Characterization of the whisker–matrix interfacial reactions in $K_2O \cdot 6TiO_2$ whisker-reinforced aluminium matrix composites

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The interfacial reaction at the whisker–matrix interface in a $K_2O \cdot 6TiO_2$/6061Al composite was investigated by high-resolution transmission electron microscopy. Magnesium segregation and titanium enrichment at the whisker–aluminium interface was revealed by energy-dispersive X-ray analysis. It was shown that TiO and $MgTi_2O_4$ layers and $MgAl_2O_4$ particles were formed at the whisker–aluminium interfaces in the composite during the manufacturing of the composite. The thickening of the reaction layer after T6 treatment may result in the decrease of the bending strength of the composite. Specific orientation relationships between $MgTi_2O_4$ and TiO, and also between TiO and $K_2O \cdot 6TiO_2$ whiskers were also found.

1. Introduction

The whisker-reinforced aluminium alloy matrix composites are of great interest for their high specific strength, high modulus, high wear resistance and thermal stability. Among the whiskers, potassium titanate whisker has several benefits compared with other ceramic whiskers. One of the most desirable features is the low cost of the whisker itself, which is one of the critical factors for commercial applications of composites. The price of potassium titanate whisker ranges from one-tenth to one-twentieth of the cost of silicon carbide whiskers [1]. Potassium titanate whisker will therefore be one of the most beneficial reinforcements for commercial base alloys.

In previous articles [2, 3], it was reported that reactions between whisker and aluminium alloy matrix seem to restrict the application of the aluminium alloy matrix composite with potassium titanate whisker. Recently, Fukunaga *et al.* [4] systematically investigated the mechanical properties of several potential whisker-reinforced aluminium matrix composites in as-fabricated (F) and T6-treated (T) states, and the results showed that the bending strength is 518.2 MPa (F) and 489.9 MPa (T) for $K_2O \cdot 6TiO_2$/6061Al ($V_f = 32.1\%$), respectively, which indicates that the bending strength has been reduced after T6 treatment. Here V_f represents the volume percentage of the whisker in the composite. It has been of great interest to study the interface structure and interfacial reactions to obtain a better understanding of the relationship between the interface characters and the mechanical properties due to the high volume percentage of the whisker–matrix interfaces in the composite. This paper presents some ultrafine structures of interfacial interaction products at the atomic level obtained by a combination of high-resolution transmission electron microscopy (HRTEM) and analytical electron microscopy techniques.

2. Experimental procedure

The diameter and the length of the $K_2O \cdot 6TiO_2$ whiskers are 0.1–2.0 and 10–30 μm, respectively. The crystal lattice of the $K_2O \cdot 6TiO_2$ whisker is monoclinic (space group $C2/m$) with the unit cell constants $a = 1.5582$ nm, $b = 0.382$ nm, $c = 0.9112$ nm and $\beta = 99.764°$. The chemical composition of 6061Al alloy was 0.8–1.2 wt% Mg, 0.4–0.8 wt% Si, 0.15–0.4 wt% Cu with the balance aluminium. The $K_2O \cdot 6TiO_2$/6061Al composite was fabricated by the squeeze-casting technique, using a pouring temperature of molten aluminium 720 °C, a whisker preheating temperature of 550 °C, preheating temperature of the dies of 480 °C, a squeeze pressure of 100 MPa, and a pressure dwelling time of 30s. The volume fraction of whiskers was 30–32%. Samples both in the as-fabricated (F) and T6-treated states were investigated for comparison. T6 treatment was carried out under the conditions of 530 °C, 1 h solid solution, water quenching, then 160 °C, 18 h ageing. Meanwhile, the $K_2O \cdot 6TiO_2$/pure aluminium sample was also investigated in order to ascertain the reasons for the formation of the interfacial reaction products.

The HRTEM observations were carried out in a JEOL-2000 EXII high-resolution transmission electron microscope operating at 200 kV with the point resolution of 0.21 nm at optimum conditions, and in a Philips EM420T analytical transmission electron microscope equipped with energy dispersive X-ray analysis (EDAX).

