

# INFILTRATION AND REACTIVITY OF TiC PARTICULATE WITH LIQUID ALUMINIUM

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**SUMMARY:** TiC particulate/aluminium composites have been obtained by means of pressure infiltration of the liquid metal into packed samples of the ceramic particles. The reactions between the metal and the particle have been investigated by heat treating the so produced composite at different temperatures. The main reaction products result to be alumina and aluminium carbide. An analysis of the possible reaction occurring during the heat treatments indicate that alumina can only be formed if the TiC particulate are oxidised prior to the infiltration process. It is shown that reactions between Al and various titanium oxides can in fact produce alumina. The likelihood of the various reactions is analysed by means of a calculation of their associated free energies. Instead aluminium carbide can be formed by direct reaction between aluminium and titanium carbide, producing either free titanium (that can eventually be dissolved into aluminium) or titanium aluminides. Thermodynamic calculations indicate that none of the possible reactions is favourable. Thus, further work is needed to reconcile our experimental results with the thermodynamic data.

## INTRODUCTION

The need for high strength, lightweight, and high stiffness materials has in recent years, attracted much interest in the development of the manufacturing processes of metal matrix composites (MMC). [1]. The most important limitation to the fabrication of MMC by liquid-phase process resides upon de compatibility between the reinforcement and the matrix. Wettability and reactivity determine the quality of the bond between both materials and, therefore, greatly influence the final properties of the composite. This compatibility is particularly important in the case of aluminium-based composites, because Al is usually covered with a thin oxide layer that hinders wetting [2], and, when uncovered, it readily reacts with most ceramics to form intermetallics. In particular, liquid aluminium reacts with TiC to produce aluminium carbide, free titanium and titanium aluminides.

Recently, theoretical [3,4] and experimental [5,6] studies on the Al-Ti-C system have been published. It has been reported that Al and TiC do not react at processing temperatures, which are commonly well above that of melting of aluminium. However, in a theoretical work Yokokawa et al. [4] predicted that Al and TiC cannot coexist in thermodynamic equilibrium at temperatures as low as 973 K. Besides, the thermodynamic study of [4] differs from that reported by Mitra et al [7].

In this work we present experimental data for pressure infiltration [8,9] of liquid aluminium into packed samples of titanium carbide particulate. Infiltration results are shown to follow Darcy law. The reactions between TiC and aluminium in infiltrated samples containing around 50% in volume of TiC particulate are also investigated. The reaction products were identified by means of optical microscopy, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), thermal programmed oxidation (TPO), TG and DTA. The interpretation of the results is carried out with the help of an analysis of the thermodynamics of the various relevant reactions.

## MATERIALS AND EXPERIMENTAL PROCEDURES

The composites were fabricated by means of pressure infiltration. The method consists of forcing the liquid metal (aluminium) to infiltrate samples of packed particulate (titanium carbide) by means of a pressurised gas. The experimental set-up and procedures have been described in Ref. [8]. Pressure was measured with a transmitter and controlled within  $\pm 2$  kPa. Pressure and temperature were registered during the whole process.

The TiC particulate were of 99.5% purity and had an average diameter of 31  $\mu\text{m}$ . Aluminium of commercial purity (99.98 wt.%) was used all throughout. The particulate was packed into quartz tubes by alternating strokes of a weight and vibrations. The resulting particle volume fraction  $V_p$  was 0.59. The side of the tube to be introduced into the melt was plugged with alumina paper of 6% theoretical density. This paper prevents depacking of the particulate and skims off the alumina scum during infiltration. Infiltration was carried out at a melt temperature of  $1023 \pm 2$  K. Pressure was applied with nitrogen gas at a rate of 50-60 kPa/s, up to the chosen pressure. After a fixed period of time (120 seconds), the chamber was vented at a rate of 30-70 kPa/s. To keep the extent of the reaction during the fabrication process at a low level the following conditions were used: an applied pressure well above the threshold, a short reaction time (15 s) and a moderate temperature (973 K).

