A METHOD FOR SIMPLE AND PRECISE MEASUREMENTS OF KINETICS OF REACTIONS BETWEEN SiC AND MOLTEN Al

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Reinforced aluminum is generally fabricated by liquid metal infiltration. The reinforcement degradation produced by molten matrix is the major problem to be considered. The relationship between conversion and thermal exposure time is an important information. In the present paper a method for measuring the conversion by weight determinations is proposed.

Aluminum reinforced with silicon carbide particles is a metal matrix composite with considerable potential as an engineering material. Any method used for producing these composites requires contact between molten Al and SiC reinforcement at some stage of their fabrication. As a result, it is important to asses the stability of SiC when exposed to molten Al and to develop techniques for measuring the extent of the reaction.
Silicon carbide is chemically unstable in molten Al and reacts to form aluminum carbide according to the reaction:

$$4\,Al_{(l)} + 3\,SiC_{(s)} \rightarrow Al_4C_{3(s)} + 3\,(Si\text{-}Al)_{(l)} \qquad (1)$$

The extent of the reaction has been monitored by measuring the intensity of the aluminum carbide and silicon X-ray peaks from the composite /1,2/. The reaction kinetics can also be followed through chemical analysis /1/ of the composite, electron microprobe analysis (EMA)/1/, calorimetric analysis (DSC) /4/ and by determining changes in the liquidus temperature /3/. In principle, the interaction can also be investigated through quantitative metallography, measuring the volume fraction of silicon phase. The aluminum carbide content can also be determined, however, the silicon phase is much easier to resolve when examining etched, diamond-polished sections (see Figures 1,2).

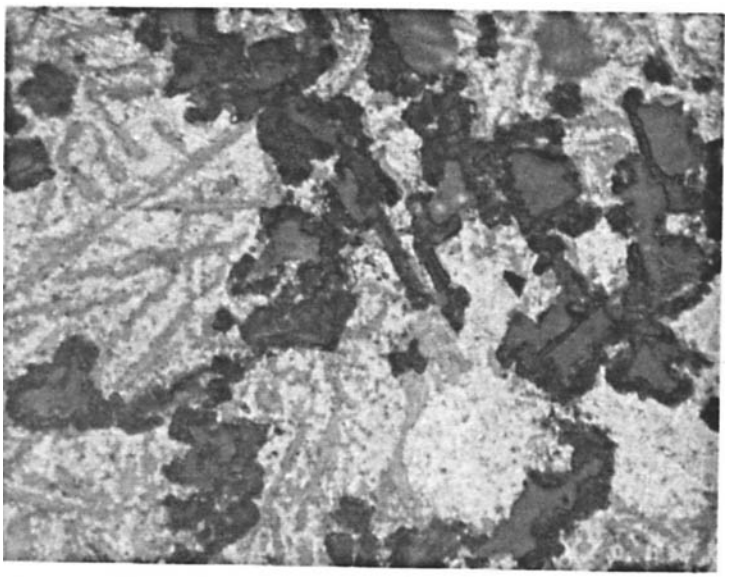

Figure 1: Microstructure of the composite after 48h at 800°C (under vacuum), showing increased Si and Al_4C_3 (as polished sample, x1008). The Al_4C_3 forms on the surface of SiC (dark azure particles) a non uniform layer of well-facetted dark crystallites.

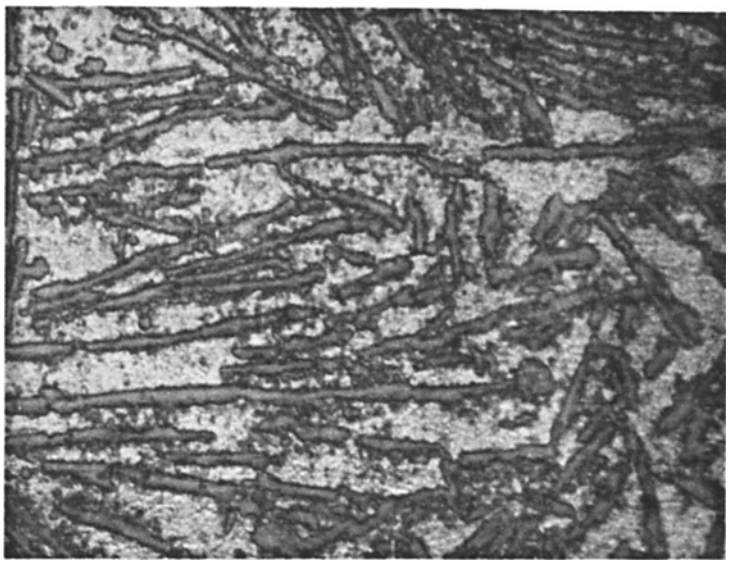

Figure 2: Metallograph photograph of an etched SiC-Al sample, heat-treated at 800°C for 48h under vacuum, showing the matrix microstructure (eutectic phase) (x1008).