3. Results and discussion

In our previous works, HRTEM observations have shown that there were two kinds of interface structures in the whisker-reinforced aluminium matrix composites. SiC [5] and Si_3N_4 [6, 7] whiskers bonded with the aluminium matrix with a nanoscale amorphous transition layer, and the interfacial reactions did not "eat" whiskers. $Al_{18}B_4O_{33}$ ($9Al_2O_3 \cdot 2B_2O_3$) [8] whiskers directly bonded with the aluminium matrix, and the whiskers themselves also took part in the interfacial reactions which occurred in specific areas of the whiskers. The $K_2O \cdot 6TiO_2$w/6061Al composites showed different types of reactions and interfacial structure in comparison with those mentioned above.

Typical morphologies of the $K_2O \cdot 6TiO_2$ whiskers in $K_2O \cdot 6TiO_2$/6061Al as-fabricated and T6-treated composites are shown in Fig. 1a and b, respectively, from which we can see that serious interfacial reactions occurred at the whisker–aluminium interfaces; the reaction layers are indicated by arrow heads. From Fig. 1a and b, it can also be seen that $K_2O \cdot 6TiO_2$ whiskers themselves took part in the interfacial reactions, and reaction products completely covered the whiskers. Moreover, it can be seen from Fig. 1 that the interfacial reactions became more serious after T6-treatment, i.e. the reaction product layer became thicker in the T6 state than in the as-fabricated state.

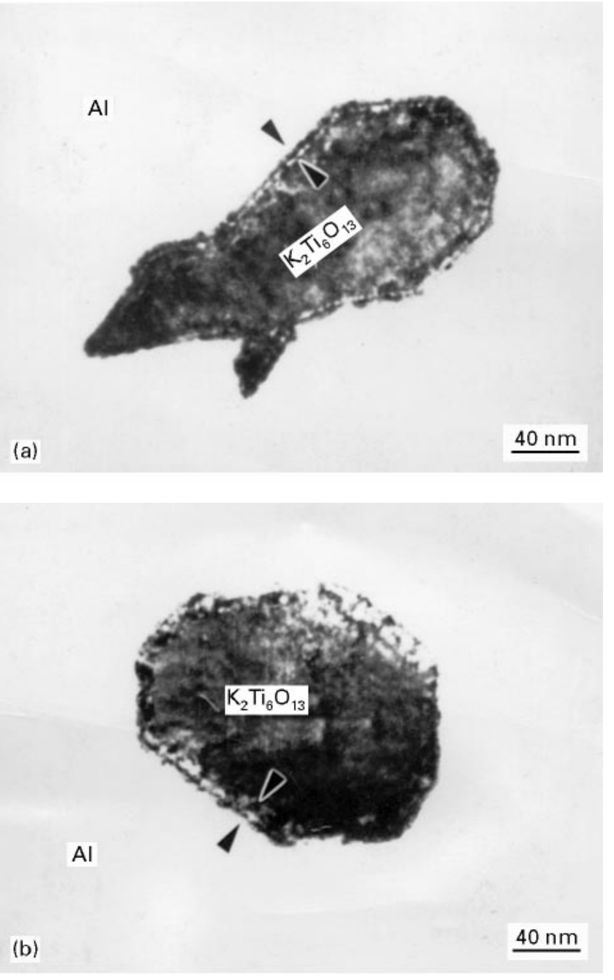


Figure 1 Diffraction contrast images of the $K_2O \cdot 6TiO_2$ whiskers in (a) the as-fabricated and (b) the T6-treated $K_2O \cdot 6TiO_2$/6061Al composite.