The infiltrated samples were sectioned to obtain discs that were subsequently heat treated in an Ar atmosphere at different temperatures. The heat treated samples were studied by X-ray diffraction, carried out in an automated powder diffractometer (Seifert model JSO Debye-Flex 2002), using a Cu  $K\alpha$  radiation source and a nickel filter. The experimental conditions were 42 kV, 35 mA and 2°/min. The morphology of the reaction products was analyzed by means of a Scanning Electron Microscope (JSM 840, from JEOL) fitted with a Link QK 200 dispersive X-ray analyzer, and by Reflecting Polarized-light Microscopy (in a Leica microscope). We also carried out TG-DTA studies, both of the infiltrated samples and the TiC particulate, in a SETARAM DSC-92 differential thermal analyser. Runs were performed in the range 673-1373 K at a heating rate of 10 K/min and under a dynamic helium atmosphere (one l/h).

As oxidation of TiC can occur during preheating of the compacts, we have also investigated the oxidation process by heat treating the particulate in an air atmosphere at different temperatures (between 673 to 1273 K) for 1 h. The compounds formed during the process have been analysed by X-ray diffraction. TiC oxidation was also investigated by TG-DTA and thermal programmed oxidation (TPO). TPO samples had an approximate weight of 100 m, whereas heating (up to 1273 K) was carried out at a rate of 10 K/min in a dynamic atmosphere (50 ml/min) of He - 20% O<sub>2</sub>. A large fraction of the evolved gas was evacuated with a rotary pump and only a small amount passed the leak valve. The gases (CO<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>) were analysed with a quadrupole mass spectrometer (VG Quadrupoles). TPO results were expressed as percentage volume per unit weight of sample.

## EXPERIMENTAL RESULTS

### Pressure Infiltration

The experimental results for the infiltrated height ( $h$ ) versus applied pressure ( $P$ ) are shown in Fig. 1. The data can be accurately fitted by a straight line, in agreement with Darcy law,

$$h^2 = \frac{2kt}{\mu(1-V_p)} \Delta P \quad (1)$$

where  $t$  is the infiltration time,  $V_p$  the particle volume fraction,  $k$  the intrinsic permeability of the packed powder and  $\mu$  the viscosity of the liquid metal. The pressure drop in the liquid metal  $\Delta P$  is given by the total pressure drop that can be taken as  $P - P_0$ ,  $P_0$  being the threshold pressure for the initiation of infiltration. Thus, the pressure axis intercept of the fitting of Fig. 1 gives the threshold pressure.

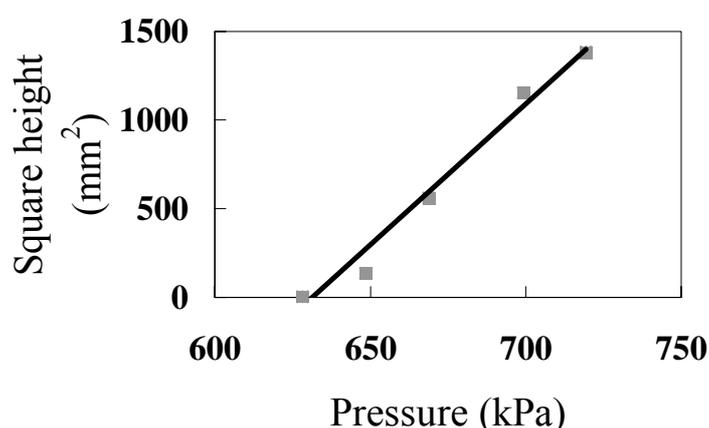


Fig. 1. Square of the infiltrated height ( $h^2$ ) as a function of the applied pressure (infiltration time, 120 s,  $T = 1023$  K) for packed samples of TiC particulate infiltrated with pure aluminium. The fitted straight line is,  $h^2(\text{Al}) = 16.3(P-633)$  mm<sup>2</sup>, with  $P$  in kPa (regression coefficient  $r = 0.991$ ).

### Reaction Products

Table 1 reports the compounds identified by means of XRD in the heat treated composites. The results indicate that extensive reaction between liquid Al and TiC has occurred,

producing mostly alumina, aluminium carbide and TiAl<sub>3</sub> (the latter mainly at the lowest temperature, see Table 1). The identification of aluminium carbide is hindered by its rapid decomposition in air. In fact while the observation of freshly heat treated composite samples by means of optical microscopy allows to identify a large amount of this compound, much less proportion is detected by XRD if diffraction diagrams are taken just a few hours after the heat treatment. While the formation of most products can be ascribed to the reaction between TiC and Al, that of alumina can only be understood by assuming the presence of titanium oxide. In the next subsection we will investigate the reactions that may lead to the formation of the compounds reported in Table 1.

