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**EVIDENCE FOR THE MICROWAVE EFFECT DURING THE ANNEALING OF
ZINC OXIDE**

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EVIDENCE FOR THE *MICROWAVE EFFECT* DURING THE ANNEALING OF ZINC OXIDE

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ABSTRACT

A microwave/conventional hybrid furnace has been used to anneal virtually fully dense zinc oxide ceramics under pure conventional and a microwave/conventional hybrid heating regime with a view to obtaining evidence for the ‘microwave effect’ during the resulting grain growth. In each case it was ensured that each sample within a series had an *identical* thermal history in terms of its temperature/time profile. The results showed that grain growth was enhanced during hybrid heating compared to pure conventional heating; the greatest enhancement, a factor of ~3 increase in average grain size, was observed in the range 1100-1150°C. The grain growth exponent decreased from 3 during conventional heating to 1.4 during hybrid heating in this temperature range, suggesting an acceleration of the diffusional processes involved. Temperature gradients within the samples were found to be too small to explain the results. This suggests that clear evidence has been found to support the existence of a genuine ‘microwave effect’.

INTRODUCTION

Many investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. This has included apparent evidence for accelerated kinetics for a range of processes in ceramic, polymeric and organic systems [1,2,3,4,5,6, 7,8,9,10]; enhanced sintering of ceramic powder compacts, including lower sintering temperatures [11,12]; and reduced activation energies [1,2,3,11]. It is now generally, though not unanimously, accepted that a ‘microwave effect’ exists, though recent research on the sintering of ceramics involving the use of a single microwave/conventional hybrid furnace appears to have provided extremely clear evidence for its existence [13]. In a parallel study to the current work, three ceramics with different microwave absorption characteristics were sintered under pure conventional and a range of microwave/conventional hybrid heating regimes using exactly the same temperature/time profile. Both the measured final densities of the samples and the use of a dilatometer showed that the presence of microwaves enhanced densification, with higher microwave power levels, finer particle sizes and, particularly, greater microwave absorption by the ceramic, resulting in greater enhancement. The largest effect occurred at temperatures that represented the early to intermediate stage of sintering; for both submicron and micron powder ZnO samples the increase in densification was equivalent to approximately a 100°C higher sintering temperature. A smaller size of effect was observed for yttria-doped zirconia ceramics, which have a lower microwave absorption, whilst for the alumina, a very poor microwave absorber at 2.45 GHz, only an extremely small, but nevertheless repeatable, increase in density was observed. These effects could not be accounted for by the presence of temperature gradients of sufficient magnitude, a potential cause of the effect, within the specimens. Two separate techniques based on optical thermometry and a thermal imaging camera both failed to detect any gradients that

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2 were larger than approximately 10°C between the centre and edge of the samples, a seventh of the size
3 required to explain the results.
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6 In the present work, the same microwave/conventional hybrid sintering furnace outlined above has been
7 used to investigate the effect of the fraction of microwave power used during hybrid and pure
8 conventional heating on grain growth in >98% dense zinc oxide ceramics, again using *identical*
9 temperature/time profiles for each series of experiments.
10

