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High-temperature oxidation process of intermetallic compound Ti–42 at% Al

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The oxidation process of two-phase (Ti_3Al and TiAl) intermetallic compound, Ti–42 at% Al, in air at 1073 and 1273 K has been investigated. The oxidation at 1273 K is much faster than that at 1073 K; however, the oxidation kinetics are similar. During heating up, TiO_2 scale forms initially on the compound surface at about 973 K, and then Al_2O_3 scale forms at about 1273 K. For the isothermal heating, TiO_2 scale slowly grows up at 1073 K, while at 1273 K both TiO_2 and Al_2O_3 scales grow up drastically. The outer oxide scale consists of TiO_2 and the inner one consists of a mixture of TiO_2 and Al_2O_3. The volume of Al_2O_3, which forms after TiO_2 formation at the initial stage of oxidation, is larger at an area adjacent to the oxide–compound interface.

1. Introduction

Intermetallic titanium aluminides are considered for application as high-temperature materials, because of their good strength-to-weight ratio even at elevated temperature [1].

Recently, however, it has been suggested that titanium aluminides such as TiAl, are susceptible to high-temperature oxidation, especially at elevated temperature above 1073 K [2]. For TiAl compound, porous Al_2O_3 scale enhances titanium diffusivity to the outside through Al_2O_3 scale, and as a result, TiO_2 scale forms at the external oxide layer [3]. On the other hand, the aluminium-rich compound $TiAl_3$ forms a protective Al_2O_3 oxide scale, due to the sufficient amount of aluminium to form Al_2O_3, so that $TiAl_3$ has better oxidation resistance than TiAl [3]. For two-phase (Ti_3 Al and TiAl) compound, a mixture of TiO_2 and Al_2TiO_5 has been reported to be identified at the external layer [4]. It has also been reported that addition of a third element (such as molybdenum) to the compounds, and surface treatment, improve the oxidation properties of titanium aluminides [5, 6].

It is, however, not clear how the high-temperature oxidation proceeds at the initial stage. This study investigated the initial stage of the oxidation process for a two-phase intermetallic compound in detail, by means of high-temperature X-ray diffractometry, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

2. Experimental procedure

The material used in this study was Ti–42 at% Al button ingot, argon arc-melted and then homogenized isothermally at 1273 K for 605 ks. Thin sheets (10 mm × 10 mm × 1 mm) were cut from the button ingot and then mechanically polished.

High-temperature X-ray diffractometry was applied to specimens heated up and heated isothermally at 1073 and 1273 K. The heating conditions are shown in Fig. 1. The heating rate was $0.33\ K\,s^{-1}$ and the maximum holding time at the isothermal temperatures was 7.2 ks. The specimens were heated in atmospheric conditions (static air).

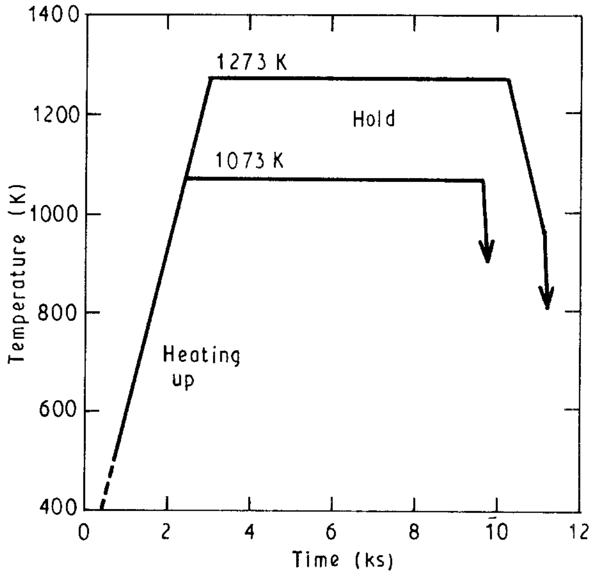

Figure 1 Heating conditions for high-temperature X-ray diffractometry measurements.