Table 1. Compounds formed in the reaction between aluminium and TiC at different Temperatures as identified by means of XRD. The superscript “t” stands for traces and “m” for minority.

Temperature (K)	Products
973	Al, Al <sub>2</sub> O <sub>3</sub> , TiC, TiAl <sub>3</sub> , Al <sub>4</sub> C <sub>3</sub>
1073	Al, Al <sub>2</sub> O <sub>3</sub> , TiC, TiAl <sub>3</sub> <sup>m</sup> , TiAl <sup>t</sup> , Ti <sub>3</sub> Al <sup>t</sup> , Ti <sub>3</sub> AlC <sup>t</sup> , Al <sub>4</sub> C <sub>3</sub>
1173	Al, Al <sub>2</sub> O <sub>3</sub> , TiC, TiAl <sub>3</sub> <sup>m</sup> , TiAl <sup>t</sup> , Ti <sub>3</sub> Al <sup>t</sup> , Ti <sub>3</sub> AlC <sup>t</sup> , Al <sub>4</sub> C <sub>3</sub>
1273	Al, Al <sub>2</sub> O <sub>3</sub> , TiC, TiAl <sub>3</sub> <sup>m</sup> , TiAl <sup>t</sup> , Ti <sub>3</sub> Al <sup>t</sup> , Al <sub>4</sub> C <sub>3</sub>

## DISCUSSION

### Formation of Al<sub>2</sub>O<sub>3</sub>

As remarked above, the formation of alumina requires the presence of titanium oxide. Extensive oxidation of TiC may have occurred during the heating of the compacts at around 1023 K. Thus, we first discuss TiC oxidation. Fig. 2 shows typical DTA and TPO curves of TiC particulate. In both curves a small peak at 723 K is observed that corresponds to the surface oxidation of TiC. At 873 K starts bulk oxidation of TiC. Three peaks are clearly noted probably associated to the formation of different titanium oxides. The TPO curve shows the formation of CO<sub>2</sub> and consumption of O<sub>2</sub>, its profile being similar to that of the DTA curve. Although this already confirms that the peaks observed in the DTA curve correspond to the oxidation of TiC, we have carried out isothermal heat treatments at temperatures in the range 673 - 1273 K (1 h at temperature) and confirmed the presence of various titanium oxides by means of XRD.

Oxidation of titanium carbide can occur through the following reactions:



