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Analysis of the Weight Loss During Sintering of Silicon-Carbide Whisker-Reinforced Alumina Composites

F. Hue, Y. Jorand,* J. Dubois & G. Fantozzi

GEMPPM URA CNRS 341, INSA de Lyon, Bat. 502, Av. A. Einstein, 69621 Villeurbanne Cedex, France

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Abstract

Good densification of Al_2O_3–SiC whisker composites usually requires use of the expensive hot-pressing technique. In this work, composites with 12 vol% whisker content have been made by pressureless sintering at temperatures above 1700°C. To evaluate the effect of the sintering environment, tests were conducted either with samples placed in different powder beds, or by gas pressure sintering. The highest densities are obtained by the use of an alumina powder bed, or by gas pressure sintering. The latter method leads to densities of 95% of theoretical. The densities achieved are strongly dependent on the chemical stability of the species at the sintering temperature. This stability was evaluated by measuring the weight loss after sintering. Then, an analysis of the sintering process with reference to chemical engineering techniques was conducted. The analysis shows the relevance of the selected sintering cycles. © 1997. Published by Elsevier Science Limited. All rights reserved.

1 Introduction

Among ceramic–ceramic composite systems, Al_2O_3–SiC whisker-reinforced composites [for clarity, in the following text this will be denoted as SiC(w)] have been extensively studied over the last few years[1,2] owing to their improved performance and reliability compared with alumina. Such composites possess high toughness, strength, hardness, thermal shock resistance and excellent properties up to 1200°C.

However, because Al_2O_3–SiC(w) composites are difficult to sinter to full density by pressureless sintering, most of the investigated materials were hot-pressed composites. Tiegs and co-workers[3,4] and Sacks and co-workers[5–7] have developed high-density pressureless-sintered Al_2O_3–SiC(w) composites through different ways. Tiegs and co-workers made their composites by dry compaction. Major parameters revealed were: (1) reduced whisker length and selected ultrafine alumina, (2) use of 2% Y_2O_3 and 0·5% MgO as sintering aids, (3) SiC(w) content not above 10 vol%. Sacks and co-workers[5–7] used slip casting technique to obtain green samples. This technique allowed them to raise green density from 53–59% to 70–71% and therefore to obtain quite dense composites without sintering aids with 15 vol% SiC(w) content. This is an important point, as it has been shown that sintering aids are detrimental to high-temperature properties[8,9] and the major interest in these composites is their potential for use at high temperature. Nevertheless, reduced length SiC(w) were also used. Sintering temperatures above 1700°C were required in these experiments and both groups noticed an important weight loss in their samples (more than 5% for Sacks and more than 10% for Tiegs) but they did not study the influence of weight loss on their composites.

Moreover, Al_2O_3–SiC has been studied extensively from chemical and thermodynamical points of view.[10–12] Misra[10] points out the effects of C and SiO_2 content in SiC liquid phase sintering, and shows that the major gaseous species are CO, Al_2O, SiO and Al vapour. But he did not consider the influence of such species on the final density of the SiC. Pijolat and Soustelle[13] have studied the influence of sintering atmosphere on the sintering rate of different oxides. They showed the significant influence of water vapour in raising the initial sintering rate of oxides like Al_2O_3 and TiO_2.

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*To whom correspondence should be addressed.

The purpose of this work is to determine the relationship between weight loss during sintering and final density attained in order to justify our interest in the use of gas pressure sintering (GPS) as another sintering method to increase the final density of the composites. Different composites have been prepared by pressureless sintering under different environments. An analysis in terms of chemical gas processing is presented, showing the prevailing influence of sintering atmosphere. This analysis refers to basic concepts used in chemical engineering.[14] We show that gas pressure sintering is an alternative way to improve final density without the use of sintering aids and with only minor additional costs in comparison to hot-pressing techniques.

