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The influence of cooling rate during alloy casting on the oxidation behaviour of TiAl-based intermetallics

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The oxidation behaviour of the intermetallic phase Ti–50 at% Al at 900 °C was studied. It was found that the oxidation behaviour strongly depends on the composition and distribution of the γ and α_2-phases in the alloy microstructure. As this microstructure strongly depends on the alloy cooling rate, the oxidation behaviour of TiAl-based intermetallics is significantly affected by the casting procedure and subsequent heat treatment. Rapid cooling from high temperature ($T \geq 1400$ °C) has a beneficial effect on oxidation behaviour.

1. Introduction

TiAl-based intermetallics are of potential interest as construction materials because of their high-temperature strength in combination with low density. Applications of this class of materials at temperatures higher than 700 °C are, however, limited due to their poor corrosion resistance [1, 2]. The oxidation behaviour of TiAl-based alloys has been extensively investigated, especially with respect to the influence of ternary and quaternary alloying additions [1, 3–5]. The published oxidation data for TiAl-based alloys show an extremely large scatter. The reason for this is that the surface oxide scale can easily change from an alumina to a titania-based layer, which leads to a very large change in oxidation rate. In the present paper it will be shown that for TiAl-based materials with around 45–50 at % aluminium, which are the most promising from the viewpoint of mechanical properties, this change from one oxide type to another is closely related to the alloy microstructure, which is merely determined by the cooling procedure during alloy casting. It is believed that this effect, which was hardly considered in the literature until now, is at least partially responsible for the large scatter observed in published oxidation rates of titanium aluminide-based intermetallics.

2. Experimental procedure

The alloy used in this study was Ti50Al (addition in at %). The detailed chemical composition of the alloy is given in Table I. The alloy was produced by melting the base metals titanium and aluminium in a vacuum induction furnace and by subsequent pouring into a ceramic cylindrical mould with a diameter of 10 mm. The ingot obtained was cut into discs with a thickness of 1 mm. The samples were ground with SiC paper up to an 800 grit surface finish and degreased in alcohol before using. The oxidation of the samples was carried out in air at 900 °C during 24 and 100 h. The alloy microstructure and the oxidation products formed were analysed by optical and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX). The chemical composition of the scale was analysed by electron microprobe analysis (EPMA).

3. Results

3.1. Alloy microstructure

The microstructure of the investigated alloy is shown in Fig. 1. It is obvious that the region near the edge of the sample possesses a different microstructure from that in the central part. The average aluminium and titanium ratios measured by EDX for the regions designated 1, 2 and 3 in Fig. 1 are collected in Table II. The outer region contains mainly two-phase grains composed of lamellae of γ-TiAl and α_2-Ti$_3$Al. In the inner region two types of grain are observed: brighter areas containing only γ-TiAl with an aluminium content which is higher than that according to the Ti–Al phase diagram [6] in the equilibrium state (region 2 in Fig. 1d), and darker areas (region 3) which are composed of two phases: γ-TiAl and α_2-Ti$_3$Al. These two-phase regions contain a smaller average concentration of aluminium than the grains with a similar structure in the outer part of the sample (Table II).

3.2. Oxide scale structure

As shown in Fig. 2, the appearance of the sample after 24 h oxidation at 900 °C is different in the inner and outer regions. On the outer part of the specimen a thin and well adhered alumina scale has formed (Fig. 3d, e and f) which did not spall after cooling. Nearer to the

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centre of the specimen titania nodules were formed (Fig. 3a, b and c). In the middle of the sample these nodules joined each other and formed a continuous, thick titania-based scale. After 100 h of oxidation a continuous titania-based scale was found on the inner part of the specimen. The results of the EPMA analyses of the scale cross-section in this area are shown in Fig. 4 and Table III. The outer part of the scale consists

TABLE I Chemical composition of the alloy studied (Ti and Al in at %, other elements in p.p.m.)

