_2, Ar-21%O_2, Ar-1%O_2, He-1%O_2 and Ar) to explain the effects of the partial pressure of oxygen on the oxidation behavior of γ-TiAl. These gases contained relatively high levels (1 to 2.6 ppm) of impurities such as CO_2, N_2, H_2O and H_2. All the oxidation curves of their study showed mass gains larger than those expected from parabolic rate laws. The oxidation curve at 1000°C in O_2 was the lowest and it became higher as the oxygen partial pressure decreased in the reactive atmosphere. Surprisingly, the oxidation kinetic results in Ar Figure (1) showed the highest mass gain at the same exposure temperature. That was probably because of the other oxidants present in the Ar such as CO_2, H_2, and H_2O. Rapid increase of the mass gain in (Ar) atmosphere was attributed by Taniguch et al. [27], as due to the presence of nitrogen (< 2ppm) in the reactive atmosphere. In fact the rapid increase of the weight gain of the experimental material used by Taniguch et al. [27] in Ar atmosphere was due to the presence of water vapour (H_2O). The significant effect of water vapour on the γ-TiAl corrosion behaviour was experimentally examined by Aljarany [28] (see Figure 2) and also by others (see Figure (3)). Also, Shigeji et al. [30] reported that water vapour in the O_2 significantly increased the oxidation rate of TiAl at 727 and 927°C. They concluded that the oxidation mass gain significantly increased as the H_2O content increased in the atmosphere and the oxidation rate followed approximately linear kinetics laws at 927°C [29]. The dramatic increase of the weight gain was attributed by Shigeji et al [30] due to the formation of high intensity of TiO_2 grains in the H_2O-containing atmospheres. Although the outer surface morphology of the scale formed on Ti-Al in the H_2O-containing atmospheres was very different from the normal morphology of such alloys in air and O_2 cited in the literature, no hydride(s) formation of Ti and/or Al was reported by Taniguchi et al [30]. Another effort to explain the effects of the partial pressure of oxygen in the oxidising environment of Ti-Al systems was undertaken by Becker et al. [31]. The study showed contrary effects of oxygen partial pressure to the finding of Taniguch et al [27]. The oxidation rate of TiAl-V reported by Becker [31] in oxygen was higher than in Ar-1%O_2 at a single temperature (900°C).

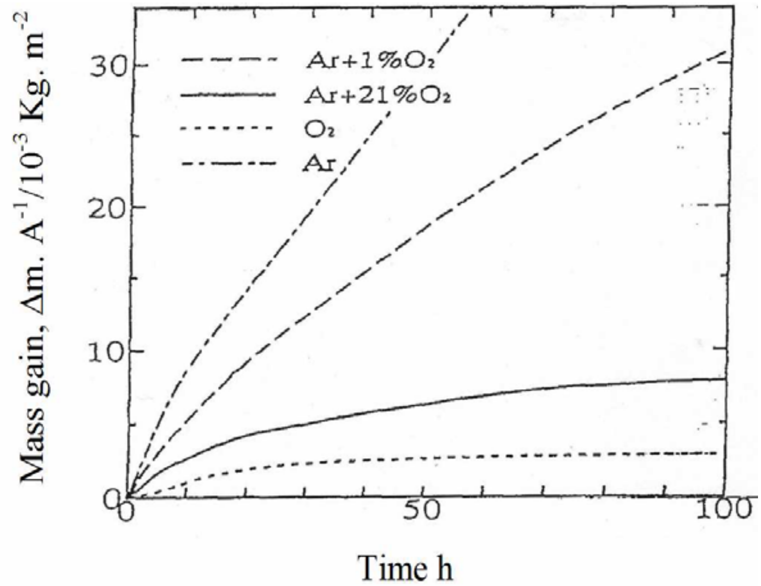

Figure 1: Oxidation curves of TiAl at 1027°C in various gases under atmospheric pressure [27]

It should be noted that the purity of the used argon-oxygen gases was not mentioned in the report of Becker [31]. In the same study, Becker et al. extensively investigated the transport processes through Ti-Al scales. The authors concluded, the formation of protective Al_2O_3 increased with the increase of oxygen partial pressure in the reactive atmosphere. This was believed due to; (i) the low solubility of Al_2O_3 in

TiO_2 at higher oxygen pressures (the exact relationship is still unclear and (ii) low defect structures in Al_2O_3 if compared to that in TiO_2. The consequences of Al_2O_3 formation at the outer part of the inner layer (at higher oxygen pressures), is that it reduced the oxygen flux through the scale. Once diffusion 'Al_2O_3' barrier has begun to form, the discontinuity at the border between the inner and outer layers of the scale increased.