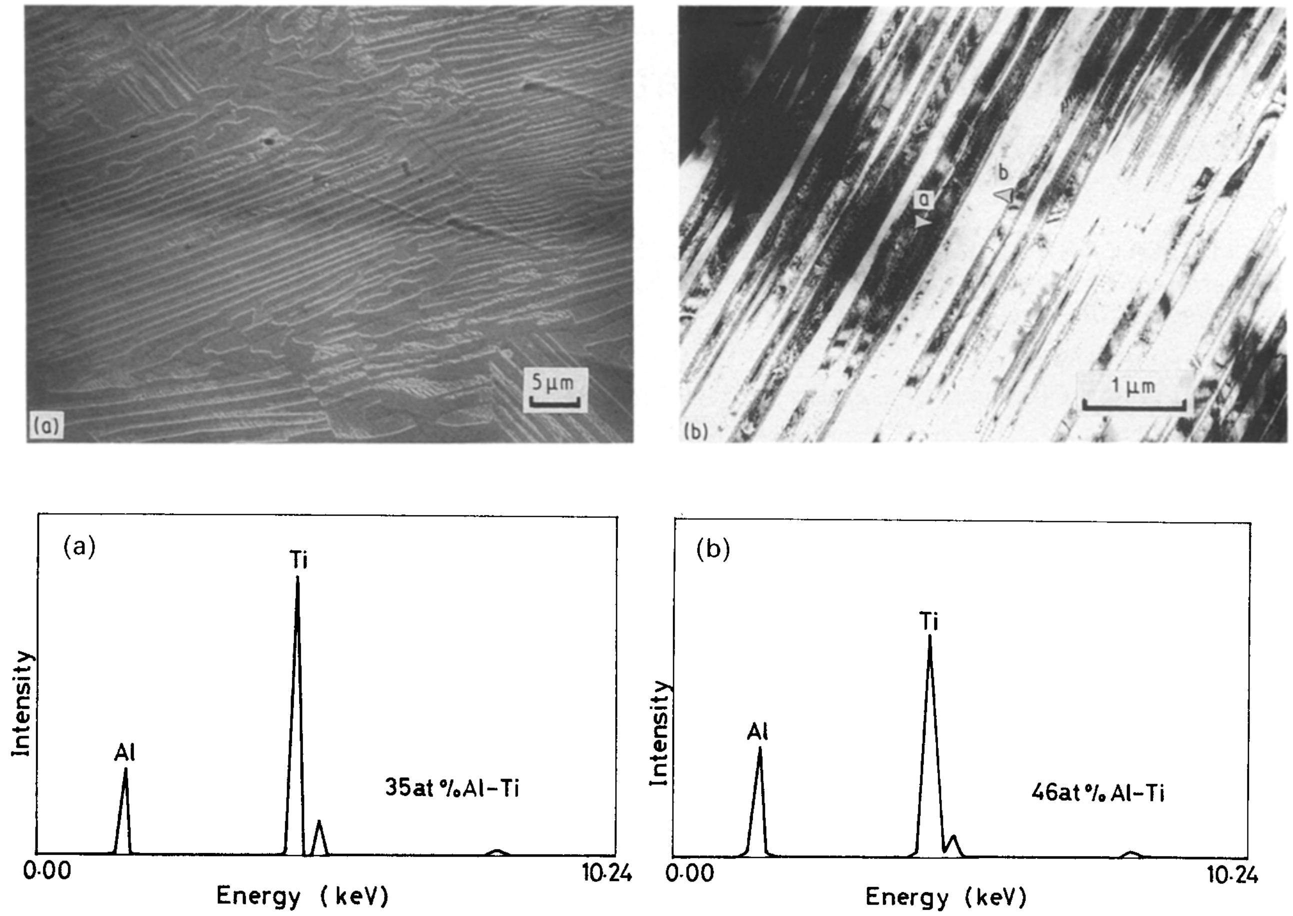

Figure 2 Microstructures of homogenized Ti–42 at % Al: (a) scanning electron microstructure, (b) transmission electron microstructure and the corresponding energy-dispersive X-ray spectra. EDX spectra denoted a and b are from the points indicated by arrows a and b in the TEM microstructure.

Weight gains were measured by thermogravimetric analysis in air, and the oxidized surfaces were observed by a SEM. The main elements (Ti, Al) of the oxides were analysed by an energy-dispersive X-ray (EDX) spectrometer. TEM observation of microstructures was also performed. The spatial resolving powers of TEM and SEM are estimated to be about 20 nmϕ and 1 μmϕ, respectively.

3. Results and discussion

Scanning and transmission electron microstructures of homogenized (1273 K for 605 ks) Ti–42 at % Al are shown in Fig. 2a and b, respectively. Both microstructures show lath/lamellar structural characteristics, and subsequent TEM–EDX analysis indicated that the microstructure consists of alternating plates of Ti_3 Al and TiAl.

Fig. 3 shows oxidation curves measured by thermogravimetric analysis. In this figure, heating conditions are also indicated. The weight gain at the temperature of 1273 K is much higher than that at 1073 K. It is obvious that oxidation has already occurred during heating up at a temperature above about 973 K. Oxidation curves at both 1073 and 1273 K follow the parabolic law for an oxidation time up to 24 ks. This means that the oxidation is not controlled by reactions between compound and oxide or oxide and air but controlled by diffusion in the oxide scale.