11 EXPERIMENTAL

12
13 A submicron zinc oxide (ZnO) powder (99.9% purity, Sigma Aldrich, UK) was used to produce disks
14 measuring 13 mm diameter by 5 mm thickness by uniaxial pressing using poly(ethylene glycol)-block
15 poly(propylene glycol)-block poly(ethylene glycol) binder (Sigma Aldrich). The green densities were
16 58% of theoretical. A hole was drilled into the centre of one face of each green disk to accommodate the
17 optical thermometer temperature measurement probe described below and then they were sintered using
18 two-stage sintering with pure conventional heating. Two-stage sintering is a new approach developed by
19 Chen and Wang [14], the aim is to enable the retention of a fine grain size whilst achieving notionally
20 full densification. Based on preliminary work, this involved heating the disks at 20C min⁻¹ to an initial
21 temperature (T1) of 850°C and then immediately cooling to the lower temperature (T2) of 820°C as fast
22 as the furnace was capable. The samples were then held at this lower temperature for 15 hrs before
23 furnace cooling back to room temperature. As a result of this sintering schedule, all of the disks used in
24 the current work were >98.4% of theoretical density and had an average grain size of ~0.6 μm.
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29 The disks were subsequently annealed in a single conventional/microwave hybrid furnace for 1, 3 or
30 5 hrs at 900, 1000, 1100, 1150 or 1200°C using either pure conventional heating or hybrid heating
31 involving 1 kW of 2.45 GHz microwave power and a balance of conventional heat sufficient to achieve
32 an *identical* temperature/time profile, figure 1. Note that all the samples were held at 500°C for 1 hour at
33 the beginning of each annealing run to ensure that thermal equilibrium was reached before the
34 temperature was increased to the final value chosen. This minimised the magnitude of any temperature
35 gradients developed.
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38 Throughout the work, the temperature was controlled using a Luxtron optical thermometer (M10,
39 Luxton Corporation, USA) inserted into the narrow hole drilled into the centre of the flat face of each
40 sample such that the temperature was measured at the centre of the body. The temperature at the edge of
41 the samples was also monitored using a second optical thermometer, this allowed the temperature
42 gradient across each sample to be determined, figure 2. The radiation from the heating elements was
43 shielded via the use of a non-metallic, very low dielectric loss ceramic tube around the optical
44 thermometers to achieve accurate temperature measurement. The accuracy of the measurements had
45 been independently assessed using a separate series of measurements involving the melting point of
46 vanadium pentoxide and found to be ±3°C [15].
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50 Green sample densities were determined by simple measurement of the sample dimensions and mass,
51 whilst the sintered and annealed densities were measured by the Archimedes method using mercury. The
52 microstructures of all the specimens were examined on both fractured and sliced, polished and
53 chemically etched surfaces using field emission gun scanning electron microscopy (FEG-SEM), the
54 latter allowing the average grain size and grain size distribution to be determined using the linear
55 intercept method and also the use of computer-based image processing software (Image Pro, Media
56 Cybernetics, inc, USA).
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RESULTS AND DISCUSSION

Figure 3 shows the polished and etched microstructures at the centre of the ZnO disks before annealing and after annealing at 1000°C and 1100°C for 5 hours using pure conventional and hybrid heating. It can be seen that grain growth was enhanced by the use of hybrid heating, a phenomenon confirmed by the grain size data shown after 5 hours of annealing in figure 4. The figure reveals that the onset of significant grain growth during conventional heating was at around 1150°C, whilst for the hybrid heated samples it occurred at about 1050°C. By 1200°C, the difference in grain size between the conventionally and hybrid annealed samples was significantly reduced, supporting the idea that microwaves have their greatest effect during the early to intermediate stages of the process [13]. This appears to be confirmed by figure 5, which shows that the slopes of the lines at 1100 and 1150°C were different for the conventional and hybrid cases although they were essentially the same at 1200°C.

Table 1 shows the temperature differences that existed across the radius of the disks that were annealed for 5 hours at each of the different annealing temperatures investigated, as measured by the two optical thermometers. The difference in temperature, ΔT , is given by the surface temperature minus the temperature at the centre of the sample, thus an inverse temperature gradient would be visible by the presence of a negative value for ΔT . It can be seen that this was not found with any of the samples, the surface was always slightly hotter than the centre of the sample, particularly at the start of the annealing soak period. Although the hybrid heated samples had a smaller temperature gradient than the pure conventional heated samples, indicating that overall the samples had been slightly hotter, this was always less than 20°C, far too little to account for the significantly larger average grain sizes at 1100 and 1150°C.

The kinetic grain growth equation can be expressed by equation 1 [16]:

$$G^n - G_0^n = Kt \quad (1)$$

Where G is the average grain size, n is an integer that depends on the diffusion mechanism, t is time and K can be expressed by the Arrhenius equation:

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where K_0 is the pre-exponential constant of the material, Q the activation energy, R the gas constant and T the absolute temperature. Hence, the kinetic grain growth equation can be written as:

$$G^n - G_0^n = K_0 \exp\left(-\frac{Q}{RT}\right) t \quad (3)$$

In this expression the initial grain size G_0 can be neglected because it is significantly smaller than the grain size G at time t . Thus, equation 3 can be simplified to:

$$G^n = K_0 \exp\left(-\frac{Q}{RT}\right) t \quad (4)$$

This has been widely applied by many researchers to calculate the grain growth exponent value n , e.g. [17], by plotting in the form:

$$\log G = \frac{1}{n} \log K + \frac{1}{n} \log t \quad (5)$$

Where the slope of the $\log G$ versus $\log t$ line is $1/n$, the grain growth exponent. Hence the smaller the value of n , the greater the rate of grain growth.