Ti	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Zr	Nb	Sn	Sb	W	Ta	Pt
49.3	50.1	44	30	50	946	9	24	40	7	160	14	2.3	2.1	23	3.0	21	1.2	< 1

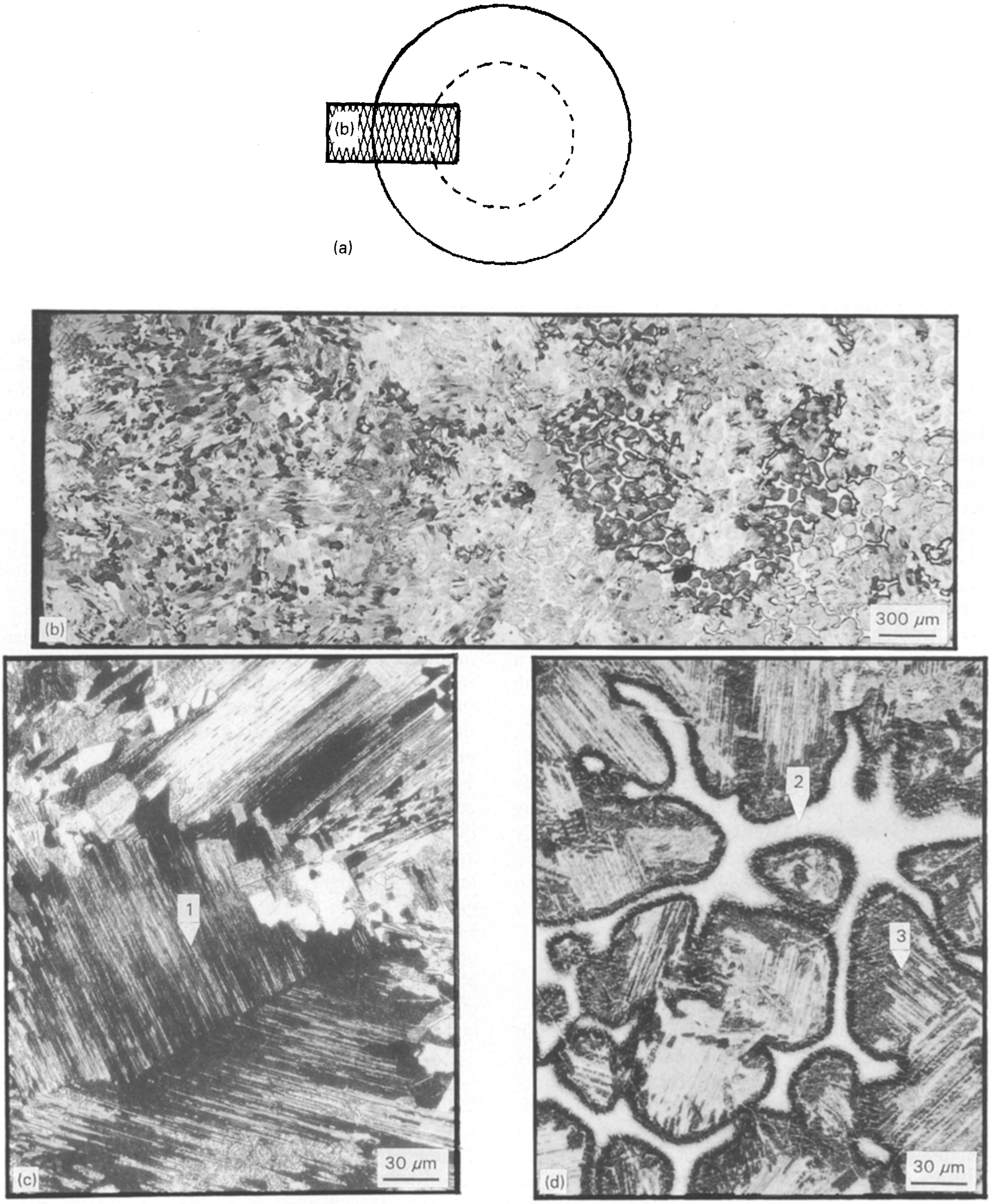

Figure 1 (a) Illustration of microstructural study of disc-shaped specimen of Ti–50 Al. (b) Polished cross-section of the alloy after etching: area indicated in (a). (c) Region near edge of specimen at higher magnification. (d) Region in the central part of the specimen at higher magnification.