The [0 1 0] HRTEM image of the whisker–matrix interface is shown in Fig. 2a, and Fig. 2b is the corresponding electron diffraction pattern (EDP). It is evident that there are two kinds of interfacial reaction products, indicated by subscripts s and t in Fig. 2b. The HRTEM image (Fig. 2a) and EDP (Fig. 2b) indicate that the interfacial reaction products possibly possess the f c c structure (along the [1 0 0] direction) with $a = 0.85$ nm (s) and $a = 0.43$ nm (t), which are likely to be the $MgTi_2O_4$ with a cell constant of 0.847 nm and Fd3*m* space group (s), and TiO with a cell constant of 0.429 nm and F*m*3*m* space group (t). In Fig. 2b, the {0 0 2} and {0 2 2} diffraction spots of TiO nearly coincide with {0 0 4} and {0 4 4} diffraction spots of $MgTi_2O_4$, respectively, because the cell constant of $MgTi_2O_4$ is nearly double that of TiO. The {0 2 2} diffraction spots of $MgTi_2O_4$ are not very clear and are marked by dark triangles. Fig. 2c shows a schematic diagram of the EDP shown in Fig. 2b. Projections of unit cells of TiO and $MgTi_2O_4$ along the [1 0 0] direction are marked in Fig. 2a. There are no transition layers between $K_2O \cdot 6TiO_2$ and TiO and between TiO and $MgTi_2O_4$. Owing to the formation of the f c c phase with $a = 0.85$ nm occurring within the TiO layer, it is reasonable to consider that the segregated magnesium reacted with TiO to form the $MgTi_2O_4$. Moreover, the following specific orientation relationships between the reaction products $MgTi_2O_4$ and TiO, and also between TiO and $K_2O \cdot 6TiO_2$ in the $K_2O \cdot 6TiO_2$/6061Al composite can be obtained:

$$[1\,0\,0]_{TiO} \parallel [1\,0\,0]_{MgTi_2O_4} \parallel [0\,1\,0]_{KTO}$$
$$(0\,1\,0)_{TiO} \parallel (0\,1\,0)_{MgTi_2O_4} \parallel (1\,0\,1)_{KTO}$$
$$(KTO = K_2O \cdot 6TiO_2)$$

Fig. 3 shows the EDAX results. Fig. 3a–c correspond to the aluminium matrix, the whisker–matrix interface and the whisker itself, respectively. The Al : Mg atomic ratios are 16 : 1 (a) and 6 : 1 (b) and the Ti : K atomic ratios are 3.6 : 1 (b) and 2.9 : 1 (c). The titanuim and potassium atoms in the whisker would influence the EDAX results for the Ti : K ratio at the interface because the size of the electron beam used was about 50 nm which is larger than the width of the