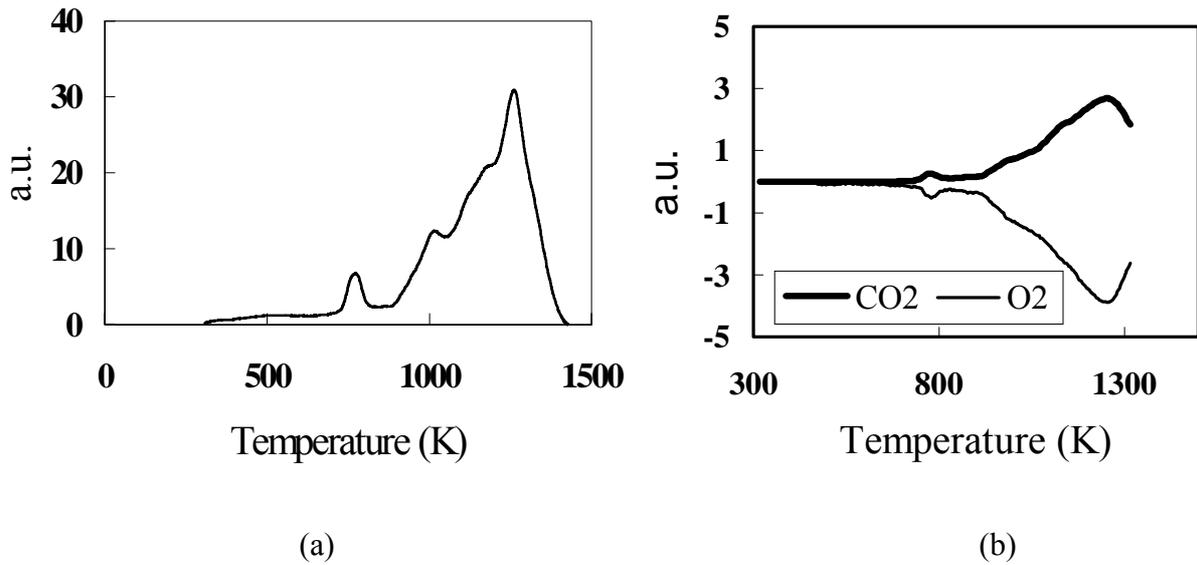


Fig. 2. DTA (a) and TPO (b) curves of TiC particulate. The runs were carried out at a heating rate 10 K/min under a He - 20% O<sub>2</sub> atmosphere. In the TPO curves both carbon dioxide formation and oxygen consumption are noted.

Fig. 3 shows the free energies related to these reactions as a function of Temperature [10]. It turns out that the most favourable is Reaction 2.

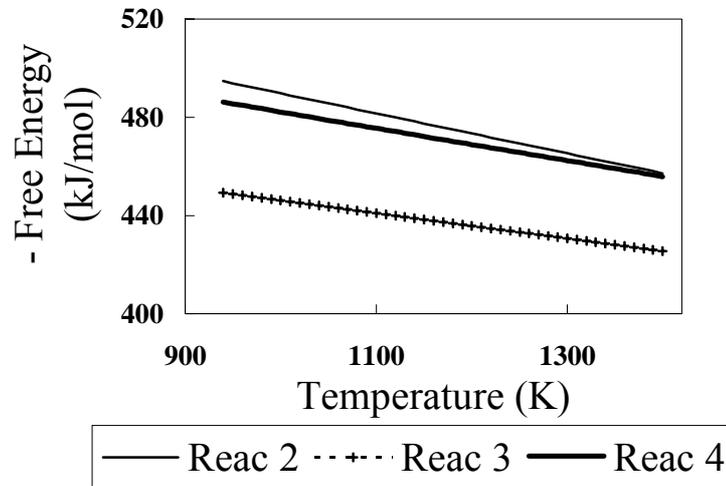
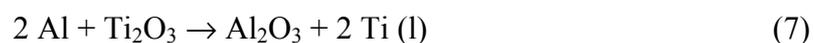
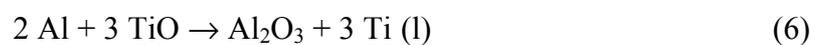


Fig. 3. -Free energy (in kJ per mol of O<sub>2</sub>) for Reactions 2-4 as a function of temperature.

Then, alumina can be produced through various reactions between liquid aluminium and the titanium oxides in Reactions 2-4,



These reactions have a negative free energy [10], particularly in the case of Reactions 6 and 7 (see Fig. 4). All three can become even more favourable if the heat of dissolution of Ti in aluminium is taken into account. Other possible reactions include the formation of titanium aluminides such as  $TiAl_3$  and  $TiAl$ . These results clearly indicate a way to form alumina in the heat treatments of the Al-TiC composites investigated here, giving support to the observations summarised in Table 1.

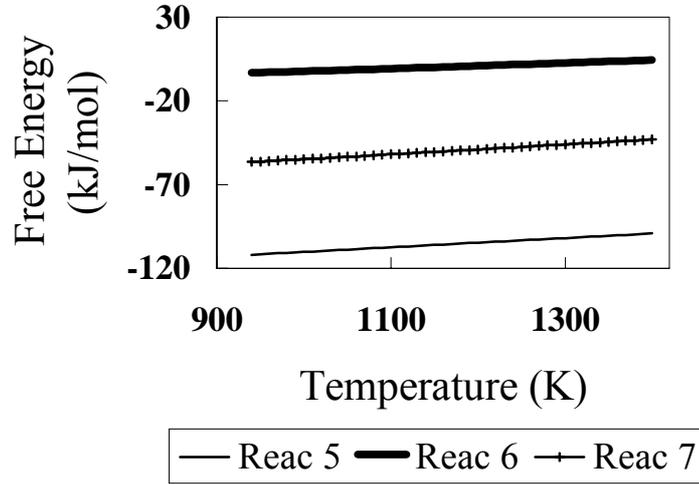
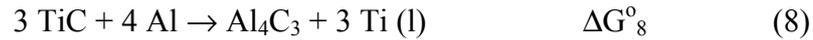


Fig. 4. Free energy (in kJ per mol of  $O_2$ ) for Reactions 5-7 as a function of temperature.