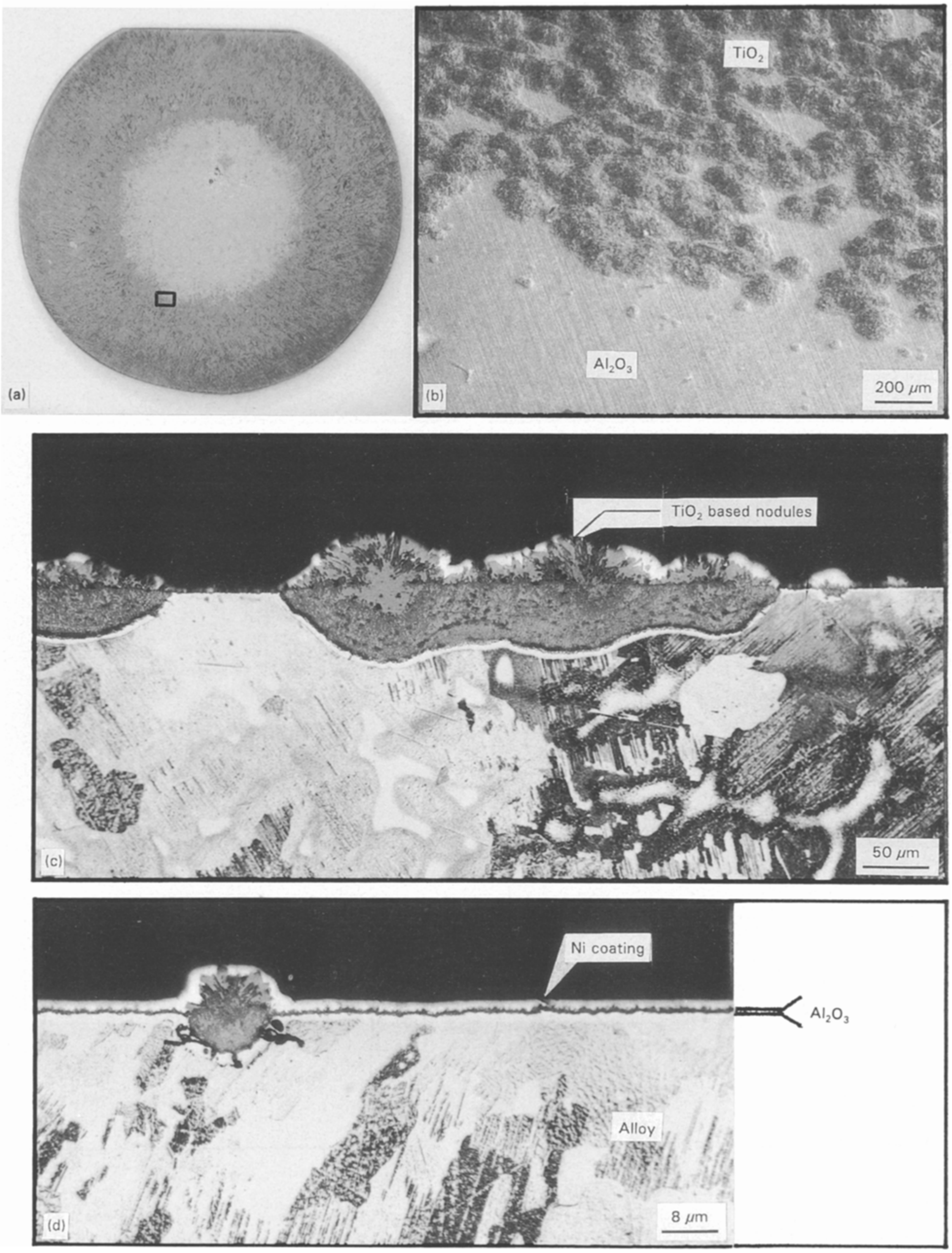

Figure 2 (a) Appearance of the sample after 24 h of oxidation at 900 °C in air. (b) Region boxed in (a) at higher magnification (SEM picture). (c) Polished cross-section of surface scale in the inner region of the specimen. (d) Polished cross-section of surface scale in the outer specimen region.

of TiO_2. Beneath this layer a thin discontinuous alumina-rich scale is found. The lighter part of the scale consists of an Al_2O_3–TiO_2 mixture. Beneath a thin aluminium-rich layer, designated as an internal oxidation zone, a depleted alloy layer exists which consists of Ti_3Al in which a considerable amount of oxygen was dissolved. Some indication was found that

TABLE II Average relative concentrations of Ti and Al (at %) in different areas of the alloy, determined by EDX; numbers refer to designations in Fig. 1