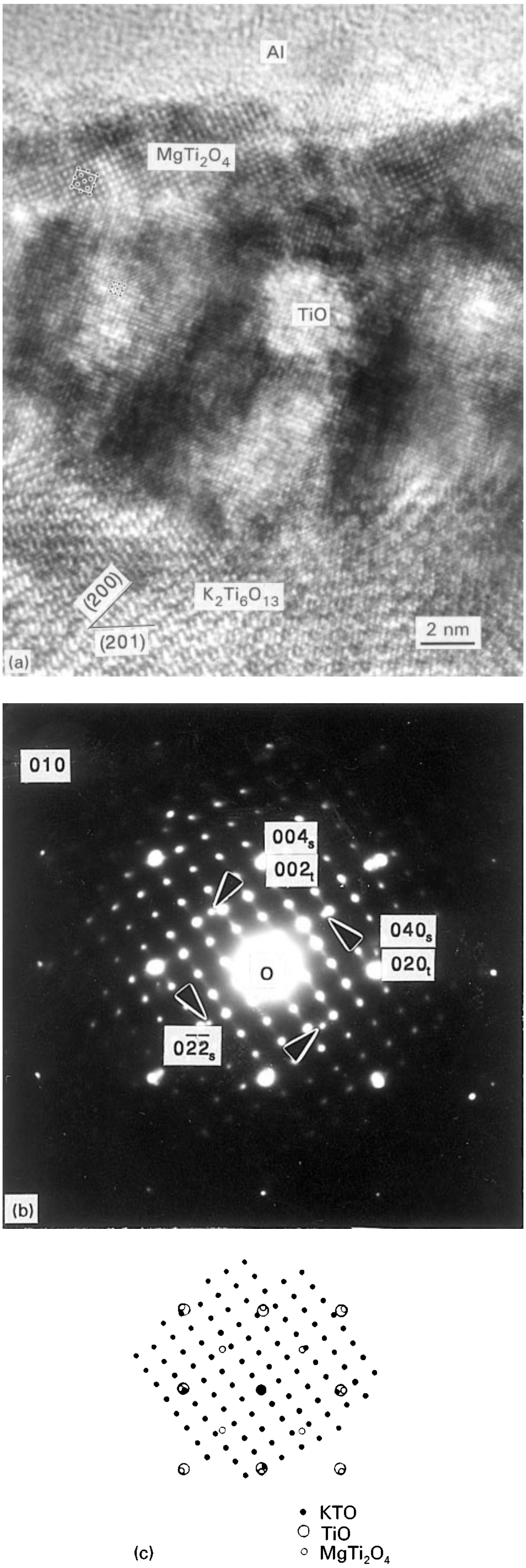


Figure 2 (a) HRTEM image of the interfacial reaction products of TiO and $MgTi_2O_4$ at the whisker–matrix interface, (b) the corresponding electron diffraction pattern, and (c) a schematic diagram of the EDP.

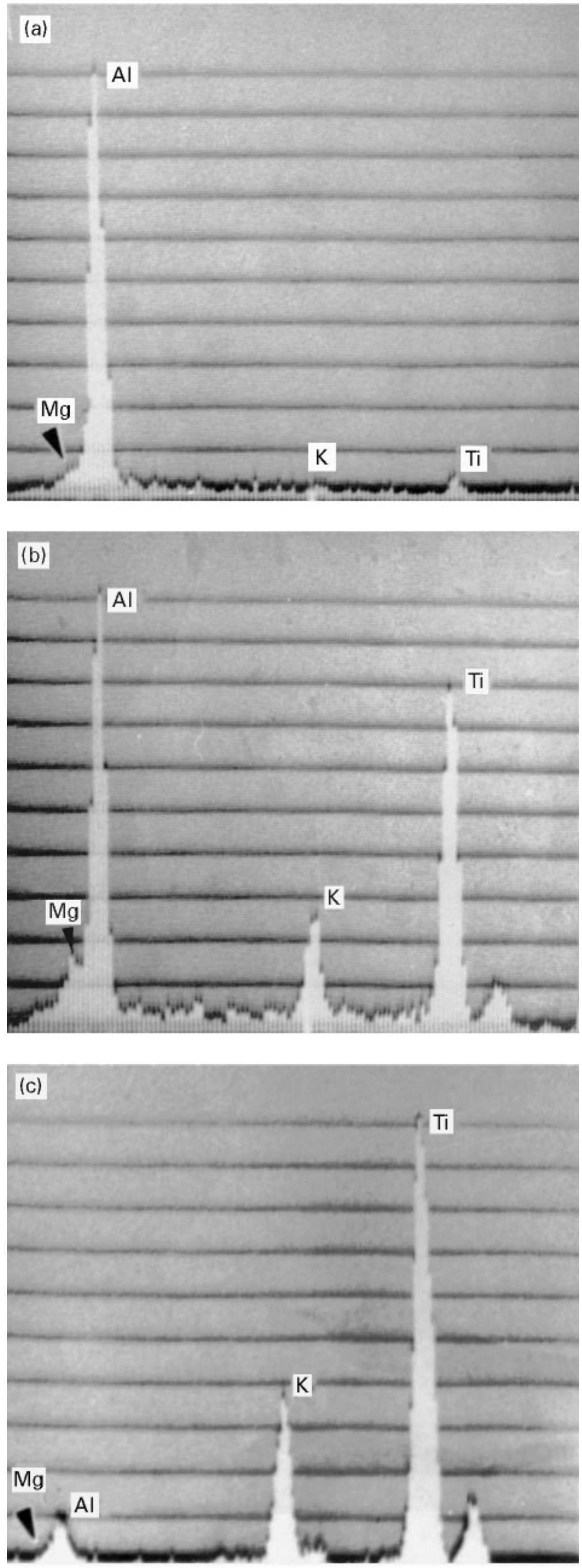


Figure 3 EDAX results at (a) the matrix, (b) the whisker–matrix interface, and (c) the whisker in the $K_2O{\cdot}6TiO_2/6061Al$ composite.

interfacial reaction layer (usually less than 30 nm). But because the Ti : K atomic ratio in the whisker is nearly equal to 3 : 1, the ratio 3.6 : 1 in Fig. 3b can also indicate the enrichment of titanium atoms at the whisker–matrix interface. Futhermore, the titanium and potassium atoms in the whisker would not influence the

EDAX results for the Al : Mg ratio. Therefore, it can be seen from the above EDAX results that magnesium has segregated and titanium enriched at the whisker–matrix interface, which further confirmed the formation of TiO and $MgTi_2O_4$ at the whisker–matrix interfaces.