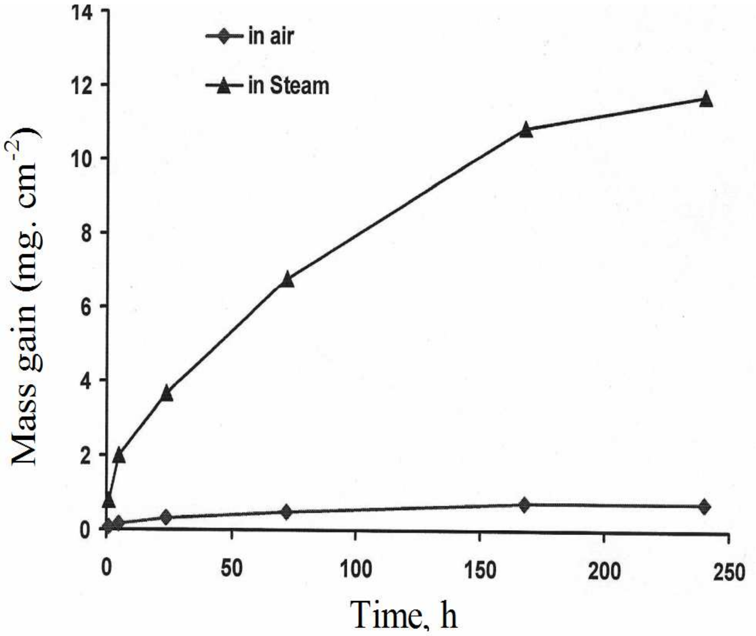

Figure 2: Effect of steam on the oxidation of Ti-46.7Al-1.9W-0.5Si alloy at 850°C [28]

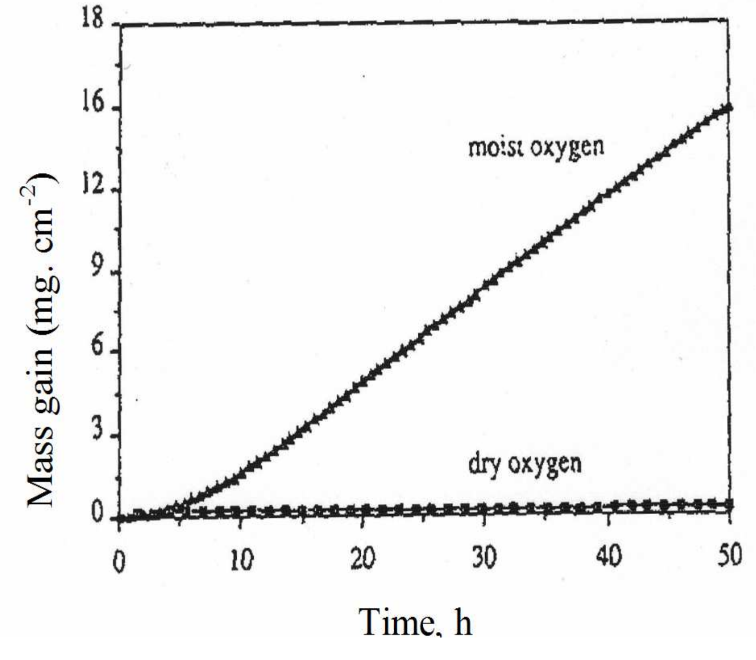

Figure 3: Effect of moisture on the oxidation of Ti-50 at% Al at 900°C [29]

EXPERIMENTAL WORK

Materials

Conventional cast Ti-46.7Al-1.9W-0.5Si (at %) alloy rods of 22 mm diameter were provided. The γ-TiAl intermetallics chemical compositions are given in Table (2).

Table 2: Chemical composition of Ti-46.7Al-1.9W-0.5Si intermetallic alloy

Element (wt %)	Fe	Al	W	Si	C	O	Cu	Ti
γ-TiAl	0.052	31.05	8.56	0.34	0.01	0.0698	0.01	Bal

Specimen Preparation and Surface Area Calculations

The 3 mm outer layer of the as-casted γ-TiAl rods was removed using lathe machine. The removal of the outer layer is to ensure that the whole surfaces of the test samples could be perfectly free from any possible scale or voids resulting from the casting processes. Half disks of 19mm diameter coupons from γ-TiAl billets and 2.5 mm thickness were cut by means of a Buehler Isomet 2000 precision saw. A hole of 1mm diameter, to facilitate suspension by platinum wire in the specimen boat, was bored in each sample of γ-TiAl using WC drills. The surfaces of the specimens were prepared by grinding on metallographic SiC papers up to 1200 grit. As a matter of record, the specimen dimensions prior to exposure were accurately measured in three locations using a digital micrometer, followed by degreasing in (IMS) and cleaning by acetone.

The samples were then weighed before and after exposure on a Mettler HLS balance capable of reading to a resolution of ±0.02mg. The sample after exposure was weighed. The total mass gain of the sample was determined by the mass change of the sample plus the alumina crucible in order to include any spalled scale. However, one possible source of error is that, without a lid, any violently spalled scale may not have been captured in the crucible. In most cases this loss was minimal. The weight changes of the material (with the spalled scale) were necessary to determine the kinetic data for each material at a fixed temperature. To reflect the realistic weight change data, the weight change of the sample after exposure was calculated by the difference in weight of the sample after exposure (with the spalled scale) and the weight of the sample before exposure.

Oxidation experiments: Rig, procedure and gases

For (Ar-O_2) gas oxidation experiments, Ar-5%O_2, Ar-20%O_2 and Ar-80%O_2 cylinders were used. to study the effect of oxygen partial pressure on the oxidation behavior of Ti-46.7Al-1.9W-0.5Si alloy. Gas cylinders contain trace amounts of impurities – see Table 3). The rig used for controlled oxidation consisted essentially of horizontal vitreous silica tube, the mid-section of which was heated by an electric resistance type furnace. The heating rate of the used furnaces was 50°C/min.