#### Formation of $Al_4C_3$ and $Ti_xAl_y$ compounds

Aluminium carbide can either be formed in a reaction which gives free Ti or in reactions that produce some titanium aluminide. We shall first explore the reaction between TiC and Al which gives free Ti (undercooled liquid titanium), taking into account the possibility that Ti dissolves in aluminium. Other reactions will be considered at the end of this Section. The mentioned reaction between TiC and aluminium is,



In order to calculate the free energy associated to this reaction we have to take into account the free energies related to the reactions,



Then, the free energy related to Reaction 8 is given by,

$$\Delta G^{\circ}_8 = \Delta G^{\circ}_{10} + 3 \Delta G^{\circ}_{11} - 3 \Delta G^{\circ}_9 \quad (12)$$

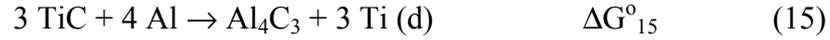
$$\Delta G^{\circ}_8 = \Delta G^{\circ}_f [Al_4C_3] + 3 \Delta G^{\circ}_f [Ti (l)] - 3 \Delta G^{\circ}_f [TiC] - 4 \Delta G^{\circ}_f [Al] \quad (13)$$

The free energy related to the formation of Ti (l) contains two terms, one related to the formation of solid titanium Ti (s) and a second one associated to the phase change  $Ti (s) \rightarrow Ti (l)$  [3], that is,

$$\Delta G^{\circ}_f [\text{Ti (l)}] = \Delta G^{\circ}_f [\text{Ti (s)}] + \Delta G^{\circ}_{\text{phase change, (s)} \rightarrow \text{(l)}} \quad (14a)$$

$$\Delta G^{\circ}_{\text{phase change, (s)} \rightarrow \text{(l)}} = 16234 - 8.368T \text{ (J/mol)} \quad (14b)$$

The results for the free energy obtained by using data reported in [10] are shown in Fig. 5. Thus, Reaction 8 is clearly unfavourable, in agreement with the conclusion of [4]. However, it becomes far more favourable if the dissolution of free titanium in aluminium is taken into account, that is if, instead of Reaction 8 we write,



The free energy associated to dissolution of titanium  $\text{Ti (l)} \rightarrow \text{Ti (d)}$  can be obtained from,

$$\Delta G^{\circ}_f [\text{Ti (d)}] = \Delta G^{\circ}_f [\text{Ti (s)}] + \Delta G^{\circ}_{\text{phase change, (s)} \rightarrow \text{(l)}} + \Delta G^{\circ}_{\text{change phase, (l)} \rightarrow \text{(d)}} \quad (16a)$$

$$\Delta G^{\circ}_{\text{change phase, (l)} \rightarrow \text{(d)}} = -113400 - 5.256T \text{ (J/mol)} \quad (16b)$$

Finally, the free energy related to Reaction 15 is given by,

$$\Delta G^{\circ}_{15} = \Delta G^{\circ}_f [\text{Al}_4\text{C}_3] + 3 \Delta G^{\circ}_f [\text{Ti (d)}] - 3 \Delta G^{\circ}_f [\text{TiC}] - 4 \Delta G^{\circ}_f [\text{Al}] \quad (17)$$

Again, we used the thermodynamic data of [10] to obtain the results shown in Fig. 5. We note that although the effect of dissolution of titanium is dramatic, the free energy is still slightly positive.