Figure 6 illustrates the results for ZnO annealed at 1100°C whilst Table 2 shows the values for n as a function of temperature. It can be seen that at 1100 and 1150°C they were 3.3 during pure conventional heating and 1.4 during hybrid heating respectively, whilst at 1200°C they both decreased to around 1.5. Many researchers have reported grain growth results during sintering of undoped ZnO using pure conventional heating and the value of n obtained is ~ 3 in the 1100-1150°C temperature range [18, 19, 20, 21], showing good agreement with the present results. The fact that the value of n at 1200°C during conventional heating and at 1100 – 1150°C during microwave-based heating is both lower and similar suggests that the effect of using microwaves is simply to accelerate the conventional process so that it happens roughly 100°C sooner, in line with the results from the sintering study [13].

CONCLUSIONS

Dense, sintered zinc oxide pellets have been annealed using both pure conventional and hybrid heating schedules involving 1 kW of microwave energy but in exactly the same equipment and ensuring that all the samples within each series saw *exactly* the same thermal history. The results showed clearly that grain growth was enhanced by approximately a factor of 3 in the range 1100 – 1150°C with hybrid heating compared to the conventional heating. Similarly, the grain growth exponent, n , decreased from ~ 3 with conventional heating to about half of this value indicating a considerable acceleration of the diffusional processes involved. Similar results were obtained by Janney et al [2] who studied grain growth in dense, fine-grained, alumina containing 0.1 wt% MgO using conventional and 28 GHz microwaves, though in separate furnaces. Whilst the microstructural changes that occurred were the same for both sets of samples, the grain growth kinetics were greatly increased by the microwave anneals; the grain growth rate at 1500°C in the microwave furnace matching that at 1700°C in the conventional furnace. In the present work, temperature gradients within the samples were found to be too small to explain the results, suggesting the existence of a genuine ‘microwave effect’ – which appears to be a simple acceleration of the conventional grain growth mechanism so that it happens at an approximately 100°C lower temperature. One possible explanation for the effect is the formation of Schottky defects which will enhance mass diffusion transport. Indirect experimental evidence was observed via increases in the levels of porosity in the samples. These also occurred at lower temperatures in the hybrid annealed pellets.

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Figure 1: Example temperature – time curves used for annealing ZnO pellets using both a) pure conventional and b) hybrid heating, the latter involving 1000 W of microwave power. The level of conventional power used is also indicated.

Figure 2: Temperature monitoring system; the sample temperature is controlled by the optical fibre thermometer at the centre of the sample body.

Figure 3: FEG-SEM micrographs of the centre of the submicron ZnO pellets: a) before annealing and after annealing for 5 hours, b) at 1000°C using conventional heating, c) at 1000°C using hybrid heating, d) at 1100°C using conventional heating and e) at 1100°C using hybrid heating. The hybrid heating anneals involved 1000 W of microwave power.

Figure 4: Average grain sizes after 5 hours for annealed ZnO samples as a function of annealing temperature and location on the cross section of the sample (see inset) with conventional and hybrid heating.

Figure 5: Average grain sizes as a function of time for annealed ZnO samples after conventional (C) and hybrid (H) heating at 1100°C, 1150°C and 1200°C.

Figure 6: Log grain size versus log time for ZnO pellets annealed at 1100°C using conventional and hybrid heating. The grain growth exponents, n , are shown on the plot.

Table 1: Temperature differences across the ZnO pellets during annealing.

Table 2: Grain growth exponent values for un-doped, submicron ZnO as a function of temperature for conventional heating and hybrid heating. Errors are those arising from the fit to the data.

Table 3: Porosity changes in the ZnO pellets as a result of conventional and hybrid annealing.