A Eurotherm proportional regulator, coupled with thyristor units, controlled the furnace operating temperature, was capable of maintaining a minimum “hot zone” (defined by an N-type thermocouple) of the working tube length in the reaction tube of 8cm with a maximum temperature fluctuation of ± 5°C. The temperature measurement and control were achieved using two separate thermocouples. The control thermocouple was located between the furnace wall and the silica reaction tube, whilst the measuring thermocouple connected with a temperature probe was used to check the hot zone temperature.

Table 3: Impurity levels of various gases supplied by B.O.C. special gases (UK)

Gas	Impurities (ppm)					
	CO	CO_2	H_2	H_2O	N_2	O_2
Ar	< 1	< 1	< 1	< 20	-	< 15
$Ar-O_2$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-

The prepared specimens were suspended – in a silica crucible – above a small alumina boat – for scale collection – using 0.1mm diameter platinum wire. At the end of the Ti-46.7Al-1.9W-0.5Si alloy isothermal air oxidation tests, the specimens were furnace cooled to room temperature after each exposure time at the test temperature. The mass change of the specimens of the intermetallics material was measured including spalled oxide scales (individual boats were used for scale collection) after each run. The controlled isothermal oxidation rig used the same type of furnace. Provision was made for the controlled oxidation – using special gases – in order to admit and exit the reactive gases at the tube ends via fabricated glass end-pieces, which incorporated appropriate taps.

The oxidation tests were performed in a flow of highly purified $Ar-5\%O_2$, $Ar-20\%O_2$ or $Ar-80\%O_2$ under atmospheric pressure. In all the $Ar-O_2$ oxidation experiments (at $Ar-5\%O_2$, $Ar-20\%O_2$ and $Ar-80\%O_2$), the reactive gas was passed through dryer and a gas flow-meter, then entering the reaction chamber. The flow of the gas is also monitored using a water bubbler at the gas outlet. At the end of the oxidation test, the Ti-46.7Al-1.9W-0.5Si alloy specimens were furnace cooled in the reactive gas. To avoid any possible contaminating impurities such as H_2O or hydrocarbons might be present in the argon, so the reactive gas ($Ar-O_2$) was used as a purging gas as well.

ISOTHERMAL OXIDATION OF Ti-46.7Al-1.9W-0.5Si ALLOY IN $Ar-5\%O_2$, $Ar-20\%O_2$ AND $Ar-80\%O_2$ ATMOSPHERES

Mass changes of Ti-46.7Al-1.9W-0.5Si alloy after isothermal oxidation in $Ar-5\%O_2$, $Ar-20\%O_2$ and $Ar-80\%O_2$ atmospheres

Isothermal kinetic weight changes of Ti-46.7Al-1.9W-0.5Si alloy in $Ar-5\%O_2$, $Ar-20\%O_2$ and $Ar-80\%O_2$ at 750, 850 and 950°C respectively for up to 240 h exposure time are shown in Figures (4 to 6). Generally, the isothermal oxidation curves and the kinetic data analysis (Table 4) obtained at the three temperatures indicated some effects of oxygen partial pressure on the oxidation behaviour of Ti-46.7Al-1.9W-0.5Si alloy especially at higher temperatures.

Table 4: Oxidation parabolic rate constants ($g^2/cm^4/s$) of Ti-46.7Al-1.9W-0.5Si intermetallic alloy after exposure for up to 240h

	750°C	850°C	950°C
$Ar-5\%O_2$	6.8×10^{-14}	3.41×10^{-13}	1.21×10^{-12}
$Ar-20\%O_2$	4.26×10^{-14}	1.89×10^{-13}	1.08×10^{-12}
$Ar-80\%O_2$	3.59×10^{-14}	1.18×10^{-13}	3.80×10^{-13}

It is apparent that the oxidation rate of the material is higher in Ar-5%O_2 than in Ar-20%O_2 and Ar-80%O_2 within the entire range of exposure time and temperatures. At 750°C, the isothermal oxidation behaviour of the alloy for up to 72h exposure time in the three Ar-O_2 atmospheres was similar (Figure 4). As the exposure time increased, more increase of weight gain of the alloy in Ar-5%O_2 was observed, whereas the alloy showed parabolic behaviour in Ar-20%O_2 and Ar-80%O_2 for up to 240h. Although the parabolic oxidation rate constants of the alloy at 750°C and 850°C in Ar-5%O_2, Ar-20%O_2 and Ar-80%O_2 were of the same order of magnitude (Table 4), the reaction rate constant of the alloy in Ar-5%O_2 is approximately two times than in Ar-80%O_2.

