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In situ Al–TiB composite obtained by stir casting

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An *in situ* Al-matrix TiB particle (10–50 μm size, ~ 10 vol %) composite was formed by stir casting at 900 °C a slurry containing liquid aluminium (2024), TiO_2, KBF_4 and Na_3AlF_6 in the weight ratio 13.5:4:1:4. The reactions among these ingredients resulted in TiB, together with small amounts of TiB_2 and $TiAl_3$.The composite (after T_6 heat treatment, but no secondary processing) exhibited tensile strength 270 MPa, modulus 91 GPa and ductility 8%.

1. Introduction

In situ composites refer to composites with the reinforcement made in place inside the composite from its precursors during composite fabrication. Reinforcements made *in situ* tend to be fine and well distributed, in addition to having good bonding with the matrix, as the reinforcement–matrix interface tends to be cleaner for *in situ* than *ex situ* reinforcements. On the other hand, the making of an *in situ* reinforcement requires the use of an appropriate reaction, so the choice of *in situ* reinforcements is much more limited than that of *ex situ* reinforcements.

Various ceramic particles, such as SiC, Al_2O_3, AlN and TiB_2 have been used as *ex situ* reinforcements in metals, such as aluminium. In particular, TiB_2 has been used as an effective *in situ* reinforcement in aluminium [1] and TiB has been used as an effective *in situ* reinforcement in titanium [2]. TiB_2 and TiB are both equilibrium intermediate phases in the binary Ti–B phase diagram. In this work, by using a reaction scheme that is similar to but different from that of [1], the authors have been able to form TiB *in situ* in aluminium. Without subjecting the composite to secondary processing, such as extrusion, the authors' *in situ* TiB reinforcement (10 vol %) resulted in a tensile strength increase of 21%, whereas the *in situ* TiB_2 reinforcement (3.4 vol %) of [1] resulted in a tensile strength increase of 5.6%.

2. Experimental procedure

2.1. Composite, fabrication

The aluminium used was commercial 2024 aluminium alloy. It contained 4.5 wt % Cu, 1.5 wt % Mg, 0.5 wt % Si, 0.6 wt % Mn and 0.1 wt % Cr.

The reaction scheme used to form TiB (together with TiB_2 and $TiAl_3$ in much smaller amounts) *in situ* in aluminium is the following. The reactants are Al, TiO_2, Na_3AlF_6 and KBF_4.

$$4Al + 3TiO_2 \rightarrow 3Ti + 2Al_2O_3 \quad (1)$$

$$Ti + 3Al \rightarrow TiAl_3 \quad (2)$$

$$2TiO_2 + 2Na_3AlF_6 \rightarrow 2Na_2TiF_6 + Na_2O + Al_2O_3 \quad (3)$$

$$2Na_2TiF_6 + 6Al \rightarrow 4NaF + 4F_2 + 2TiAl_3 \quad (4)$$

$$Al_2O_3 + 2Na_3AlF_6 \rightarrow 3NaO + 4Al + 6F_2 \quad (5)$$

$$2Na_2TiF_6 + 4Al + KBF_4 \rightarrow TiAl_3 + TiB + 4NaF + AlF_3 + KF + 4F_2 \quad (6)$$

$$2Na_2TiF_6 + 3Al + 2KBF_4 \rightarrow TiAl_3 + TiB_2 + 4NaF + 2KF + 7F_2 \quad (7)$$

$$Na_2TiF_6 + KBF_4 \rightarrow TiB + 2NaF + KF + 4F_2 \quad (8)$$

Note that Al_2O_3 formed in Equation 1 is reduced by Na_3AlF_6 in Equation 5. The reactant TiO_2 is reduced by Na_3AlF_6 to form Na_2TiF_6 in Equation 3; Na_2TiF_6 is akin to K_2TiF_6 used in [1]. The main reactions are Equations 6 and 8, which form TiB from Na_2TiF_6 and KBF_4. The product TiB_2 is also formed from Na_2TiF_6 and KBF_4 (Equation7), but the proportion of KBF_4 is higher in Equation 7 than Equation 6, so that Equation 7 forms TiB_2 whereas Equation 6 forms TiB. The reactions used in [1] are akin to Equations 7 and 8, except that Na_2TiF_6 is replaced by K_2TiF_6 and the proportion of KBF_4 to the other reactants in Equation 8 is higher, so that TiB_2 instead of TiB is formed. By-products Na_2O, NaF, F_2, KF, F_2 and AlF_3 are not useful and were removed by skimming (as slag) or natural volatilization prior to casting.