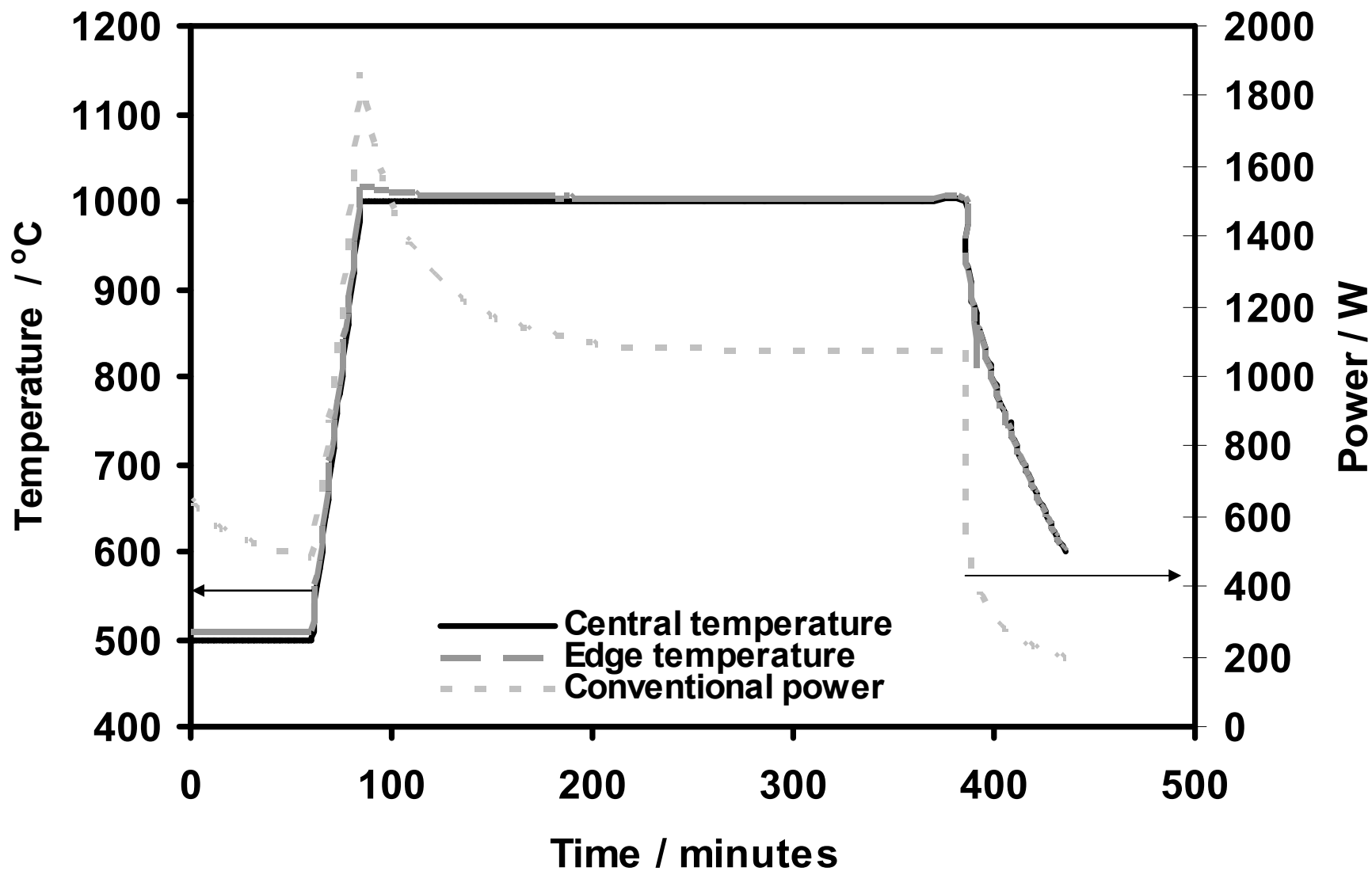


Fig 1a

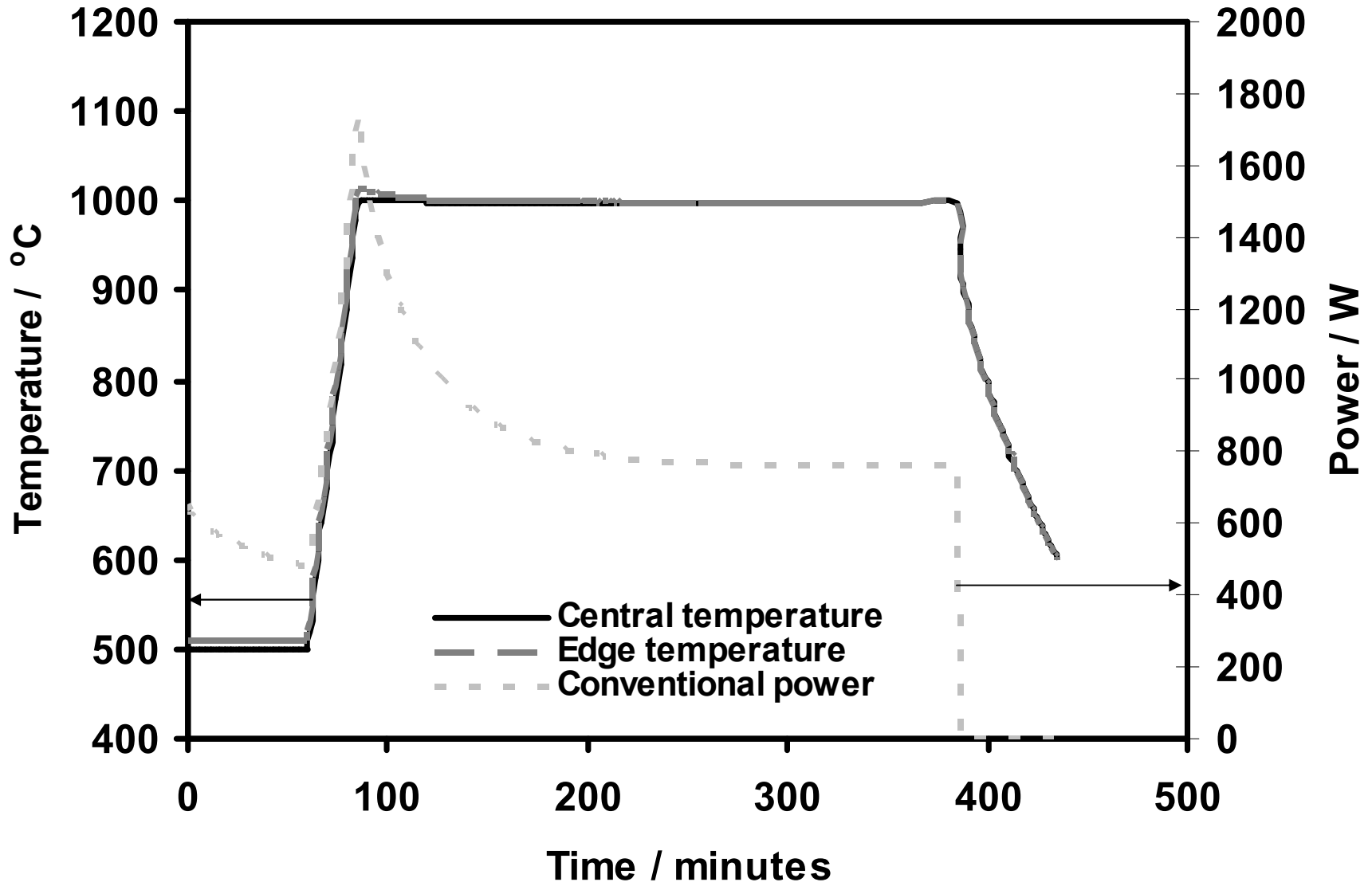


Fig 1b