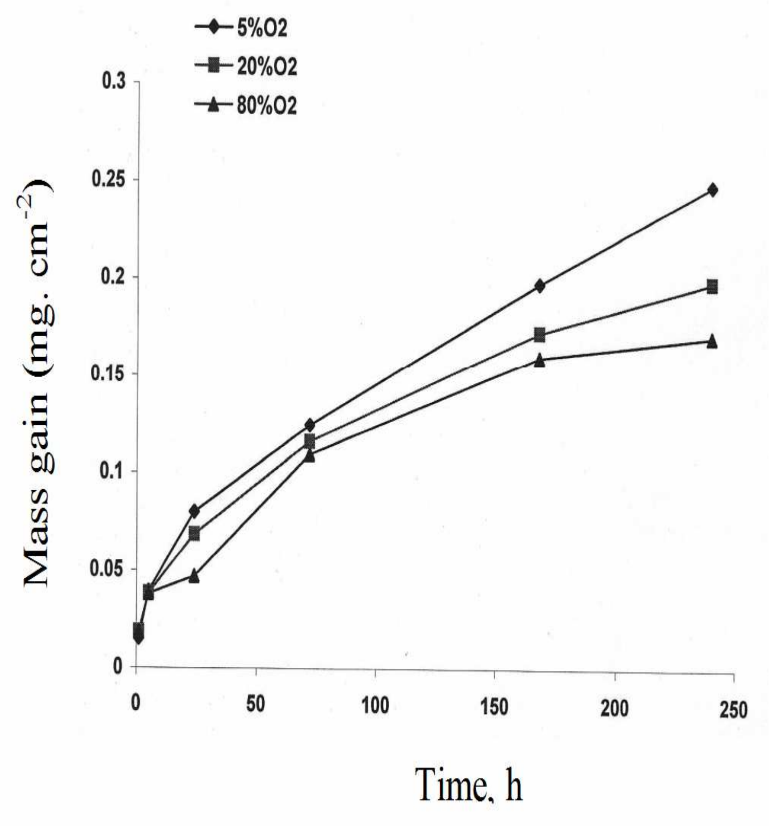

Figure 4: Weight gains versus exposure time for the Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation up to 240h

The divergence of mass gain data of the alloy in the three Ar-O_2 atmospheres at 850°C is very similar for up to 240h (Figure 5). At 950°C, the effect of oxygen partial pressure became more noticeable and the oxidation parabolic rate constant in Ar-5%O_2 is one order of magnitude higher than in Ar-80%O_2 (Table 4). In Ar-5%O_2 and Ar-20%O_2 at 950°C, the alloy showed parabolic oxidation behaviour, whereas in Ar-80%O_2 atmosphere quasi-parabolic ‘protective’ oxidation kinetic behaviour was observed (Figure 6).

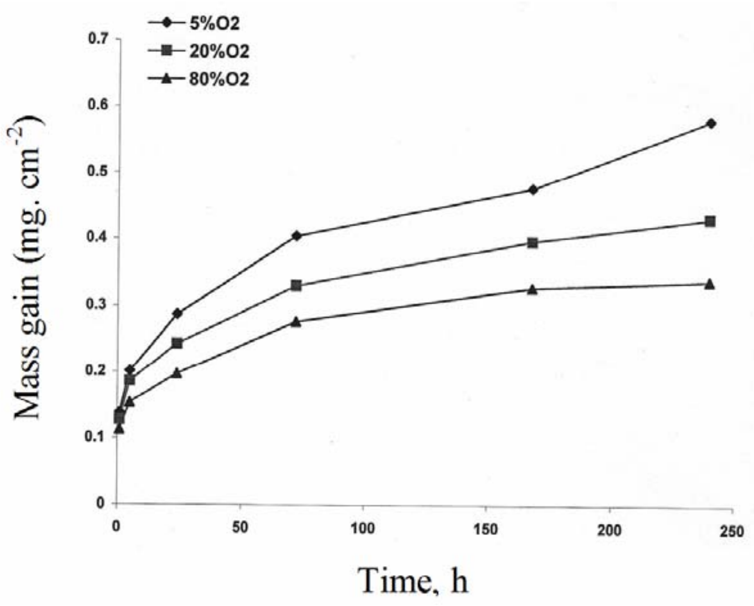

Figure: 5 Weight gains versus exposure time for the Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation for up to 240h

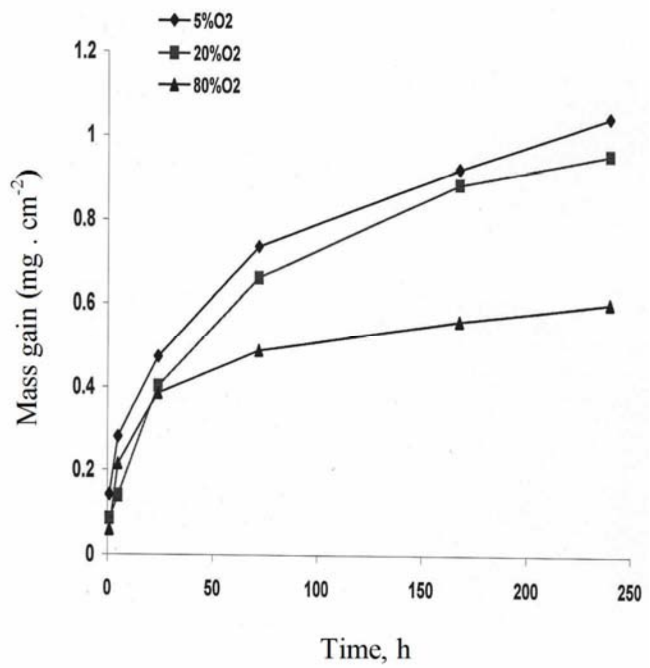

Figure 6: Weight gains versus exposure time for the Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation for up to 240h

Scale Morphology and Composition of Ti-46.7Al-1.9W-0.5Si Alloy after Isothermal Oxidation in Ar-5%O_2, Ar-20%O_2 and Ar-80%O_2 Atmospheres