The *in situ* composite was made by stir casting, using the following procedure. TiO_2 particles (40 μm size, Johnson Matthey Co.), sodium hexafluoroaluminate Na_3AlF_6 (98.5%) particles (40 μm size, Johnson Matthey Co.), and potassium tetrafluoroborate KBF_4 (99%) particles (not sized, Johnson Matthey Co.) were mixed in the weight ratio 4 : 4 : 1 and then heated at 300 °C for 4 h (for drying). The mixture was then slowly added to the surface of the liquid aluminium at 900 °C. The amount of the mixture was 40% of the

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weight of the aluminium. After this, the slurry was stirred intermittently at 900 °C for a period of about 30 min in order to allow the reactions to occur. All of the TiO_2 (white) was reacted, but the by-products (black) were removed before casting. Immediately after stirring the slurry and subsequently allowing the slurry to sit for 5–10 min, the slurry was poured into a cylindrical steel mould of diameter 30 mm and height 40 mm at room temperature. After casting and subsequent solidification at a cooling rate of about $200\,^{\circ}C\,min^{-1}$, the composite was heated at $525 \pm 5\,^{\circ}C$ for 7 h, then quenched into water at room temperature, and then heated at $175 \pm 5\,^{\circ}C$ for 9 h, in accordance with the T_6 heat treatment procedure for the 2024 aluminium alloy.

For the sake of comparison, the 2024 alloy itself was subjected to the same casting and heat treatment procedure, and its properties were compared to those of the composite.

2.2. Composite characterization

X-ray diffraction (using CuK_{α} radiation) showed that the composite consisted of aluminium and TiB mainly, in addition to small amounts of $TiAl_3$, TiB_2 and $TiSi_2$. The diffraction pattern in Fig. 1 was obtained after etching away the aluminium (in a solution with 20 wt % HCl, 20 wt % H_2SO_4 and 60 wt % H_2O at room temperature). This etching was necessary in order to reveal the presence of the minor phases, as aluminium was by far the majority phase. The $TiSi_2$ was present mainly due to the use of a graphite–clay crucible and the silicon contamination from the clay.

Optical microscopic examination was conducted on the polished and lightly etched sections of the aluminium by itself (Figs 2a and 3). The etching was performed by using an aqueous solution with 0.5 wt % HF. The grain size was 2.0 mm (Fig. 2(a)). The bright regions in Fig. 3 are the aluminium dendrites; the dark regions are the θ (Al_2Cu) phase, which is a consequence of the T_6 heat treatment. The dendrite width was about 50 μm. Similar observation of the composite (Fig. 2(b)) revealed neither grains nor dendrites, but just particles of reinforcement. The microstructure was much finer for the composite than the aluminium by itself (Fig. 2).

Optical microscopic and scanning electron microscopic (together with X-ray spectroscopy) examination was conducted on the polished (but not etched) sections of the composite (Figs 4 and 5). The TiB particles (some equiaxed, some rectangular) were of size 10–50 μm. The TiB volume fraction was ~ 10%. Also present was needle-shaped $TiAl_3$ of length ~ 50 μm and width ~ 4μm, in the amount of ~ 3 vol %. Due to the presence of TiB and $TiAl_3$, the aluminium dendrites could not be observed.

Table I gives the hardness (Brinell) and microhardness (Vickers) of the aluminium by itself and of the composite. The composite was much harder than the aluminium by itself, whether in the as-cast or T_6 heat treated condition.