2 Experimental Procedure

The processing of Al_2O_3–SiC(w) composites by hot-pressing or by pressureless sintering has already been described.[1–7,15] The general processing scheme used is shown in Fig. 1.[16] Concerning the raw materials, special attention was given to the SiO_2 content, which is known to inhibit sintering[17] and to induce low toughness in Al_2O_3–SiC(w) composites.[18] A very high-purity and high-reactivity alumina powder (Baïkowski SM8) with a specific surface area of 10 $m^2 g^{-1}$ and medium particle size of 0·35 μm was used. SiC whiskers (Tateho SiC whiskers, grade SCW1) with an average diameter of 0·5 μm and an average aspect ratio of 20:1 were used. Slurries were made by mixing the two batches previously dispersed in water, each in a deflocculated condition. After drying (80°C, under low vacuum), powder granulation was made by screening to 60 mesh. Samples were first pressed uniaxially up to 25 MPa, and then isostatically up to 400 MPa, which led to sample green densities between 53 and 60% of the theoretical density. Table 1 shows a slight decrease in green sample density up to 12 vol% whisker content, followed by a rapid decrease as the whisker content reaches 30 vol%. Sintering cycles were realized under flowing high-purity argon in a graphite furnace at temperatures between 1500 and 1800°C (1·5°C min^{-1} heating rate, dwell time 2 h). The samples were put in the furnace under different conditions: (1) in an open graphite crucible without powder bed, (2) in a closed graphite crucible, without powder bed, (3) in open graphite crucible containing alumina powder bed or silicon carbide powder bed. Final densities were calculated by Arthur's method[19] based on Archimedes' principle. Weight losses after sintering were evaluated by considering the initial sample weight after burn out of lubricant and other polymeric phases at 600°C (2 h, 0·5°C min^{-1}). The SiC whisker amounts are given in volume percent, weight loss and lubricant amount in mass percent.

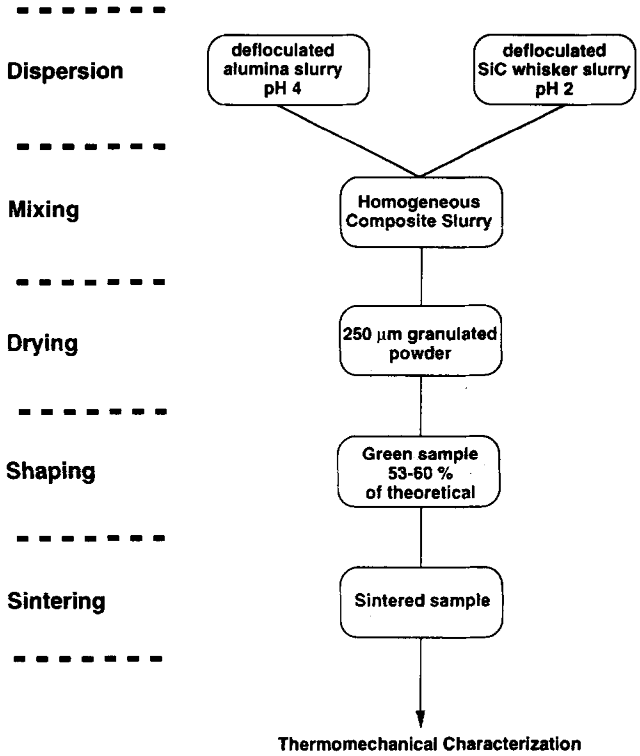

Fig. 1. Schematic of the route to produce Al_2O_3–SiC(w) composites.

Table 1. Relative green sample density (25 MPa uniaxial pressing followed by 400 MPa isostatic pressing)

	Pure SM8 alumina	*Al_2O_3 + 6·2% SiC(w)*	*Al_2O_3 + 12% SiC(w)*	*Al_2O_3 30% SiC(w)*
Green sample density (%)	59 ± 1	58 ± 1	59 ± 1	53 ± 1

3 Results

Figure 2 shows a decrease in final density with increasing SiC(w) content. This result confirms the role of the whiskers as sintering inhibitors, as previously reported.[3–7] The final densities obtained in this study are drastically lower than those of Sacks and co-workers,[5–7] as a consequence of the lower green densities.