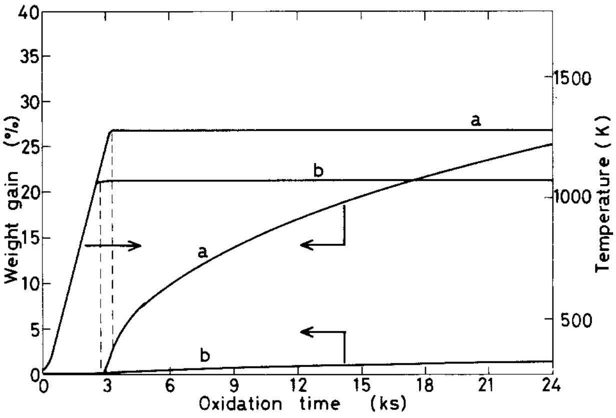

Figure 3 Oxidation curves of Ti–42 at % Al at temperatures of (a) 1273 K and (b) 1073 K.

The oxidized outer surfaces at 1073 K are shown in Fig. 4. Fine-particle oxide scale, observed for the shorter oxidation time, grows larger with increasing oxidation time. This is confirmed by comparing Fig. 4a with Fig. 4b. A portion of the compound surface still remains for the specimen oxidized for 7.2 ks, although the surface oxidized for 19.8 ks is fully covered with oxide.

The oxidized outer surfaces at 1273 K are shown in Fig. 5. In comparison with Fig. 4, the oxide grains at 1273 K become larger than those at 1073 K. EDX

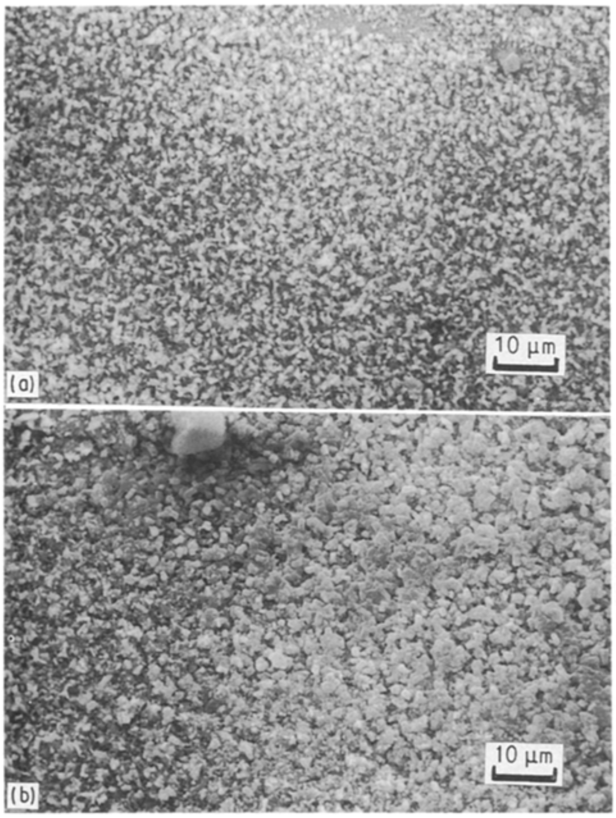

Figure 4 Scanning electron micrographs of outer-layer oxide scales oxidized at 1073 K for (a) 7.2 ks and (b) 19.8 ks.

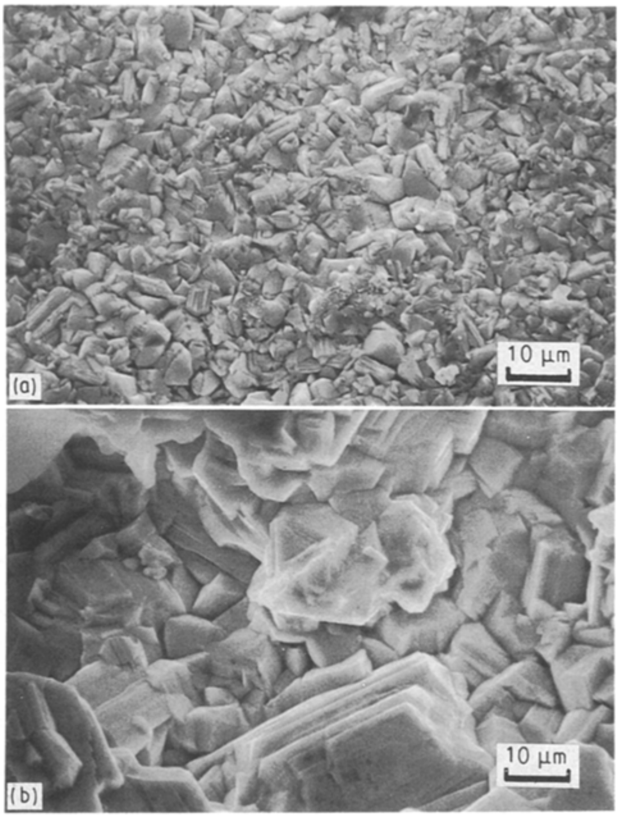

Figure 5 Scanning electron micrographs of outer-layer oxide scales oxidized at 1273 K for (a) 1.8 ks and (b) 19.8 ks.