Table II gives the tensile properties, which were obtained on dog-bone shaped specimens, using a Sintech two-dimensional (2/D) screw-type mechanical testing system and strain gauges for measuring the modulus. The ductility was obtained by measuring the

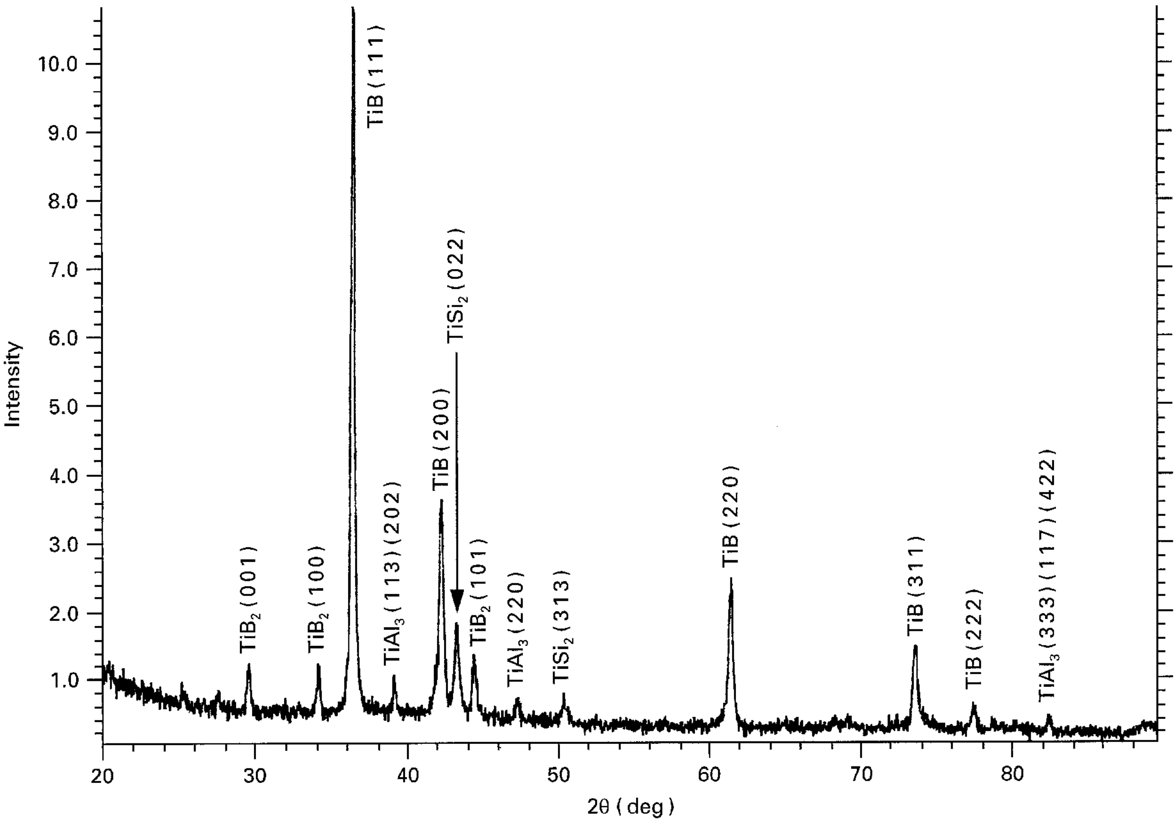

Figure 1 X-ray diffraction pattern of the composite.