Figure 2 also shows the influence of the use of a powder bed. The highest densities were always obtained with an alumina powder bed. Surprisingly, use of an SiC powder bed led to important decreases in the final densities. This phenomenon was predominant for low whisker contents. Results of weight loss during sintering are presented in Fig. 3. Depending on SiC whisker content, the weight loss can reach values greater than 10%.

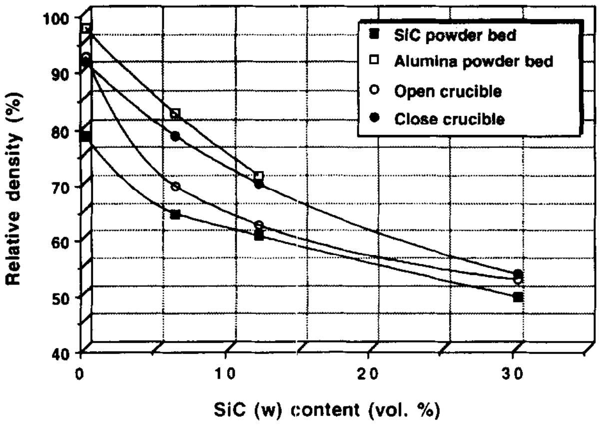

Fig. 2. Final composite density versus SiC whisker content. Sintering cycle: 1700°C/2 h/1 atm argon.

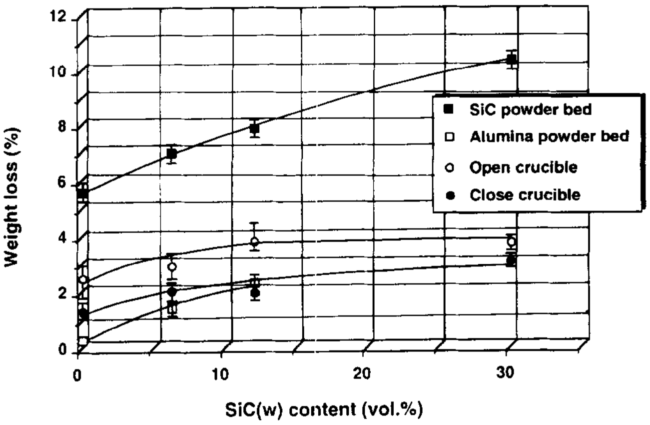

Fig. 3. Weight loss after sintering cycle versus SiC whisker content. Sintering conditions: 1700°C/2 h/1 atm argon.

Figure 3 shows an increase in weight loss with increasing SiC(w) content, for different sample environments. SiC powder bed led to the highest weight loss, while Al_2O_3 powder bed reduced the weight losses. These results are related to final density values shown in Fig. 4 for pure alumina and 6·2 vol% SiC(w) composites. Indeed, it is quite clear that for the same initial sample sintered at 1700°C/2 h in several environmental conditions, an increase in weight loss leads to a decrease in final density. The chemical reactions promoting weight loss are endothermic solid–gas reactions occurring on the powder surface (alumina or silicon carbide or both). They promote chemical surface degradation and surface energy lowering by reaction instead of densification. This suggests that another way to improve the final density of these materials could be reduction of the weight loss, i.e. by limiting chemical degradation reactions. Moreover, a reduction of the chemical degradation of the composite should allow the use of higher sintering temperatures, and thus promote densification.