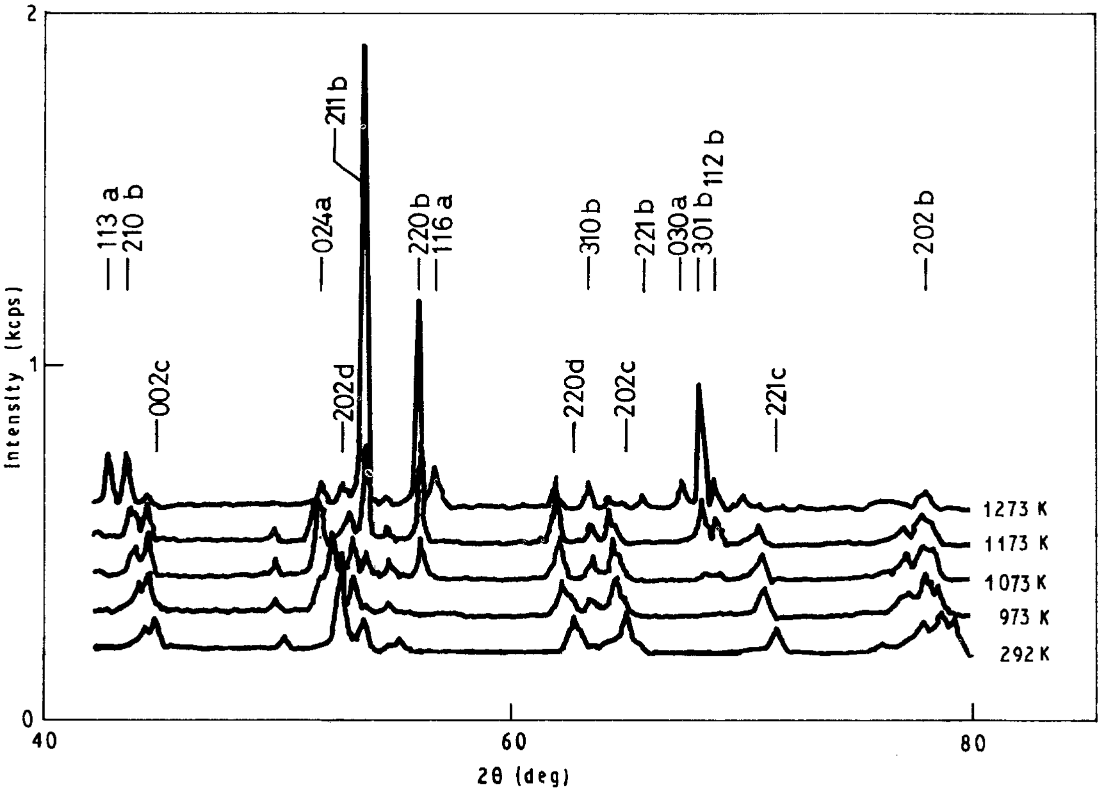

Figure 6 High-temperature X-ray diffraction spectra for Ti–42 at % Al specimen heated up from room temperature to 1273 K. (a) Al_2O_3, (b) TiO_2, (c) TiAl, (d) Ti_3Al.

analysis indicated that the oxidized outer surfaces at 1073 and 1273 K were titanium oxide.

X-ray diffraction profiles during heating up from 292 to 1273 K are shown in Fig. 6. The X-ray profile at 292 K (room temperature) shows that the compound consists of two kinds of crystal, i.e. Ti_3Al and TiAl. During heating up, each spectrum of Ti_3Al and TiAl shifts to the lower 2θ angle side because of thermal