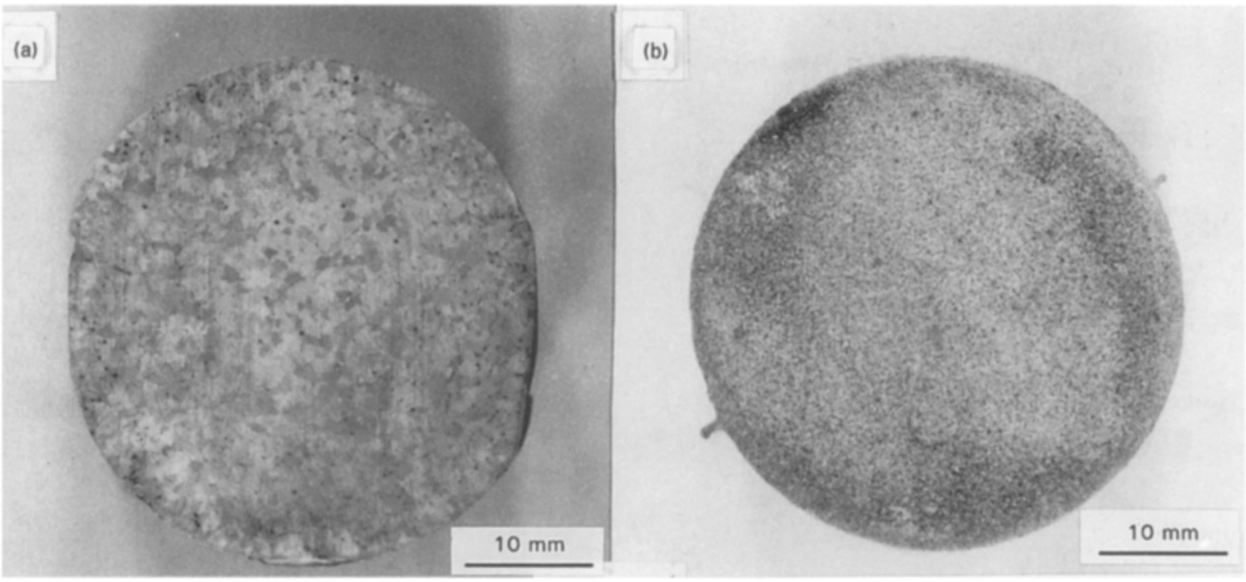

Figure 2 Optical micrographs (obtained after polishing and light etching) of (a) aluminium by itself, and (b) the composite.

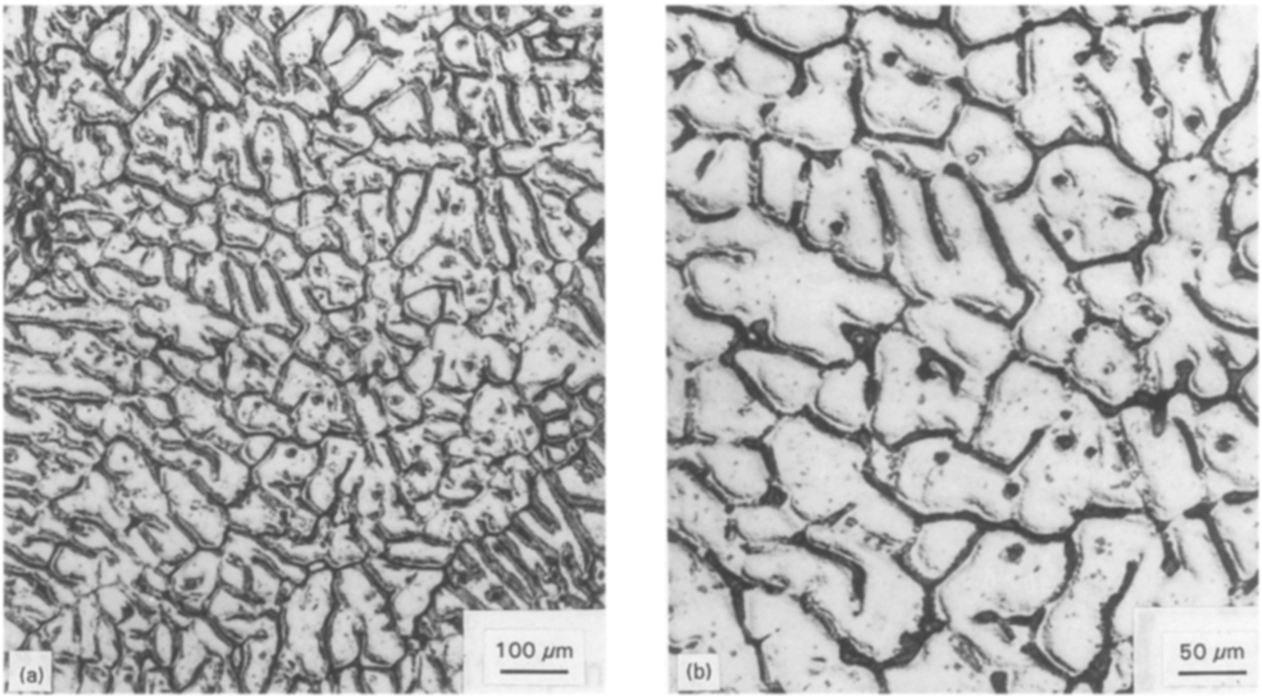

Figure 3 Optical micrographs (obtained after polishing and light etching) of aluminium by itself.

change in distance between two lines drawn perpendicular to the stress axis. The tensile strength and modulus were higher in the composite than aluminium by itself, but the ductility was slightly lower.