Following these preliminary experiences, some improvements were made concerning some minor points of the processing scheme. Samples containing 12% SiC(w) were prepared by: (a) reduction of the whiskers' aspect ratio by grinding for 10 h with alumina media, this operation leads to a final aspect ratio of about 10:1; (b) use of 4% poly(ethylene glycol) 1500 as a lubricant to avoid microcracks during sample compaction; (c) uniaxial compaction at 100 MPa followed by 400 MPa isostatic pressing to promote planar whisker orientation; and (d) sintering cycle at 1650°C/2 h/1 atm with alumina powder bed or at 1800°C/0·5 h/150 atm under flowing argon* with the GPS technique. Results presented in Table 2 show benefit on final density of reducing the aspect ratio of the whiskers: final relative density reached 82% at 1650°C compared with 70% previously reached at 1700°C without aspect ratio reduction of the whiskers. This increase corresponds to the results reported by Tiegs and co-workers.[3,4]

Nevertheless, the final densities were still too low to obtain good mechanical properties.

Consequently cycles at 1800°C/150 atm were conducted, and led to a noticeable increase in final densities: the values obtained are equivalent to those reported by Tiegs and Becher[3] with sintering aids and by Sacks *et al.*[5] with the slip casting technique.

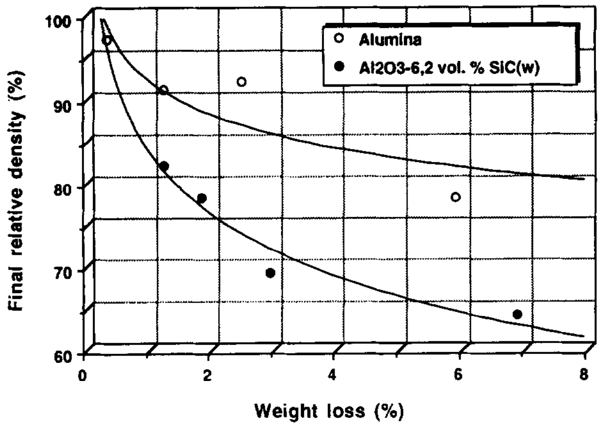

Fig. 4. Final density versus weight loss. Sintering conditions: 1700°C/2 h/1 atm argon.

Table 2. Final densities for Al_2O_3 + 12% SiC(w) composites containing low aspect ratio whiskers

	1650°C/2 h/1 atm	*1800°C/0·5 h/150 atm*
Green density (%)	59 ± 1	59 ± 1
Final density (%)	82 ± 1	95 ± 2
Weight loss during sintering (%)	< 1	—

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*Gas pressure sintering cycles were conducted by Ceram-etal/Mamer/Luxembourg.

Table 3. Some of the chemical reactions occurring in the Si–C–O system under inert atmosphere

(1)	$SiC(s) + Al_2O_3(s) = SiO(g) + Al_2O(g) + CO(g)$	$\Delta G°(2000\ K)$: 286 kJ mol^{-1}
(2)	$SiC(s) + 2\ Al_2O_3(s) = SiO(g) + 2Al_2O_2(g) + CO(g)$	$\Delta G°(2000\ K)$: 899·7 kJ mol^{-1}
(3)	$4\ SiC(s) + 2\ Al_2O_3(s) = Al_4\ SiC_4(s) + 3\ SiO_2(s)$	$\Delta G°(2000\ K)^a$: 487·2 kJ mol^{-1}
(4)	$SiC(s) + 2\ SiO_2(s) = 3\ SiO(g) + CO(g)$	$\Delta G°(2000\ K)$: 94 kJ mol^{-1}
(5)	$3\ Al_2O_3(s) + 2\ SiO_{2(l)} = 3\ Al_2O_3.2\ SiO_2(s)$	$\Delta G°(2000\ K)$: 23·97 kJ mol^{-1}
(6)	$2\ Al_2O_3(s) + 9\ C(s) = Al_4C_3(s) + 6\ CO(g)$	$\Delta G°(2000\ K)$: 283·7 kJ mol^{-1}
(7)	$Al_2O_3(s) + 3\ C(s) = 2\ Al(g) + 3\ CO(g)$	$\Delta G°(2000\ K)$: 187·3 kJ mol^{-1}
(8)	$2\ Al_2O_3(s) + 3\ SiC(s) = 4\ Al(g) + 3\ CO(g) + 3\ SiO(g)$	$\Delta G°(2000K)$: 607·2 kJ mol^{-1}
(9)	$SiO(g) + 2\ C(s) = SiC(s) + CO(g)$	$\Delta G°(2000\ K)$: −77·5 kJ mol^{-1}