Generally, the scale formed in Ar-5%O_2 at 750°C was similar to that in Ar-20%O_2 but slightly different in Ar-80%O_2. During the initial periods of oxidation at 750ºC (up to 5h), no corrosion product was detected in the three Ar-O_2 atmospheres. After 72h exposure at 750°C, very low intensity peaks of TiO_2 and Al_2O_3 in the XRD pattern was identified. With the increase of exposure time to 240h, the scale became visible at high magnification (Figure 7). The proportion of TiO_2 and Al_2O_3 islands in the scale in the three Ar-O_2 atmospheres was very hard to distinguish at 750°C for up to 240h exposure. However, the intensities of TiO_2 peaks in Ar-5%O_2 were higher than those in Ar-80%O_2. Although the XRD patterns (presented elsewhere) of the oxidised samples indicates the presence of both TiO_2 and Al_2O_3, the EDX results (presented elsewhere) of the corresponding samples revealed a mixed scale of TiO_2 and Al_2O_3 was formed in both Ar-5%O_2 and Ar-80%O_2 atmospheres. However, it is more obvious in Ar-5%O_2, the scale showed transverse micro-cracks perpendicular to the scale/alloy interface – Figure (8). Also a very thin depleted layer of aluminium at 750°C after 240h oxidation in Ar-5%O_2 and Ar-80%O_2 atmospheres was detected by EDX analysis. However, it was not possible to identify this thin layer by the available XRD. Figure (9) shows the surface morphologies of the scale formed on Ti-46.7Al-1.9W-0.5Si alloy after oxidation in Ar-5%O_2 and Ar-80%O_2 at 850°C for 5h exposure. The rutile in Ar-5%O_2 started to overgrow (Figure 9a) resulting in a scale predominant of TiO_2 with some islands of Al_2O_3 (TiO_2/Al_2O_3) scale, as revealed by EDX analysis. Whilst for the scale in Ar-80%O_2, the concentration of TiO_2 and Al_2O_3 has changed over, i.e. more Al_2O_3 can be observed (Figure 9b) and the scale becomes predominant in Al_2O_3 (Al_2O_3/TiO_2), A very thin layer rich in titanium in Ar-5%O_2 and Ar-80%O_2 was detected by EDX. However, this layer was not possible to be identified by XRD in both atmospheres. The intensity of the SiO_2 peak is higher in Ar-5%O_2 than that in Ar-80%O_2. By increasing the exposure time at 850ºC to 72h, more islands of TiO_2 were observed in Ar-5%O_2 than that at Ar-80%O_2. After 240h of oxidation in Ar-5%O_2 and Ar-80%O_2 atmospheres the top surface of Ti-46.7Al-1.9W-0.5Si alloy is almost covered with TiO_2 in both atmospheres, Figures (10a and 10b). However, still Al_2O_3 islands could be seen after oxidation in Ar-80%O_2 for 240h at 850ºC, Figure (11b). Also localised oxidation was observed in Ar-5%O_2 atmosphere especially in places where W was observed, Figure (11a) whilst, the scale in Ar-80%O_2 was protective and almost flat to the substrate (Figure 11b). Generally the thickness of the aluminum-depleted layer identified by XRD as Ti_3Al increased with the increase in exposure time and temperature in both Ar-5%O_2 and Ar-80%O_2 atmospheres.

At 950°C, the surface morphologies of the oxidized samples in Ar-5%O_2, Ar-20%O_2 and Ar-80%O_2 were covered with rutile Figure (11). However, the cross-sectioned scales of the samples oxidized in Ar-5%O_2 , Ar-20%O_2 showed substantially thicker TiO_2 layer Figure (11a and 11b), whereas, the scale in Ar-80%O_2 is consisting almost of "protective" Al_2O_3 containing very thin of discontinuous layers of rutile Figure (11c),. More interesting features of the cross-sectioned scales were observed at 950°C in both Ar-5%O_2 and Ar-80%O_2 atmospheres: The thickness of the depleted layer increases as the exposure time increased in both atmospheres. However, the depletion band of aluminum increased as the oxygen partial pressure increased at a temperature. For example, the thickness of the depleted layer at 950°C after 240h oxidation in Ar-80%O_2 is about two times than in Ar-5%O_2. Another important feature of the scale formed in Ar-5%O_2 and Ar-80%O_2 at 950°C is that, after 240h the existence of porosities within the inner layer of the scale in Ar-5%O_2 and voids at the scale/alloy interface in Ar-80%O_2 can be observed. Generally, the XRD results of the oxidized samples in Ar-O_2 atmospheres revealed no sign of nitridation of the Ti-46.7Al-1.9W-0.5Si substrate were detected.