The segregation of magnesium on the whisker–matrix interface in $K_2O \cdot 6TiO_2$/ 6061Al composite has been recognized earlier [1] is generally thought to be the formation of MgO. Indeed, MgO has the f c c structure (space group F*m*3*m*) with a unit cell constant of 0.421 nm, which are quite similar to those of TiO. In order to make sure that the interfacial reaction product is TiO and not MgO, the interface in the $K_2O \cdot 6TiO_2$/pure aluminium sample was also observed.

Fig. 4a shows a $K_2O \cdot 6TiO_2$ whisker in a $K_2O \cdot 6TiO_2$/pure aluminium composite and Fig. 4b is the electron diffraction pattern corresponding to the whisker–aluminium interface. It is obvious that there existed an interfacial reaction layer at the whisker–aluminium interface, too. The electron diffraction pattern shows that the reaction product also possibly has the f c c structure with $a = 0.43$ nm. Because there is no elemental magnesium in the $K_2O \cdot 6TiO_2$/pure aluminium composite, the interfacial reaction product should be TiO and not MgO. Fig. 4 also shows the EDAX results for whiskers (c) and at the whisker–matrix interface (d). The Ti : K atomic ratios obtained from Fig. 4c and d were 3.0 : 1 and 4.2 : 1, respectively. The enrichment of titanium atoms is evident and no elemental magnesium could be detected. These results clearly confirm that the interfacial product is TiO.

In our observations, the dominant interfacial reaction product is TiO in the as-fabricated $K_2O \cdot 6TiO_2$/6061Al composite and in many cases no $MgTi_2O_4$ exists. Fig. 5a shows an HRTEM image of the whisker–matrix interface in the composite with only one interfacial reaction product, TiO, in a much greater proportion than that shown in Fig. 2a. In an extremely small number of cases, the $MgAl_2O_4$ phase has been observed at the whisker–matrix interface in the composite. Fig. 5b shows an HRTEM image of this case, where the orientation of the $MgAl_2O_4$ particle is [1 0 0]. There is also no transition layer between TiO and $MgAl_2O_4$.

Therefore, we are of the opinion that reactions occur during the process of $K_2O \cdot 6TiO_2$/6061Al composite