[a] Data from Misra.[10]

4 Thermochemical Analysis

During sintering cycles of Al_2O_3–SiC(w) composites, the four initial solid constituents are Al_2O_3, SiC, C present in the graphite crucible or in SiC as an impurity, and SiO_2 as the main impurity. Despite the raw material being chosen carefully, SiO_2 is present as a thin layer surrounding SiC due to manipulation in aqueous medium. This was revealed by TEM and ESCA experiments[9,20] on the whiskers. Other elements present in Al_2O_3 or in SiC as impurities are not considered. Considering thermodynamical data for the system Al_2O_3–SiC(w) composites, we can envisage many reactions at high temperature[10–12,21] (see Table 3). This system can be solved using different calculating methods like the THERMODATA† system to determine reactivity and volatility of this four-component system at high temperatures as a function of phase content, impurities eventually present and temperature. Misra[10] has studied the system Al_2O_3–SiC with SiC as the major phase. He concluded that the predominent gaseous species in the SiC–Al_2O_3 system were CO, SiO, Al_2O and Al vapour.

In our experiments, very pure argon was used ($P_{O_2} < 10$ ppm). Therefore, no reaction involving O_2 has been considered. According to Misra,[10] reactions (3) and (6) are not considered because his calculations reveal the presence of Al_4C_3 or Al_4SiC_4 at temperature above 2220 K (1947°C). Reaction (5) leads to mullite formation and does not have an effect on weight loss. This reaction is very limited considering the amount of silica present as a layer on silicon carbide. Furthermore, all these solid–liquid reactions can promote densification and do not lead to composite weight loss.

As seen in Table 3, all reactions leading to gas formation involve degradation of solid species, especially Al_2O_3 and SiC as the major species present. All are endothermic reactions and absorb energy from the system, leading therefore to poorer final densities. Even if the amount of gaseous species is largely dependent on impurities and sintering conditions, we assume that, during the cycle, the equilibrium gas pressure is reached inside the crucible so that each vapour pressure is constant.

P_{CO}, for example, can be calculated as a function of different parameters

$$P_{CO} = F\,(SiC,\ C,\ Al_2O_3,\ SiO_2,\ impurities,\ T)$$

Then, with reference to chemical process engineering methods (which are currently used in other domains), we will consider the sample inside the furnace as a continuous stirred tank reactor,[14] as described in the Appendix. During sintering dwell, equilibrium is reached inside the reactor (meaning no variation in temperature, gas concentration or pressure). The CO gas pressure can therefore be calculated inside the sample by conservation of CO concentration inside and at the exit of the chemical reactor. This is expressed by:

$$\frac{F_{oCO}}{F_{oT}} = \frac{P_{oCO}}{P_{oT}} \qquad (1)$$

where F_{oT} and F_{oCO} respectively are the total and the CO exit flow rates (in mol s^{-1}), P_{oT} and P_{oCO} are the total and the CO pressures inside the reactor and at the outlet (in Pa).

Considering no inlet CO flow, CO exit flow can be calculated from P_{oCO} and relation (1):

$$F_{oCO} = \frac{P_{oCO}}{P_{oT}}\, F_{oT} \qquad (2)$$

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† THERMODATA: Domaine Universitaire de Grenoble, 38402 St. Martin d'Hêre Cedex, France.