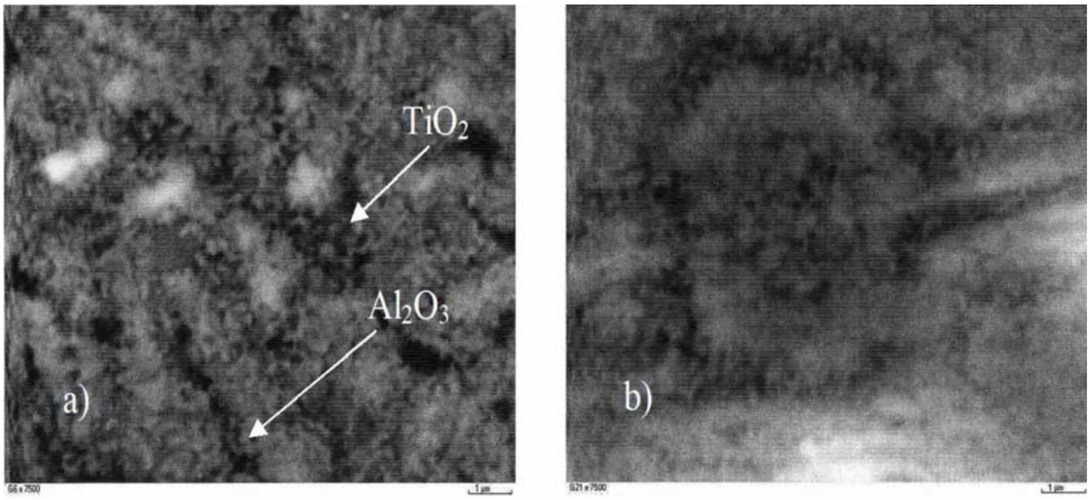

Figure 7: SEM micrographs of Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation at 750^{o}C for 240h (a) in Ar-5%O$_2$ and (b) in Ar-80%O$_2$

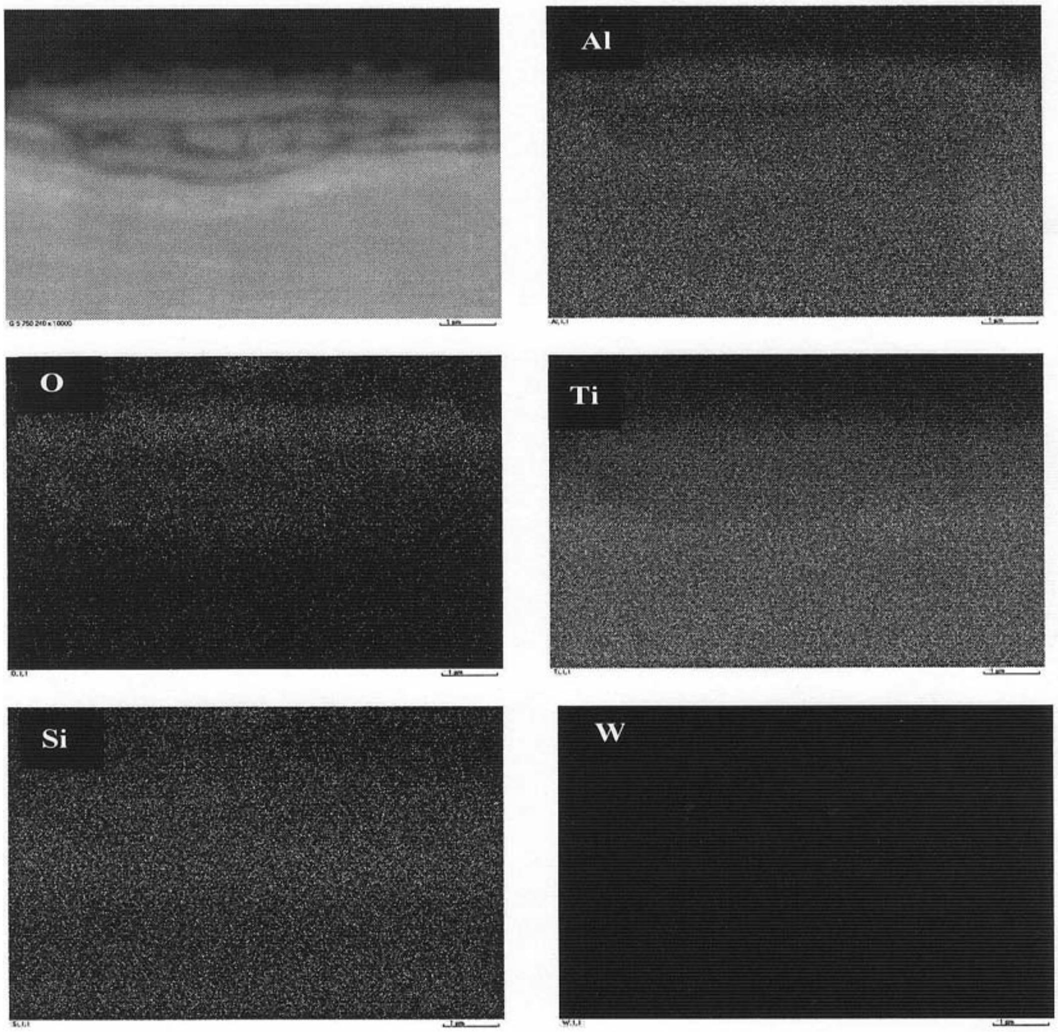

Figure 8: Back scattered electron Digimaps of Ti-46.7Al-1.9W-0.5Si intermetallic alloy oxidised in Ar-5%O$_2$ at 750°C for 240h