	1	2	3
Ti	49	42	51.5
Al	51	58	48.5

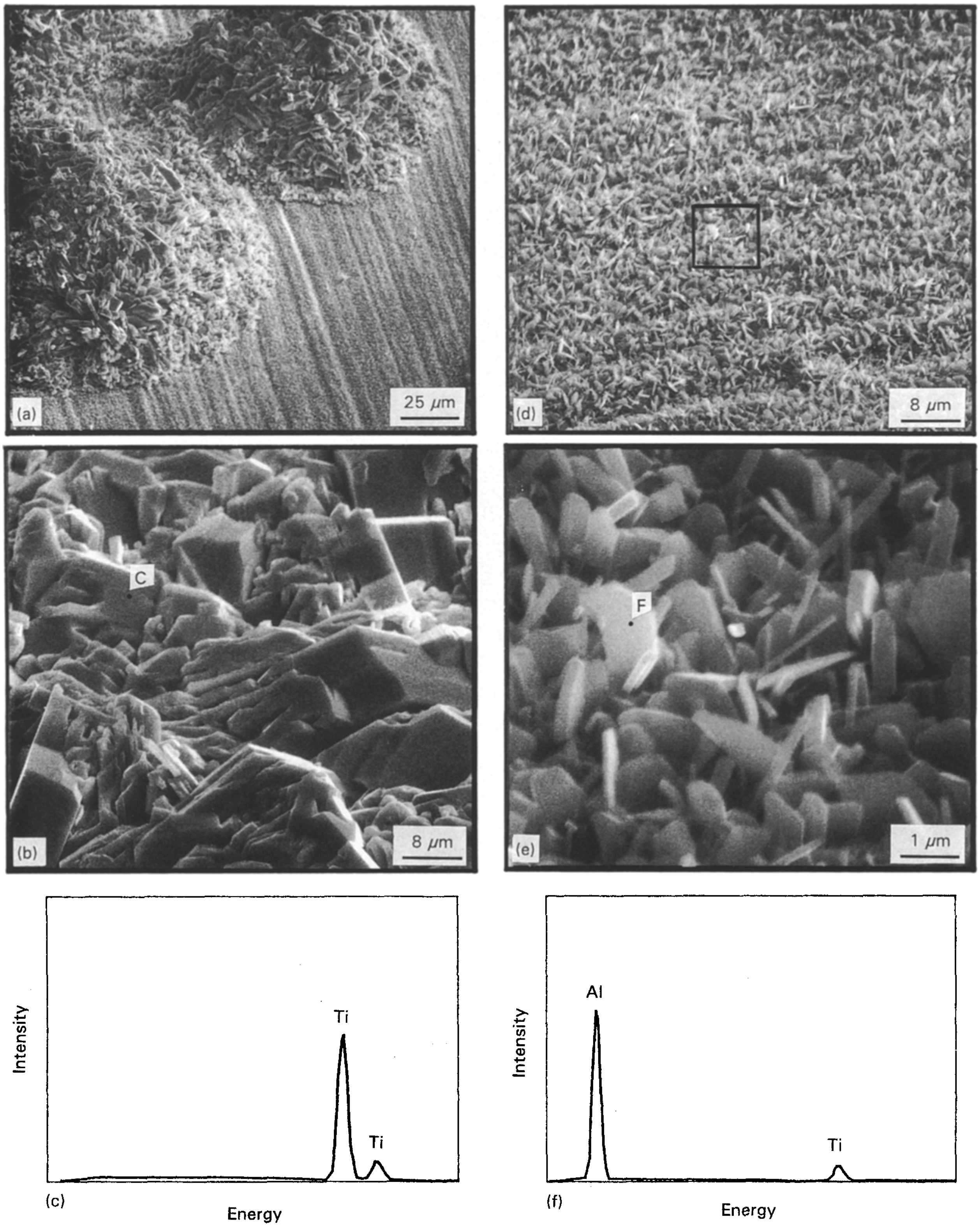

Figure 3 (a) Oxide morphology in the inner part of the specimen after 24 h of oxidation at 900 °C in air. (b) Morphology of nodules in (a) at higher magnification. (c) EDX spectrum of point designated C in (b). (d) Morphology of scale in the external part of the sample. (e) Higher magnification of area boxed in (d). (f) EDX spectrum of point designated F in (e).

TABLE III EPMA analyses (at %) of places designated in Fig. 4.

	Ti	Al	O
1	33.2 ± 0.2	0.080 ± 0.002	66.7 ± 0.1
2	1.0 ± 0.8	37.6 ± 1.3	61.4 ± 0.1
3	20.5 – 33	1.4–18.3	61–65
4	53.5 ± 1.8	32.5 ± 1.0	14.0 ± 0.1
5	51.0 ± 0.3	49.0 ± 0.3	–

this layer (4 in Fig. 4) consisted of two phases which differed in oxygen content.