Nevertheless, this method is difficult to apply because there is no homogeneity within the composite microstructure. Therefore, an analysis on a large number of high resolution micrographies becomes necessary. Matrix imperfections (e.g. shrinkages produced during the composite solidification, see Figure 3) and damages from abrasion and polishing make stereological analysis more difficult. This paper discusses an easy alternative method for measuring the conversion of (1) using weight determinations by precision balance.

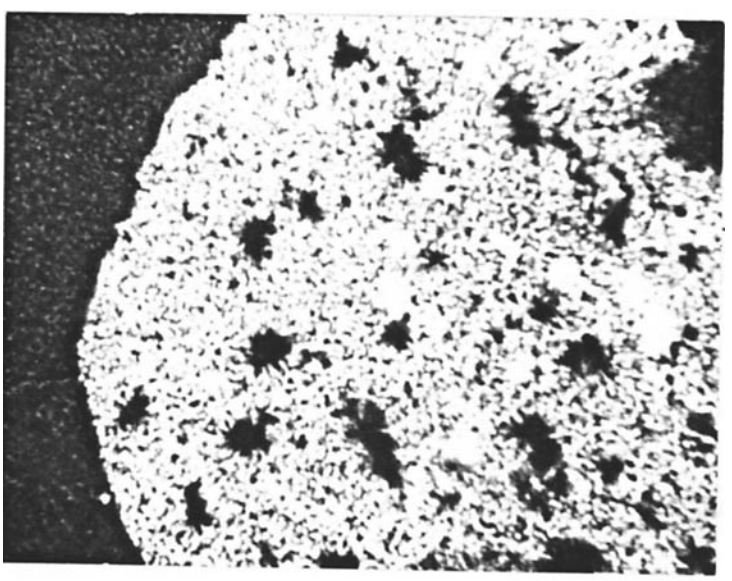

Figure 3: Matrix imperfections produced during the composite solidification (etched SiC-Al sample, x202).

If the composite material is attacked with an acidic solution, the following reactions occur:

$$Al_4C_{3\,(s)} + 12\,H^+_{(aq.)} \rightarrow 4\,Al^{3+}_{(aq.)} + 3\,CH_{4\,(g)}\uparrow \qquad (2)$$

$$2\,Al_{(s)} + 6\,H^+_{(aq.)} \rightarrow 2\,Al^{3+}_{(aq.)} + 3\,H_{2\,(aq.)}\uparrow \qquad (3)$$

The mass variation (Δw) is equal to the mass of evolved gas:

$$\Delta w = w_{CH_4} + w_{H_2} \tag{4}$$

from the stoichiometry of the reaction (2) it follows:

$$w_{CH_4} = 3\ M_{CH_4}\ n_{Al_4C_3} \tag{5}$$

and from the stoichiometry of the reactions (1) and (2) it follows:

$$w_{H_2} = \frac{3}{2} M_{H_2} \left(n^{\circ}_{Al} - 4 n_{Al_4C_3} \right) \tag{6}$$

where w_i are the masses, M_i are the atomic and molecular weigths and n_i are the moles of the i-th component. Substituting (5) and (6) into (4) and deriving $n_{Al_4C_3}$, it can be written:

$$n_{Al_4C_3} = \frac{\Delta w - \frac{3}{2} M_{H_2} n^{\circ}_{Al}}{3\left(M_{CH_4} - 2M_{H_2}\right)} \tag{7}$$

and since:

$$n^{\circ}_{Al} = \frac{w_c}{M_{Al}} \left(1 - \frac{\text{wt. pct of SiC}}{100} \right) \tag{8}$$

where w_c is the composite mass, the equation (7) can be rewriten as:

$$\boxed{\text{wt. pct of } Al_4C_3 = a \left(\frac{\Delta w}{w_c} \right) - b} \tag{9}$$

with:

$$a = \frac{100\, M_{Al_4C_3}}{3\left(M_{CH_4} - 2\, M_H\right)} \approx 342{,}09 \tag{10}$$

and

$$b = \frac{50 M_{H_2} M_{Al_4C_3}}{M_{Al}\left(M_{CH_4} - 2M_{H_2}\right)} \left(1 - \frac{\text{wt pct of SiC}}{100} \right) \approx 44{,}772 \left(1 - \frac{\text{wt pct of SiC}}{100} \right) \tag{11}$$

The wt pct of SiC can be obtained from the volume fraction of reinforcement (typically known quantity) as follows:

$$\text{wt pct SiC} = V_c r_c * 100 / \left[V_m \rho_m + V_c \rho_c \right] \tag{12}$$

where V_c and V_m=1-V_c are the volume fractions of silicon carbide and matrix, and ρ_c and ρ_m are the densities of silicon carbide (3.217 g/cc) and matrix (2.7 g/cc), respectively.