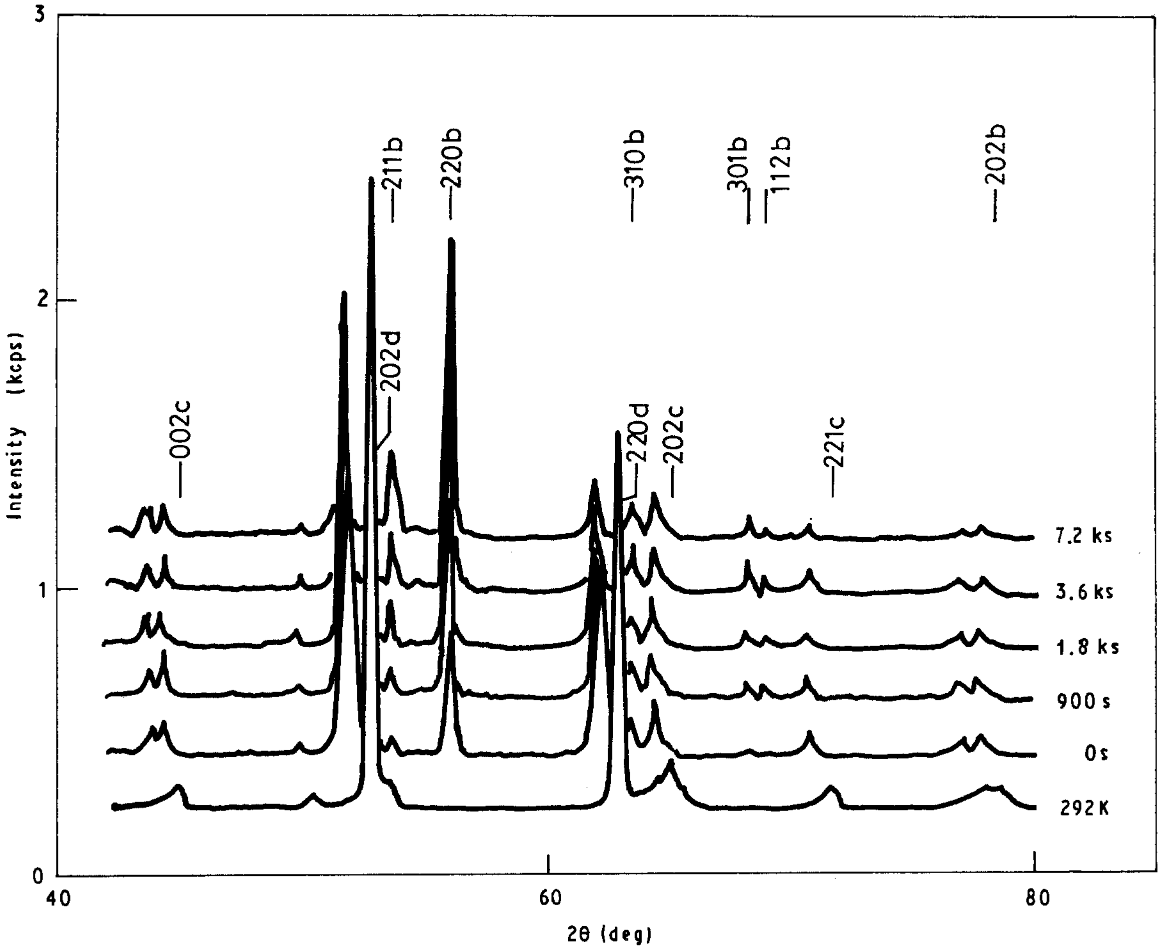

Figure 7 High-temperature X-ray diffraction spectra for Ti–42 at % Al specimen heated isothermally at 1073 K for heating times from 0 to 7.2 ks; the X-ray diffraction spectrum at 292 K (room temperature) is also included. (b) TiO_2, (c) TiAl, (d) Ti_3Al.