4. Discussion

A strong difference in the oxidation behaviour between the outer and inner parts of the cast titanium aluminide bar was observed. These differences in oxi-

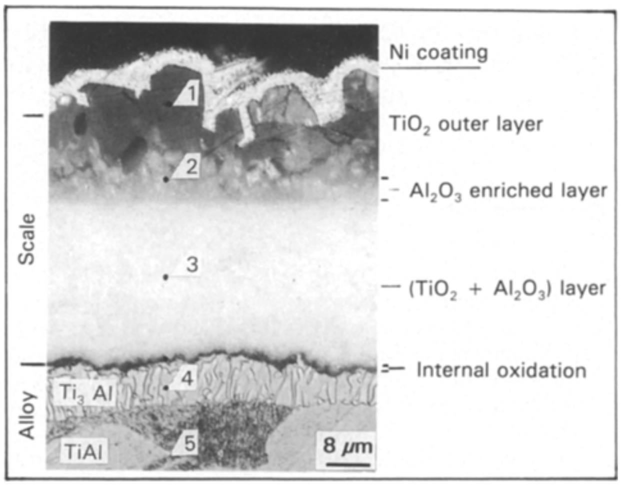

Figure 4 Cross-section of scale formed after 100 h oxidation in air at 900 °C. Numbers refer to compositions given in Table III.

dation behaviour can be explained by differences in alloy microstructure. The differences in microstructure between the inner and outer parts of the cast bar are related to the casting procedure applied. Because the molten alloy was poured into a cool ceramic crucible, the crystallization process occurs initially very fast and starts in the outer part of the ingot. Initially α-Ti is precipitated whereas the melt is enriched in aluminium. Because of the rapid cooling the α-Ti and γ-TiAl phases do not reach their equilibrium compositions as given by the phase diagram (Fig. 5). On reaching the eutectoid temperature (1125 °C) the α-Ti rapidly transforms to a fine lamellar microstructure of $\alpha_2 + \gamma$. The α_2-Ti_3Al phase contains a higher aluminium content than expected from the equilibrium phase diagram. This mechanism is confirmed by the fact that in the outer region of the specimen the average composition nearly equals that of the original alloy, whereas it consists nearly totally of a two-phase mixture formed by eutectoid reaction.

In the inner part of the ingot, the solidification process of the alloy proceeds much more slowly. Therefore the solidification occurs in a stage which is nearer to the thermodynamic equilibrium condition between solid and liquid phases. Upon cooling of the melt of composition A in Fig. 5, α-Ti of composition B in Fig. 5 will precipitate. At the same time the melt becomes enriched in aluminium (see arrow). If total equilibrium prevailed, solidification would be finished when the composition of the α-Ti phase was equal to that of the original alloy (point C in Fig. 5). Because no total equilibrium occurs, the melt will eventually become enriched in aluminium according to the liquidus line as indicated by the arrow in Fig. 5. This leads to formation of γ-TiAl with a high aluminium content (Fig. 1d and Table II).

The primary α-Ti phase will lower its aluminium content during further cooling before reaching the eutectoid temperature. Therefore the average aluminium content in the microstructure formed by eutectoid reaction is lower than that of the corresponding microstructure in the outer part of the ingot (Table II and Fig. 1c and d).

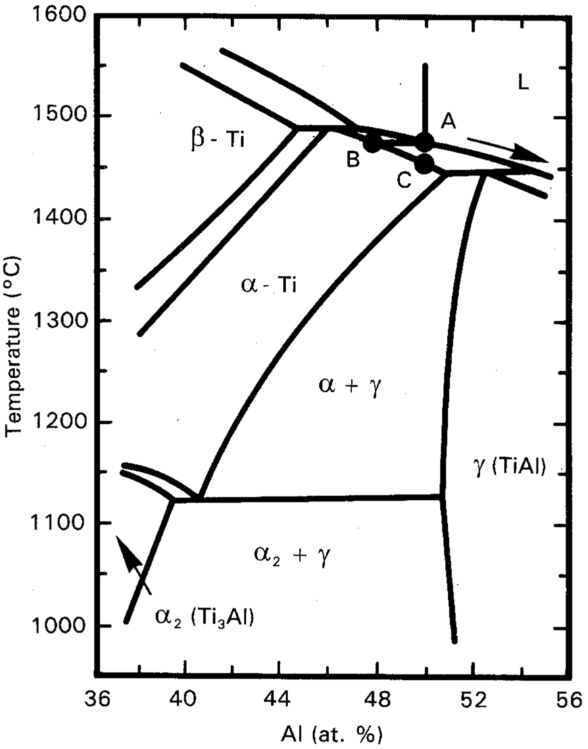

Figure 5 Ti–Al phase diagram [6]. Symbols A, B, C and the arrow at A are explained in the text.