During dwell, CO production can thus be calculated from relation (2)

$$n_{CO} = \int_{t_0}^{t} F_{oCO} \mathrm{d}t \qquad (3)$$

$$n_{CO} = \frac{P_{oCO}}{P_{oT}} F_{oT} (t - t_0) \qquad (4)$$

Relation (4) has been established for CO species. It is also available for each of the other gaseous species produced by reaction of the system during sintering dwell: Al_2O, SiO, Al, etc.:

$$n_j = \frac{P_{oj}}{P_{oT}} F_{oT} (t - t_0) \qquad (5)$$

where j represents the different species except argon (in g mol^{-1}).

Therefore total weight loss during dwell (W) can be expressed by mass conservation:

$$W = \sum_j M_j n_j = \sum_j M_j P_{oj} \frac{F_{oT}}{P_{oT}} (t - t_0) \qquad (6)$$

where M_j is the molar mass of species j except argon (in g mol^{-1}).

From relation (6) we can conclude that:

(1) Increasing dwell time $(t - t_0)$ could lead to an increase in weight loss W. However, dwell time is necessary to enhance sample density.

(2) An increase in total flow F_{oT} enhances W. This flow has to be reduced in order to improve final density, for instance by a reduction of the flowing argon (see Appendix), or by the use of a bed powder as described in the following section. It can also be reached by enhancing composite density, i.e. green density, and reducing the size of the open porosity as per the results of Sacks.

(3) Weight loss can also be reduced by increasing P_{oT}, the total pressure inside sample, as it is reached in gas pressure sintering.

5 Practical Applications

5.1 Power bed

From eqn (6) it can be seen that a reduction in total flow rate F_{oT} around and inside sample leads to a decrease in weight loss. As the use of a powder bed reduces flow inside crucible to part of the total flow in the furnace by limiting transport of reactants, it reduces W and then leads to an increase in density. This result deals with experimental results shown in Fig. 2 except in the case of the SiC powder bed.

The different effects of the SiC and alumina powder beds are more difficult to explain. For SiC powder, reaction between SiC and alumina occurs preferentially at the surface of the sample, where the gas flow is more important than inside. Due to the SiC(w) content in the composites (mostly 0 to 12%), reaction can occur without lack of alumina, leading to an important weight loss. In the case of an alumina powder, the reaction is the same but presence of SiC(w) at the surface of the sample is limited by the SiC(w) content in sample. After a short time, no more SiC(w) remains at the surface and reaction occurs inside sample with a drastically reduced gas flow.

On the other hand, we can suppose that the use of SiC or alumina as a powder bed influences composite sintering mechanisms as described by Pijolat and Soustelle[13] for water vapour in the first stage of oxide sintering, but this has to be studied and confirmed.

5.2 Gas pressure sintering

Equation (6) shows the effect of raising the total pressure around sample on the reduction of species exit flow. Weight loss is therefore drastically reduced and the composite final density is enhanced. This analysis deals with experiments made with gas pressure sintering as shown in Table 2. In all experiments, the use of the GPS technique allowed the density of Al_2O_3–SiC(w) composites to reach between 89 and 97% of theoretical without sintering aids.

Another promoting factor is the pressure effect on the sample after porosity closure. Increase of the pressure on closed porosity acts like a HIP cycle at low pressure and allows another additional improvement of the final density. The combination of all those mechanisms finally leads to the highest densities being obtained without the need for hot-pressing.

6 Conclusion

Pressureless sintering of Al_2O_3–SiC(w) composites requires temperatures above 1700°C. During sintering cycles, a connection has been noticed between weight loss and final composite density. A chemical engineering analysis considering vapour formation has been conducted to reduce weight loss, leading to an increase in final density. Weight loss reduction is obtained by an increased residence time of the vapour species. The use of

SiC and Al_2O_3 powder beds around samples has been shown to modify significantly the final density, depending on the intensity of the chemical reactions that occur. Alumina powder bed leads to the highest densities.