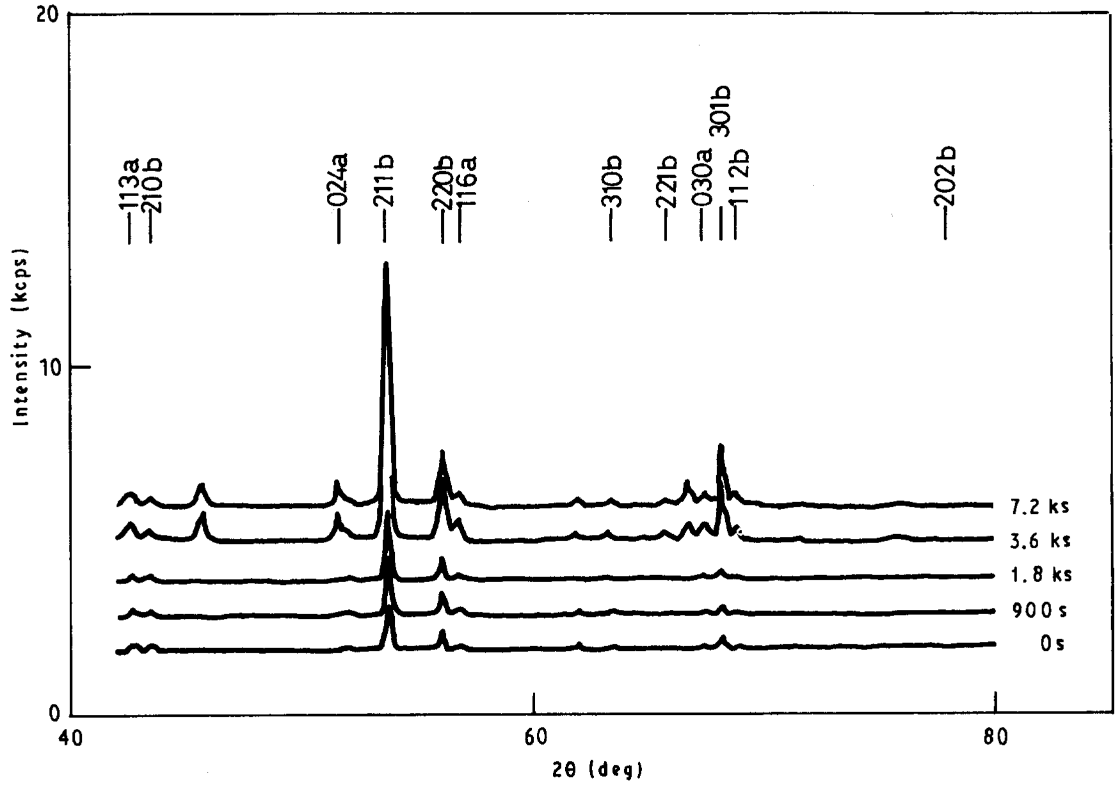

Figure 8 High-temperature X-ray diffraction spectra for Ti–42 at % Al specimen heated isothermally at 1273 K for heating times from 0 to 7.2 ks. (a) Al_2O_3, (b) TiO_2.

expansion. At the elevated temperature of 973 K, (2 1 1) and (3 1 0) weak diffractions of TiO_2 scale are identified. The X-ray intensities of these spectra increase with increasing temperature, indicating growth of TiO_2 scale. The spectra of Al_2O_3 scale are initially identified at the elevated temperature of 1273 K although these X-ray intensities are well grown up. It is, then, considered that Al_2O_3 scale initiated at a temperature between 1173 and 1273 K during heating up. X-ray intensities of Ti_3Al and TiAl at temperatures up to 1173 K decrease slowly with increasing temperature, which suggests that TiO_2 scale grows up slowly.

X-ray diffraction profiles for the specimen heated isothermally at 1073 K are shown in Fig. 7. The difference in X-ray intensities between Fig. 6 and Fig. 7 is due to the difference of specimens. TiO_2 scale grows up with increasing holding time at the isothermal temperature, although Al_2O_3 is not identified for the maximum holding time up to 7.2 ks.

X-ray diffraction profiles for the specimen heated isothermally at 1273 K are shown in Fig. 8. Each X-ray intensity for a holding time from 0 to 1.8 ks is almost similar, indicating that the oxidation rate is comparatively slow from 0 to 1.8 ks. When the