3. Discussion

The reactants used in [1] to form Al–TiB_2 *in situ* composites were Al, K_2TiF_6 (source of titanium) and KBF_4 (source of boron). The Na_3AlF_6 (known as cryolite) was used in [1] as a reducing agent to lessen the oxidation of liquid aluminium; see Equation 5. In contrast, the reactants used in this work to form the Al–TiB *in situ* composite were Al, Na_3AlF_6, TiO_2 (source of titanium) and KBF_4 (source of boron). The Na_3AlF_6 served to react with TiO_2 to form Na_2TiF_6, which is akin to the K_2TiF_6 used in [1]. The advantage of using TiO_2 instead of K_2TiF_6 as the source of titanium is that both TiO_2 and Na_3AlF_6 are inexpensive compared to K_2TiF_6.

The composites of [1] differ from that of this work not only in the reinforcement species (TiB_2 in [1] and TiB in this work), but also in the reinforcement volume fraction (up to 3.4% in [1] and 10% in this work) and reinforcement particle size (~ 0.5–2 μm in [1] and 10–50 μm in this work), reinforcement location (interdendritic regions in [1] and everywhere in this work) and aluminium alloy type (A356 in [1] and 2024 in this work). Without secondary processing, the TiB_2 reinforcement of [1] resulted in a tensile strength increase of up to 5.6%, whereas the TiB reinforcement of this work resulted in a tensile strength increase of

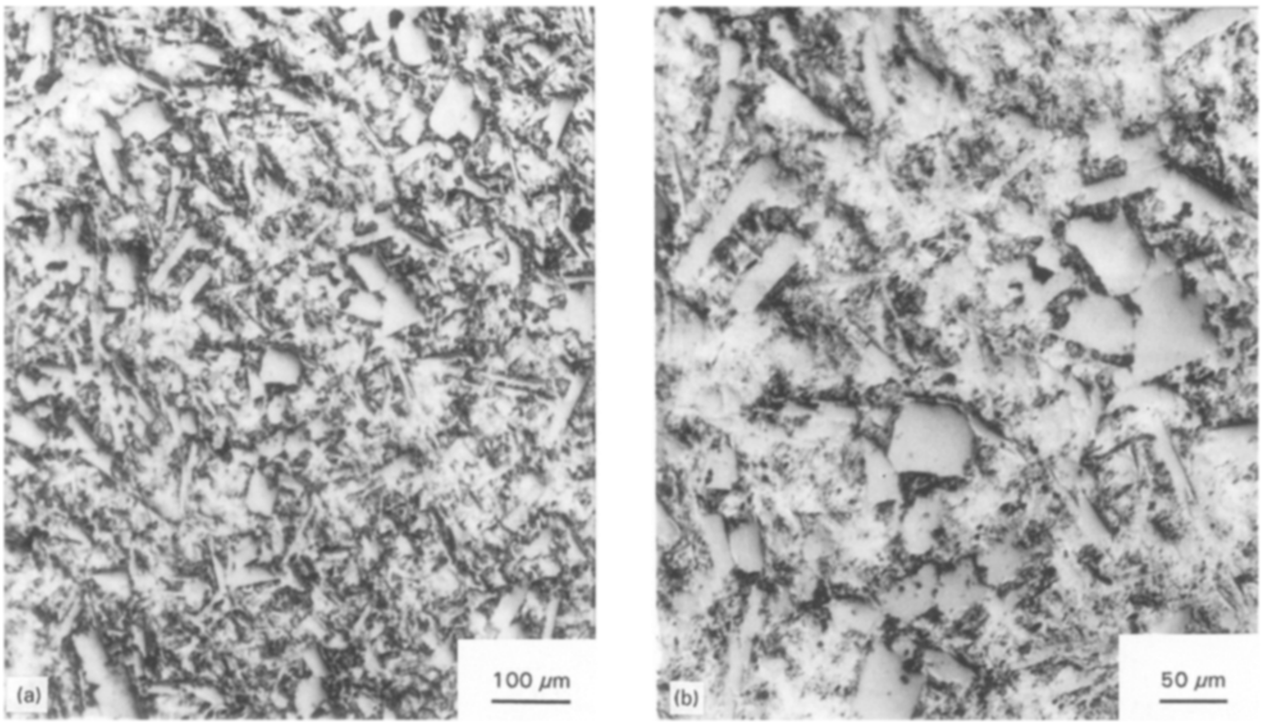

Figure 4 Optical micrographs (obtained after polishing but no etching) of the composite.