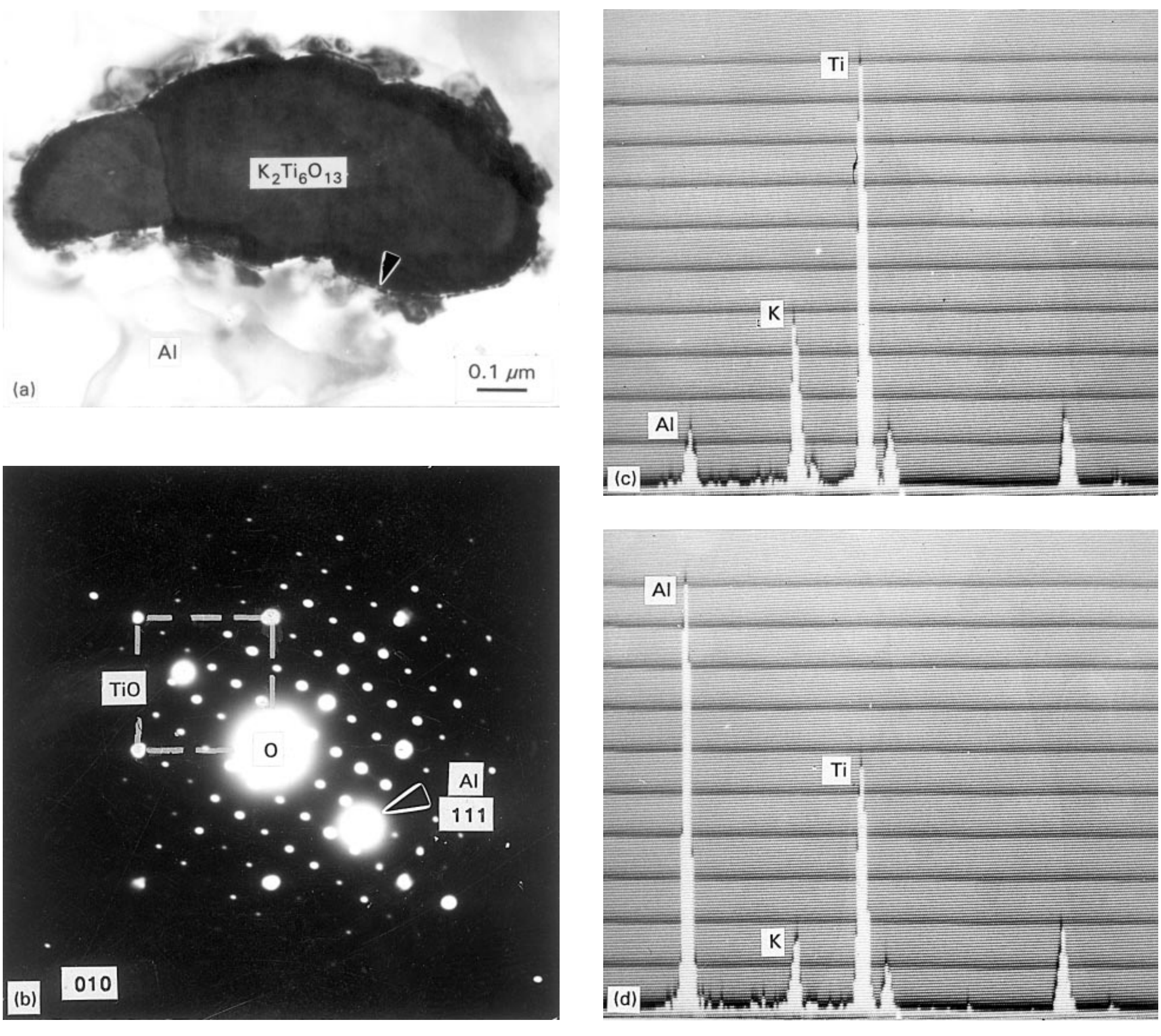
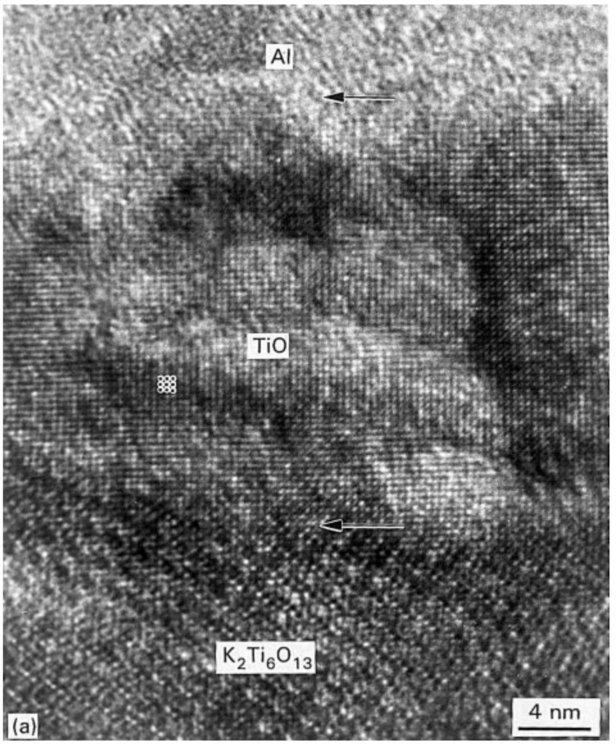


Figure 4 (a) Diffraction contrast image of $K_2O \cdot 6TiO_2$ whisker, (b) the electron diffraction pattern corresponding to the whisker–aluminium interface, EDAX results at (c) the whisker, and (d) the whisker–matrix interface in the $K_2O \cdot 6TiO_2$/ pure aluminium composite.