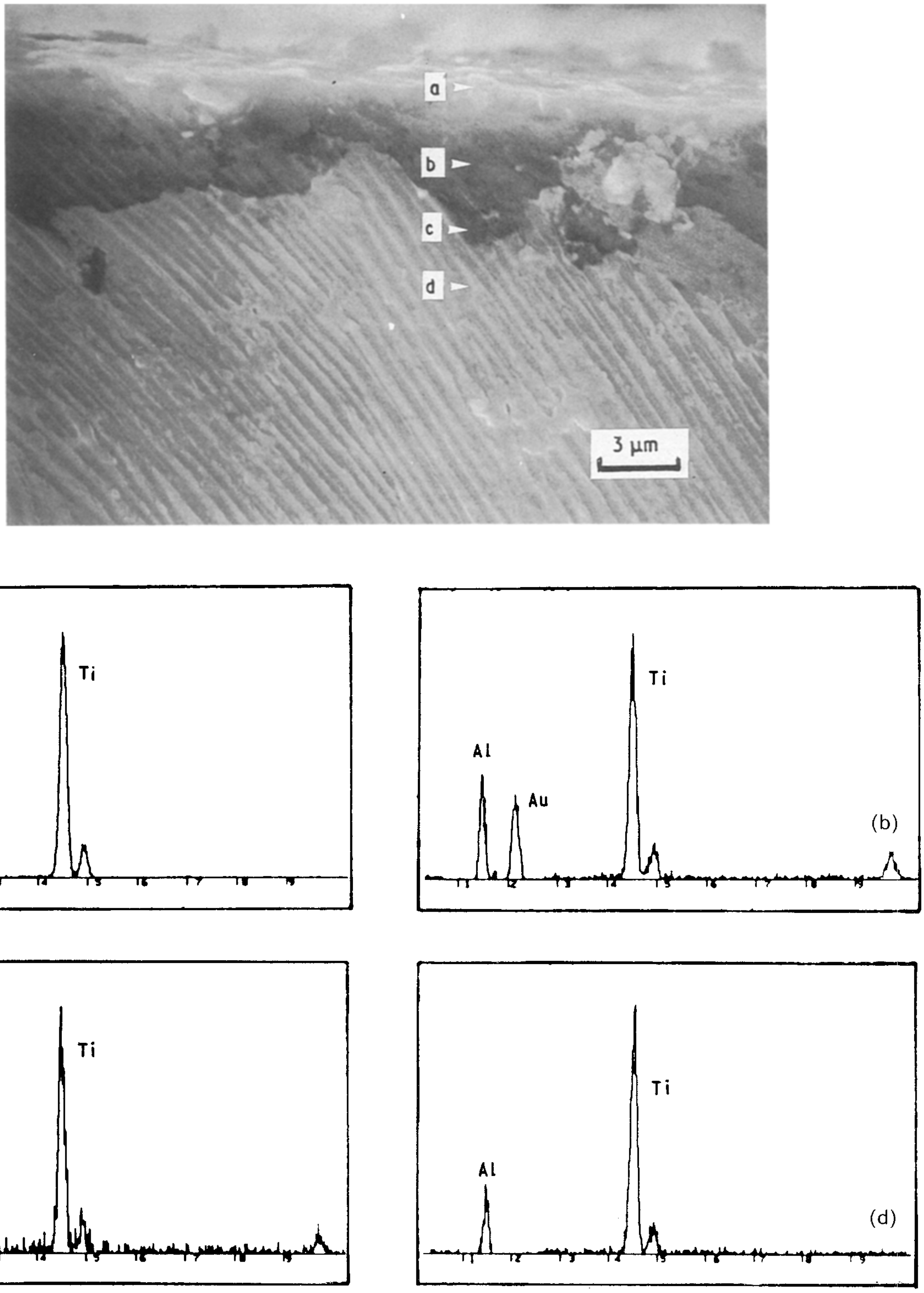

Figure 9 Scanning electron micrograph of cross-section of specimen heated at 1073 K for 19.8 ks and the corresponding energy-dispersive X-ray spectra.