Operatively, Δw can be evaluated e.g. with the following analytical method. The weight of a solid inorganic acid (e.g. $H_2C_2O_4$) in an amount higher than what is stoichiometrically required is carefully determined (w_{HA}) and then dissolved in distilled water. An exactly known amount of composite (w_c) is placed into the solution, following the total dissolution of the sample (weight

invariance), the solvent is evaporated and the residual weight measured ($w_{prod.}$). The Δw value is determined as:

$$\Delta w = w_c + w_{HA} - w_{prod} \tag{13}$$

The degree of accuracy depends upon several factors: firstly, it is important to avoid water splashes during gas evolution (e.g. using a vessel with a small opening such as a volumetric flask); moreover, since methane and hydrogen are hydrophobic gases they can be entirely removed during water evaporation; also the homogeneity of the reacted composite affects the method accuracy, therefore, it is necessary to use large-enough sized samples (i.e. w_c not less than 10 grams). Silicon carbide and silicon crystals (β-crystals of eutectic phase) do not dissolve in acidic solution. Neither does the aluminum contained in the β-crystals, but its amount is negligible (0.17 wt.%).
This method for determining the chemical interaction conversion is a very convenient one because it is utilizable for composites with any level of reinforcement.
Figure 4 shows the changes in Al_4C_3 content with increasing remelt temperature after 1h of annealing, using pure metallic aluminum (99.8wt.%) reinforced with SiC particles (15vol.%, grain size<13μm) produced by sintering.

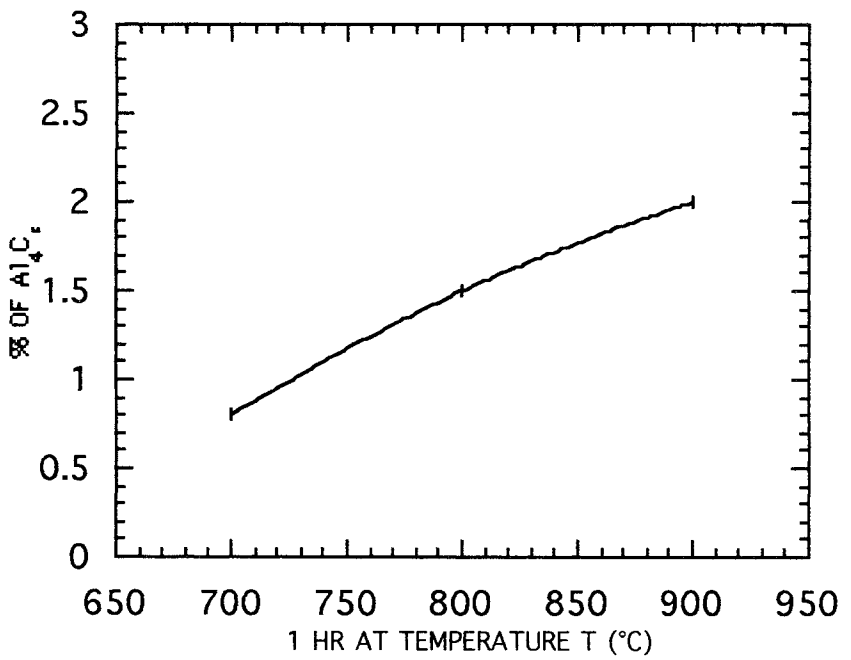

Figure 4: Changes in the Al_4C_3 content of composite after 1h at different temperatures.

The heat-treatment was carried out by heating the samples, in a glass vial and sealed in a vacuum to limit oxidation reactions, in a horizontal tubolar furnace. A Mettler AE 240 balance was used and the acid was absolute sulphuric acid (oleum). The tests were conduced at room temperature. For error evaluation, Equation (9) can be represented by a functional relationship of the form $f=f(x_1, x_2,....)$ where x_1, x_2, ... are measurement parameters or parameters that can be calculated from measurements. In estimating the errors for the values w_C, w_{HA}, and $w_{prod.}$, cross-correlated terms are neglected and, therefore, covariant uncertainties are not considered. Consequently, the uncertainty in this functional relationship can be written as:

$$\Delta f = \left(\frac{\partial f}{\partial x_1}\right)^2 \Delta x_1^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \Delta x_2^2 + ... \tag{14}$$

Applying this expression to (9) and (13) yields the following:

$$\Delta f = a\sqrt{2 + \left(\frac{w_{HA} - w_{prod.}}{w_c}\right)^2}\left(\frac{\delta w_c}{w_c}\right) \quad (15)$$

Since the amount of inorganic acid is elevated ($w_{HA} \approx w_{prod}$), it follows that

$$\Delta f \approx a\sqrt{2}\left(\frac{\delta w_c}{w_c}\right) \quad (16)$$

Using composite samples of about 1g Δf is ± 0.003g.
This method is extremely easy and, since it is founded on simple weight measurements, it is certainly more accurate than other complicated methods described in literature, that are based upon the use of very expensive and sophisticated equipment.

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