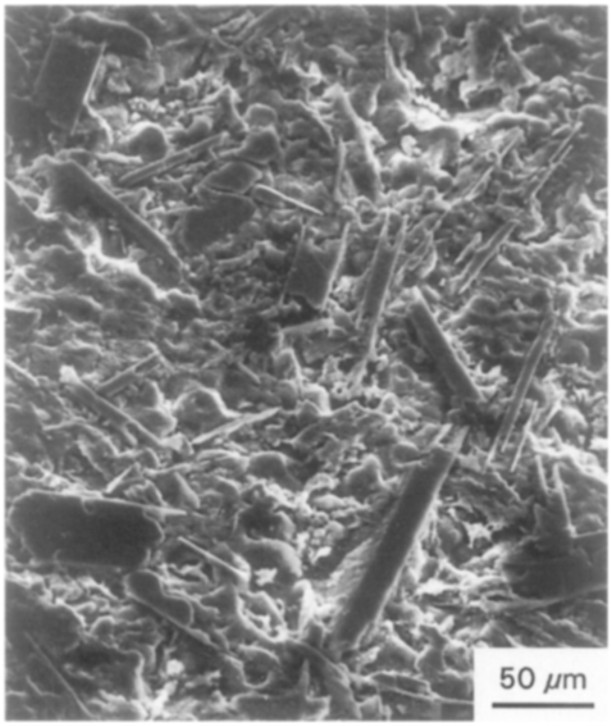

Figure 5 Scanning electron microscope photograph (obtained after polishing, but no etching) of the composite.

TABLE I Hardness and microhardness (the standard deviations, based on three data points for each type of specimen, are shown in parentheses)

	Hardness (BHN)		Microhardness (H_V)	
Material	As-cast	T_6	As-cast	T_6
Al	53.9(± 1.2)	91.4(± 2.4)	101(± 8.8)	120(± 4.5)
Al–TiB	84.6(± 1.1)	122.3(± 3.3)	138(± 2.7)	155(± 6.1)

TABLE II Tensile properties (the standard deviations, based on three data points for each type of specimen, are shown in parentheses)

Material	Strength (MPa)	Modulus (GPa)	Ductility (%)
Al	222(± 2.3)	73.7(± 0.8)	9.0(± 1.5)
Al–TiB	269(± 4.5)	91.4(± 0.5)	8.0(± 1.0)

21%. This difference in degree of strengthening is attributed mainly to the higher reinforcement volume fraction of this work.

In spite of the high TiB volume fraction (~ 10%), the TiB caused the ductility to decrease just from 9 to 8%. On the other hand, a low TiB_2 volume fraction of 3.4% in [1] caused the ductility to decrease from 13 to 7% (in spite of the small TiB_2 particle size). The high ductility of the Al–TiB composite suggests good bonding between Al and TiB–apparently a consequence of the reaction scheme used to form TiB. The presence of the needle-shaped $TiAl_3$ particles in the Al–TiB probably also contributed to the high ductility.

The volume fraction $TiAl_3$ compared to that of TiB appears negligible in X-ray diffraction (Fig. 1), but not negligible in microscopy (Fig. 4). This is because the X-ray diffraction was conducted after etching away the aluminium in the composite. Due to the much larger particle size of TiB than $TiAl_3$, TiB particles could be removed more easily than $TiAl_3$ particles from the filter paper used to isolate the particles from the etching solution. As a result, the $TiAl_3$ quantity shown by X-ray diffraction is lower than the quantity shown by microscopy.

4. Conclusions

An *in situ* composite with ~ 10 vol % TiB as the reinforcement and aluminium (2024) as the matrix was prepared by stir casting. The TiB particles of size 10–50 μm were formed *in situ* through reactions among Al, TiO_2 (source of titanium), KBF_4 (source of boron) and Na_3AlF_6. Also formed *in situ* were much smaller amounts of TiB_2 and $TiAl_3$. The $TiAl_3$ was in the form of fine needles (about 50×4 μm) in the amount of ~ 3 vol %. The composite exhibited much higher hardness, microhardness, tensile strength and modulus, but slightly lower ductility than the aluminium by itself.

References

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