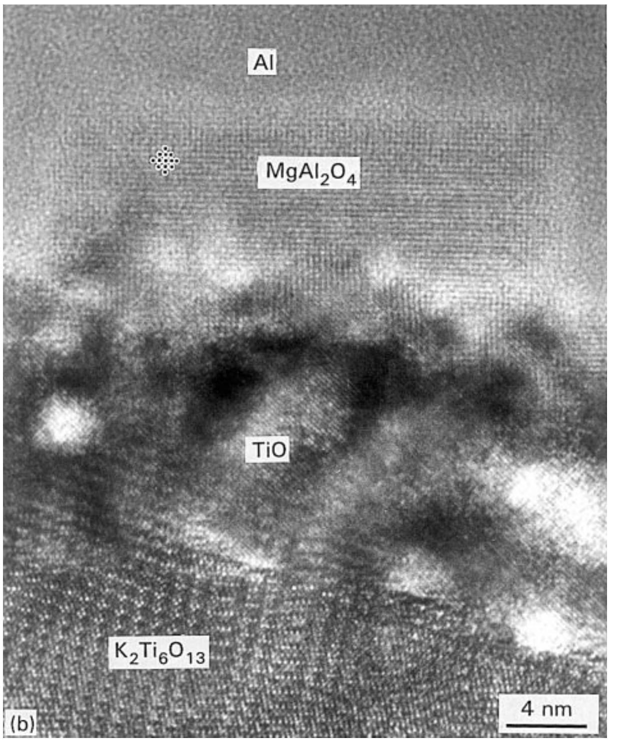


Figure 5 HRTEM images of the interfacial reaction products of (a) TiO, (b) TiO and $MgAl_2O_4$ at the whisker–matrix interface in the $K_2O{\cdot}6TiO_2$/6061Al composite.

fabrication: $K_2O{\cdot}6TiO_2$ whiskers are very stable, when they come into contact with melting metals, they are easily decomposed, the main product being TiO, which formed an even, continuous layer at the whisker–matrix interface. Magnesium atoms in the 6061Al matrix segregated on the whisker–matrix interface and reacted with the TiO phase and elemental aluminium and oxygen, to form the interfacial phases $MgTi_2O_4$ and $MgAl_2O_4$. The thickening of the reaction layer after T6 treatment results in the reduction of the effective volumes of whiskers, and further decreases the bending strength of the composite. Moreover, the seriousness of the interfacial reactions leads to depletion of magnesium from the matrix, and it is one of the elements which can strengthen the matrix by precipitation of Mg_2Si [9]. So the matrix will be weakened due to the reduction of magnesium from the matrix.

4. Conclusions

1. Interfacial chemical reactions occurred at the whisker–matrix interfaces during the fabrication of the $K_2O{\cdot}6TiO_2$/6061Al composite. The interfacial reaction products were determined to be TiO, $MgTi_2O_4$ and a very small amount of $MgAl_2O_4$ by means of HRTEM and EDAX.

2. Interfacial reactions occurred at the whisker–matrix interfaces of the $K_2O{\cdot}$ $6TiO_2$/pure aluminium composite. The interfacial reaction product was again TiO.

3. The magnesium segregation at the whisker–matrix interface, found by EDAX, resulted in the formation of $MgTi_2O_4$ and $MgAl_2O_4$ at the interface after T6 treatment. The thickening of the reaction product layer may result in a decrease of the bending strength of the composite after T6 treatment.

4. The following specific orientation relationships were found: $[1\,0\,0]_{TiO} \parallel [1\,0\,0]_{MgTi_2O_4} \parallel [0\,1\,0]_{KTO}$ and $(0\,1\,0)_{TiO} \parallel (0\,1\,0)_{MgTi_2O_4} \parallel (1\,0\,1)_{KTO}$.

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