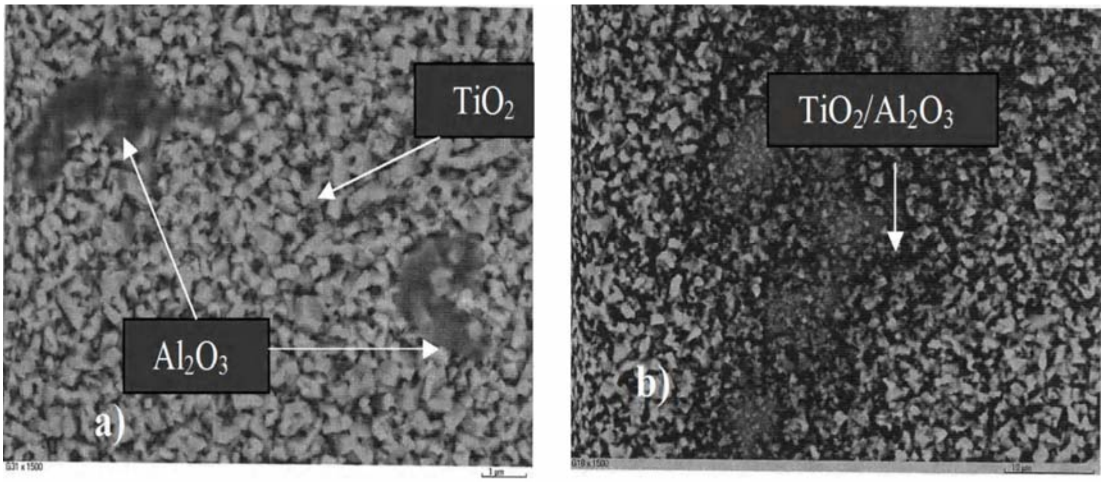

Figure 9: Back scattered SEM micrographs of Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation at 850°C for 5h (a) in Ar-5%O_2 and (b) in Ar-80%O_2

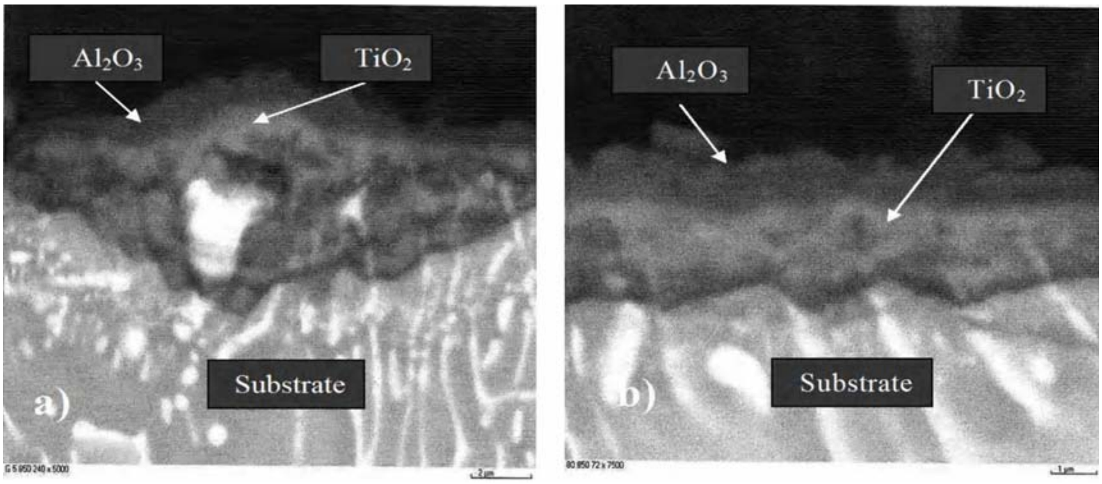

Figure 10: Back scattered SEM cross-sectioned micrographs of Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation at 850°C for 240h (a) in Ar-5%O_2 and (b) in Ar-80%O_2

DISCUSSION OF THE RESULTS

In general the scale microstructures and the kinetics of scale formation in all the three different partial pressures of oxygen (0.05, 0.2 and 0.8) x 10^5 Pa are different. Comparison of the present oxidation results of the Ti-46.7Al-1.9W-0.5Si alloy in different oxygen partial pressures revealed the differences in the scale properties and kinetics at the three atmospheres. Such differences can be understood, to some extent, by considering the defect structures in the scale, which are influenced by the oxygen partial pressures in the reactive atmospheres. Previous studies on the TiO_2 and Al_2O_3 concluded that the transport processes in TiO_2 are more rapid than in Al_2O_3 due to the defect structure of TiO_2. Also, the solubility of Al_2O_3 and TiO_2 decreased as the partial pressure of oxygen increased in the environment. These findings are consistent with the obtained results in this study and will be used for the interpretation of our experimental observations.

For illustration, the cross-sectional morphology (Figure 11) of the scale formed on Ti-46.7Al-1.9W-0.5Si alloy at 950ºC after 240h exposure in Ar-5%O_2, Ar-20%O_2

and Ar-80%O_2 is employed to explain the effect of oxygen partial pressure on the oxidation behaviour of Ti-46.7Al-1.9W-0.5Si alloy. After oxidation of Ti-46.7Al-1.9W-0.5Si alloy at 950ºC in all Ar-O_2 atmospheres proceeds, a multi-layered scale of alternating TiO_2 and Al_2O_3 is formed. The composition of the inner layer of the scale was different at various oxygen partial pressures in the oxidising atmosphere as illustrated in Figure 11. In Ar-5%O_2, the inner layer consisted predominantly of TiO_2 with some Al_2O_3 (Figure 11a). As the oxygen content increased in the reactive atmosphere (Ar-20%O_2), the Al_2O_3 content in the inner layer of the scale increased at the expenses of TiO_2 (Figure 11b).