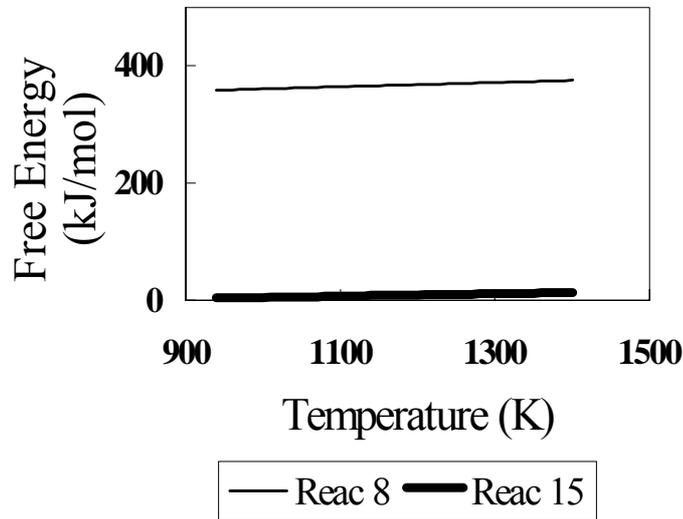
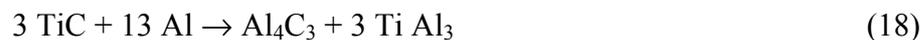
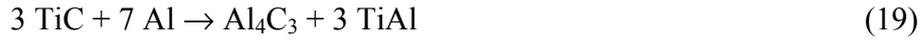


Fig. 5. Free energy versus temperature for Reactions 8 and 15.

The formation of aluminium carbide may be favoured if reactions involving the formation of titanium aluminides are considered. These reactions are,





The free energies associated to these reactions, as reported in [7], are shown in Fig. 6. The behavior of the free energy related to Reaction 19 is qualitatively consistent with the results of Table 1 in the sense that the amount of  $\text{TiAl}_3$  decreases as the temperature of the heat treatment is increased. However, we note that, approximately beyond 1000 K neither of these two reactions is clearly favourable. Further work is needed to resolve the inconsistency between the thermodynamic calculations (for Reactions 8 and 18-19) and the experimental observations summarised in Table 1. Finally we note that possible reactions for the formation of  $\text{Ti}_3\text{AlC}$  are discussed in [5] and that, to our knowledge, no reactions for the formation of  $\text{Ti}_3\text{Al}$  have yet been reported.

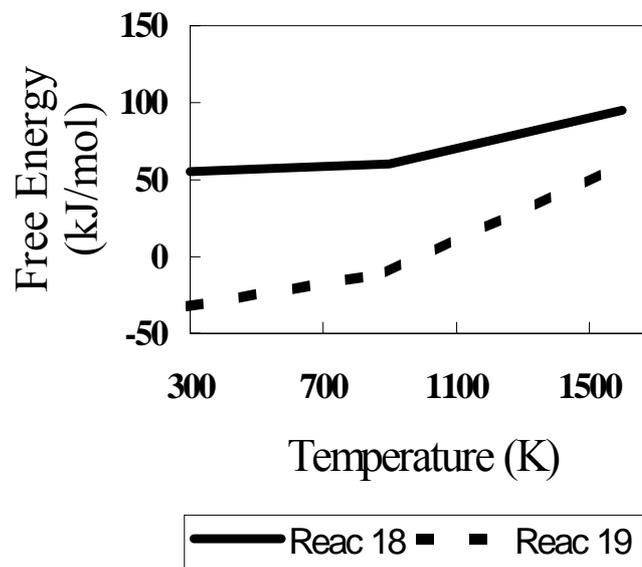


Fig. 6. Free energy versus temperature for Reactions 18 and 19 as reported in [7].

## CONCLUSIONS

In this work we have investigated the reactions between TiC and aluminium in composites of these materials produced by pressure infiltration of the liquid metal into packed samples of the ceramic particulate. Samples of the composites were heat treated at different temperatures and the reaction products identified by means of a variety of experimental techniques. The mechanisms through which those products are formed were also investigated. The main reaction products observed in the heat treated composites were alumina and aluminium carbide. It was concluded that alumina can only be produced if titanium oxides were previously formed. It is shown that the reactions between aluminium and some of the titanium oxides to produce alumina and free titanium, are thermodynamically favourable, thereby providing a mechanism for the formation of alumina. Instead, none of the reactions between aluminium and TiC which give aluminium carbide (plus either free titanium or titanium aluminides) seem to be clearly favourable in the range of Temperatures explored in this work. Further analysis of the thermodynamics of those reactions is required in order to find a mechanism for the formation of aluminium carbide and the  $\text{Ti}_x\text{Al}_y$  compounds.

## ACKNOWLEDGEMENTS

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