Rahmel and Spencer [7] showed by thermodynamic calculation that for titanium aluminides containing about 50 at % aluminium or less, titanium rather than aluminium oxide is the stable phase. Misra [8] in studying diffusion couples of various titanium aluminides with Al_2O_3 verified this fact experimentally.

For an understanding of the oxidation behaviour of titanium aluminides, it is important to consider that in the as-cast state, binary alloys with the stoichiometric composition of 50 at % Ti and 50 at % Al consist of two phases, γ and α_2. Recent studies by the present authors [9] showed that on high-temperature exposure the γ phase is an alumina former, whereas the α_2 phase forms titania. This difference in oxidation behaviour is caused by the large difference between titanium and aluminium content in the two phases.

If in the alloy microstructure the α_2 phase is finely distributed along with the γ phase in the eutectoid, as occurs after rapid cooling, alumina scale formation dominates the overall oxidation behaviour. If the secondary γ phase formed becomes enriched in aluminium due to slower cooling as described above (Fig. 1d, point 2) the aluminium content in the eutectoid will be lower than in the rapidly cooled part of the sample and consequently the amount of α_2 will be relatively high. On high-temperature exposure in an oxidizing environment, this low-aluminium eutectoid microstructure forms rapidly growing titania-rich scales as shown in Fig. 2c and Fig. 4.

In practical cases these differences in microstructure, which lead to the above mentioned tremendous differences in oxidation behaviour, will mainly depend on the exact casting and cooling condition of the ingot and can even occur in one ingot as shown in the present study.

5. Conclusion

The oxidation behaviour of cast ingots of TiAl-based intermetallics with an aluminium content of around 48–50 at %, which are the most promising from the viewpoint of mechanical properties, strongly depends on the actual casting conditions. The as-cast material consist of two phases, α_2-Ti_3Al and γ-TiAl. The exact composition of these phases and their distribution in the alloy are determined by the prevailing cooling rates during casting. As the aluminium content in the α_2 phase is significantly smaller than that in the γ phase, the α_2 phase forms a titania-based scale on exposure to high temperature. Whether a rapidly growing titania-based scale or a slowly growing alumina layer will form on the alloy strongly depends on the relative amounts and composition of α_2 and γ, and especially on the way in which the two phases are distributed in the alloy. Rapid cooling leads to a fine eutectoid structure of α_2 phase and γ-TiAl. On this microstructure alumina is formed on high-temperature exposure, leading to low oxidation rates. Slower cooling rates lead to formation of γ-TiAl which is oversaturated in aluminium. Consequently the aluminium content in the α_2–γ eutectoid structure is low, which causes this part of the alloy to form a titania-based surface scale on high-temperature exposure. After longer times this titania-based scale dominates the overall oxidation process of the alloy.

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References

1. N. S. CHOUDHURY, H. C. GRAHAM and J. W. HINZE, in "Properties of High Temperature Alloys", Edited by Z. A. Foroulis and F. S. Pettit (Electrochemical Society, 1976) p. 668.
2. L. SINGHEISER, H. W. GRÜNLING and K. SCHNEIDER, in Proceedings of Conference on High-Temperature Materials for Power Engineering, Liege, September, 1990, Part II edited by E. Bachelet et al. (Kluwer Academic, Dordrecht, 1990) p. 1687.
3. R. PERKINS, K. CHIANG and G. MEIER, *Scripta Metall* **21** (1987) 1505.
4. J. SUBRAMANYAM, *J. Mater. Sci* **23** (1988) 1906.
5. U. FIGGE, W. J. QUADAKKERS, H. SCHUSTER and F. SCHUBERT, in Proceedings EUROCORR'92, Espoo, Finland, June 1992, Vol. I, edited by P. J. Tunturi, The Corrosion Society of Finland (Uusimaa Oy, Porvoo, 1992) p. 591.
6. S. C. HUANG and P. A. SIEMERS, *Metall. Trans.* **20A** (1989) 1899.
7. A. RAHMEL and P. SPENCER *Oxid. Met.* **35** (1991) 53.
8. A. K. MISRA, *Metall. Trans.* **22A** (1991) 715.
9. A. GIL, H. HOVEN, E. WALLURA and W. J. QUADAKKERS Corr. Sci. **34** (1993) 615.

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