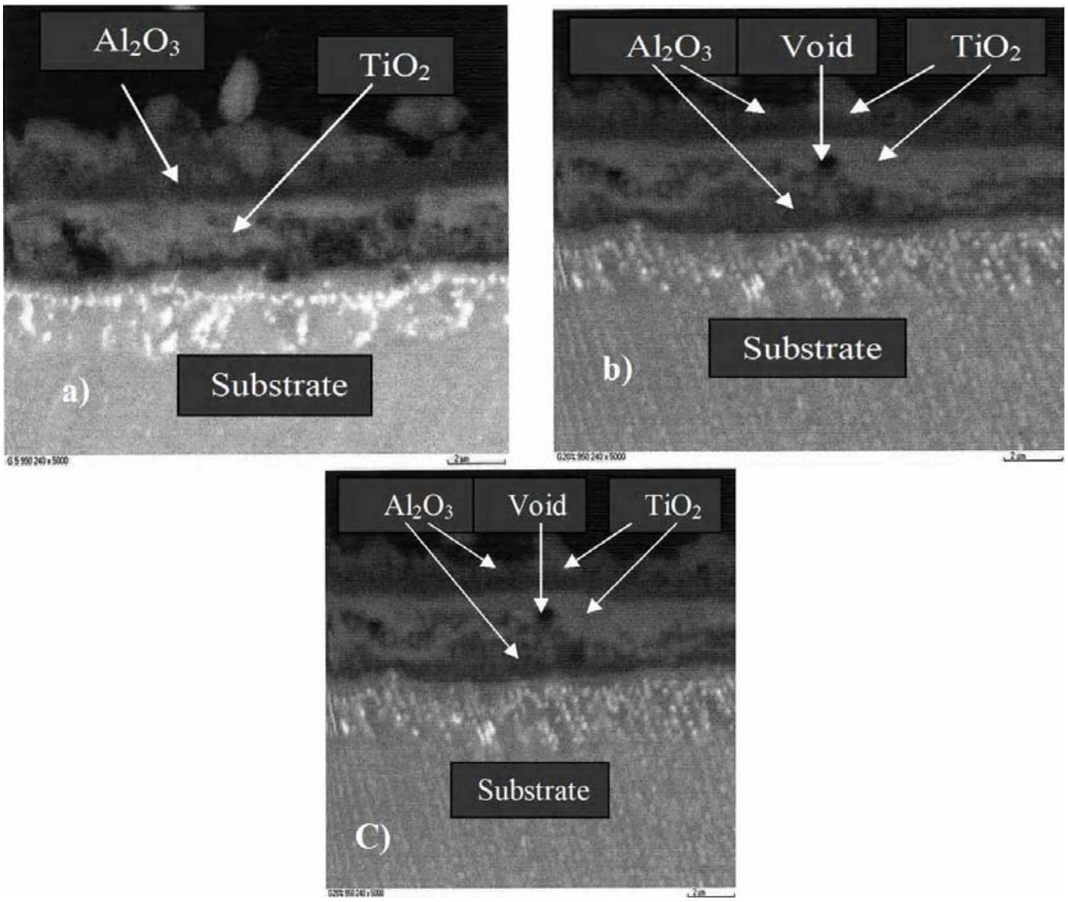

Figure 11: SEM cross-sectioned micrographs of Ti-46.7Al-1.9W-0.5Si intermetallic alloy after oxidation at 950°C for 240h (a) in Ar-5%O_2, (b) in Ar-20%O_2 and (c) in Ar-80%O_2

Further increase of oxygen in the Ar-O_2 gas mixture (Ar-80%O_2), led to the formation of oxide scale consisting of mostly Al_2O_3 with discontinuous TiO_2 (Figure 11c). The gradual increase of Al_2O_3 in the scale with the increase of oxygen partial pressure in the reactive atmosphere is due to the following reasons: (i) the lower solubility of Al_2O_3 in TiO_2 at higher oxygen partial pressures in the reactive atmosphere, (ii) lower defect structure in Al_2O_3 if compared to that in TiO_2. The consequences of the Al_2O_3 formation in the scale at higher oxygen partial pressures is that minimum possible flux of oxygen vacancies in the scale significantly lower than that at lower oxygen partial pressures. In fact, the process of Al_2O_3 barrier formation at various oxygen contents in the environment has been reported by Becker et. *al.* [31] and the present experimental observations is consistent with their schematic model. Furthermore, the process of Al_2O_3 dissociation reported in the same study of Becker et. al. [31] explains the existence of porosity at the outer part of the inner layer at low oxygen content in the atmosphere (e.g. Ar-5%O_2 Figure (11a). The dissociation of Al_2O_3 at higher oxygen partial pressures (Ar-20%O_2 and Ar-80%O_2) in the scale probably changes the defect concentration in TiO_2.

CONCLUSION

The observed reduction of Ti-46.7Al-1.9W-0.5Si alloy scale thickness in Ar-80%O_2 with the likely reduction in the rate of diffusion of the reacting species (oxygen, aluminium and titanium) throughout the scale were associated to:

- The increased tendency of the formation of relatively pure Al_2O_3 – rather than mixed scale of TiO_2 and Al_2O_3 (observed at Ar-5%O_2).
- The low defect structure of the formed Al_2O_3 compared to that of TiO_2.
- The low solubility of Al_2O_3 in TiO_2 at higher oxygen pressure.

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