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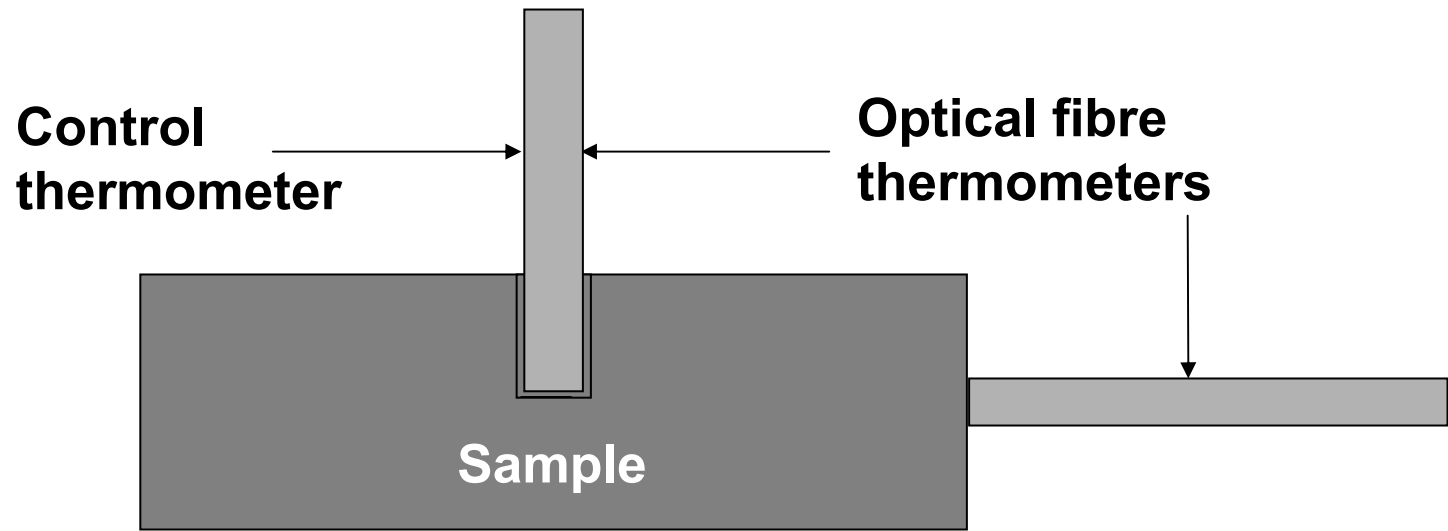