Gas pressure sintering has also been shown to improve final composite density. Final densities up to 95% of theoretical are reached, resulting from the combination of reduced chemical reactions with the pressure effect on the sample containing a small open porosity at the end of the sintering cycle. Experimental results are in accordance with theoretical analysis.

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Appendix: Modelling of a Continuous Stirred Tank Reactor (from Villermaux[14])

In the case of an ideal gas included in a batch reactor, we can write the following relation:

$$P_j V = n_j RT \text{ for each species } j \qquad \text{(A1)}$$

where V is the volume of the gas, P_j is the partial pressure of gas j, n_j is the number of moles of gas j, R is the ideal gas constant and T is the temperature in Kelvin.

Similarly, for the total system,

$$P_T V = n_T \, RT \qquad \text{(A2)}$$

where P_T is the total pressure of gas and n_T is the total number of moles in the system.

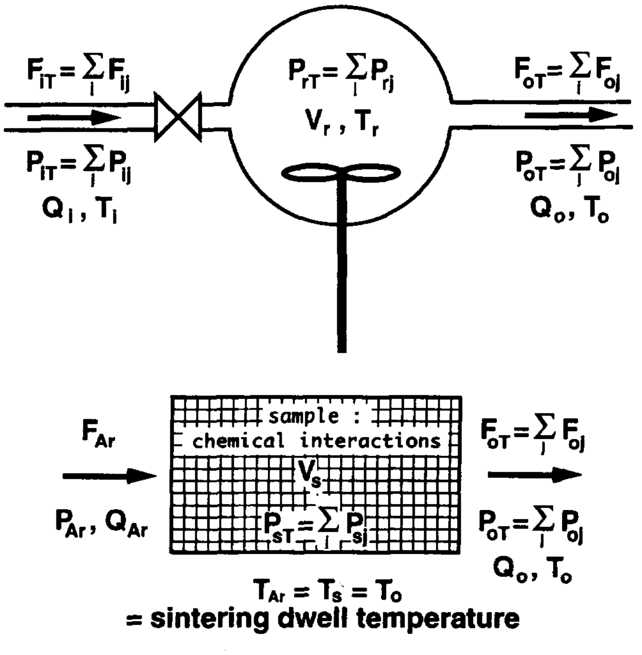

Fig. A1. Top, schematic of a continuous stirred tank reactor (from Ref. 14); bottom, sample during sintering dwell modelled as a continuous stirred tank reactor.

Considering now a continuous reactor with ideal gas (see Fig. A1), relations (A1) and (A2) are modified as follows

$$P_{oj}\,Q_o = F_{oj}\,RT \qquad \text{(A3)}$$

with Q_0 the flow outlet reactor expressed in mass/t, P_{oj} the outlet pressure of species j (the same as the pressure inside reactor for a continuous stirred tank reactor) and F_{oj} the outlet flow of j species expressed in mole/t.

Also, for the total system,

$$P_{oT}Q_o = F_{oT}\,RT \qquad \text{(A4)}$$

where subscript T represents total species.

Dividing relation (A3) by relation (A4) and considering CO as the gas species, we find the relation (1) in Section 4:

$$\frac{F_{oCO}}{F_{oT}} = \frac{P_{oCO}}{P_{oT}} \qquad (1)$$

Assuming equilibrium to be reached in the continuous stirred tank reactor, the mass balance criterion can be written as follows:

$$F_{ij} + V\,R_j = F_{oj} \qquad \text{(A5)}$$

where F_{ij} represents flow inlet in the reactor in mol s^{-1} and $V\ R_j$ represents flow of production of j species by reaction inside the reactor. Assuming equilibrium is reached, no accumulation flow remains.

During the experiments, only argon was used as a flowing gas. Therefore, for each species except argon, F_{ij} is nil. Then the production flow inside the reactor is equal to the number of moles of j produced in unit time at the outside, which is expressed by:

$$n_{CO} = \int_{t_0}^{t_1} F_{oCO}\,dt \qquad (3)$$