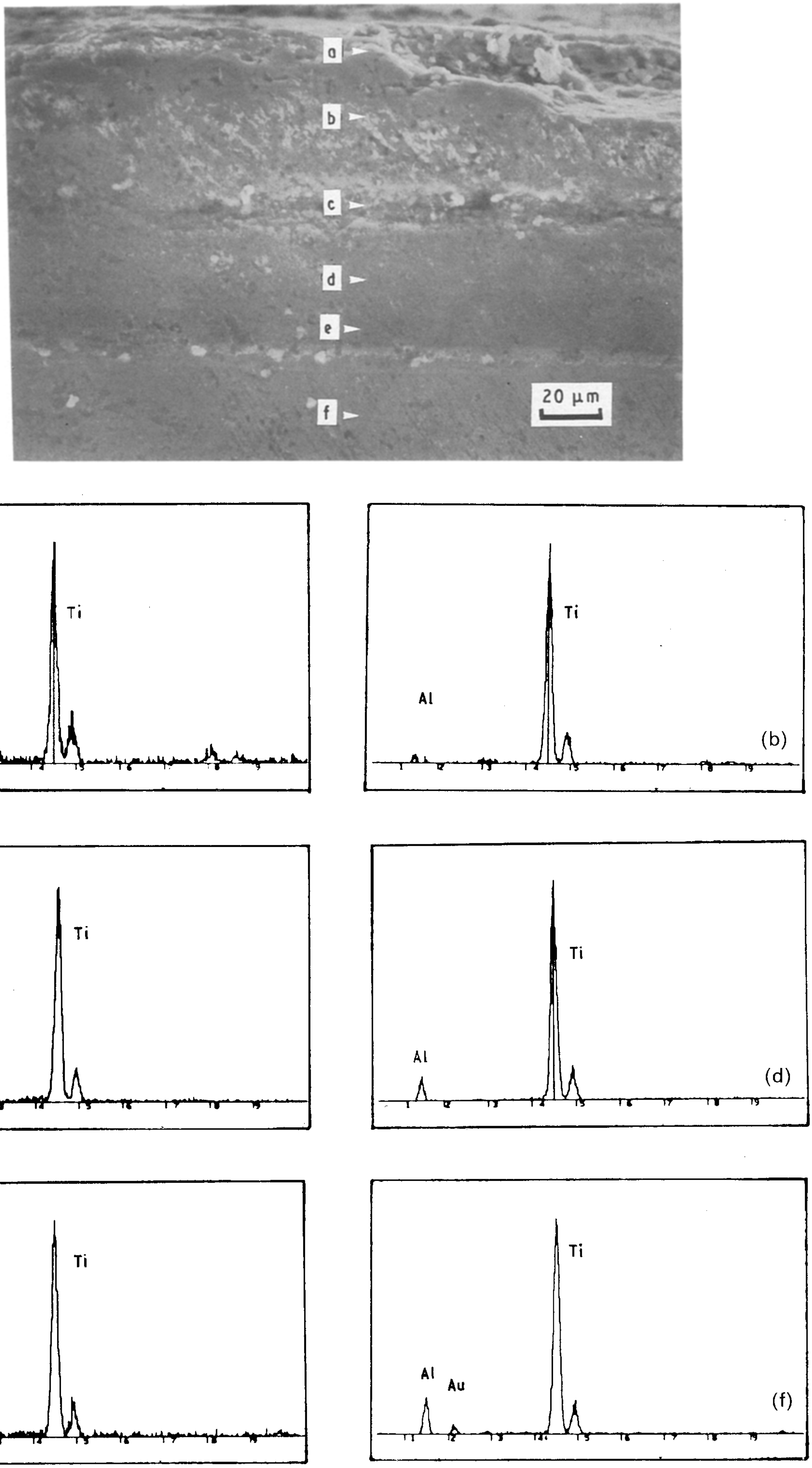

Figure 10 Scanning electron micrograph of cross-section of specimen heated at 1273 K for 19.8 ks and the corresponding energy-dispersive X-ray spectra.

holding time exceeds 1.8 ks, X-ray intensities of both TiO_2 and Al_2O_3 scales drastically increase, and the spectra of the original compound (Ti_3Al and TiAl) are not identified due to the well-thickened oxide surface.

Fig. 9 shows an SEM micrograph of a cross-section of the specimen heated at 1073 K for 19.8 ks and the corresponding EDX spectra. In the EDX profiles Au peaks are due to an ion sputter-coating used for surface preparation. It is found that the outer scale contains only Ti (spectrum a) and Al concentration increases at an area adjacent to the oxide–compound interface (spectrum c). This shows that the outer scale is TiO_2 and the inner a mixture of TiO_2 and Al_2O_3. It is, however, considered in connection with the high-temperature X-ray diffractometry results that Al_2O_3 scale would not appear at the initial stage of the oxidation at 1073 K.

Fig. 10 shows an SEM micrograph of a cross-section of the specimen heated at 1273 K for 19.8 ks and the corresponding EDX spectra. As for specimen heated at 1073 K, the outer scale is TiO_2 (spectrum a) and the inner scale (spectra c, d and e) is a mixture of TiO_2 and Al_2O_3. The amount of Al_2O_3 is comparatively high at the oxide mid-area (spectrum c) and at an area adjacent to the compound–oxide interface (spectrum f), as in Fig. 9. At the oxide mid-area a crack-like zone is observed. It is considered that Al_2O_3 produces numerous pores at the oxide mid-area, and enhances titanium diffusion to the outer surface.

4. Conclusions

The initial stage of the oxidation process of two-phase (Ti_3Al and TiAl) intermetallic compound, Ti–42 at % Al, in air at 1073 and 1273 K was investigated. The results are summarized as follows.

1. The oxide scale consisted of TiO_2 and Al_2O_3. The outer scale was TiO_2 and the inner one a mixture of TiO_2 and Al_2O_3. The volume of Al_2O_3 increased at an area adjacent to the oxide–compound interface.

2. During heating up of a specimen from room temperature to 1273 K, TiO_2 scale formed initially on the compound surface at about 923 K, and then Al_2O_3 scale formed at about 1273 K.

3. During isothermal heating at 1073 K for heating times up to 7.2 ks, TiO_2 scale grew up slowly, but Al_2O_3 scale did not appear.

4. During isothermal heating at 1273 K, both scales (TiO_2 and Al_2O_3) grew up slowly for heating times up to 1.8 ks, but for heating times above 1.8 ks both scales drastically increased.

5. The weight gain due to oxidation at 1073 K was much less than that at 1273 K. The oxidations at 1073 and 1273 K follow the parabolic low.

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