Fig 2

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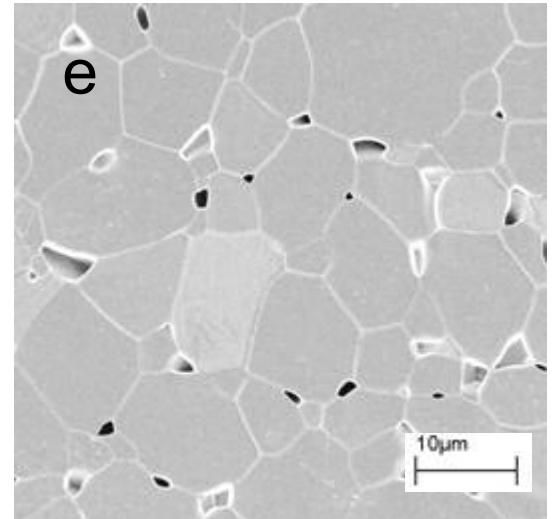
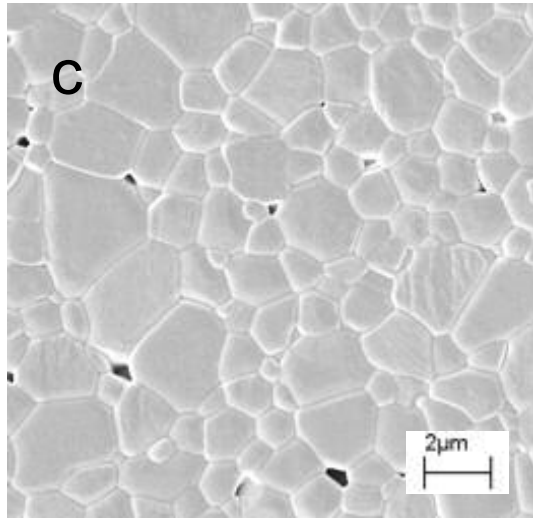
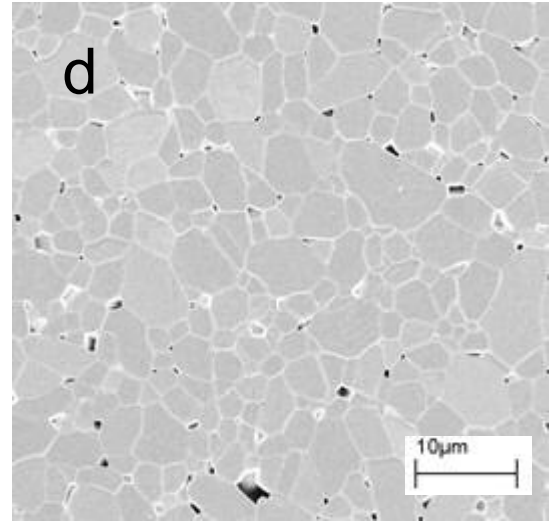
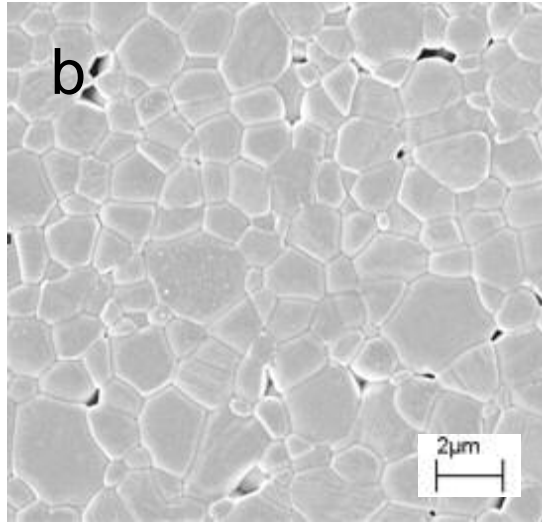
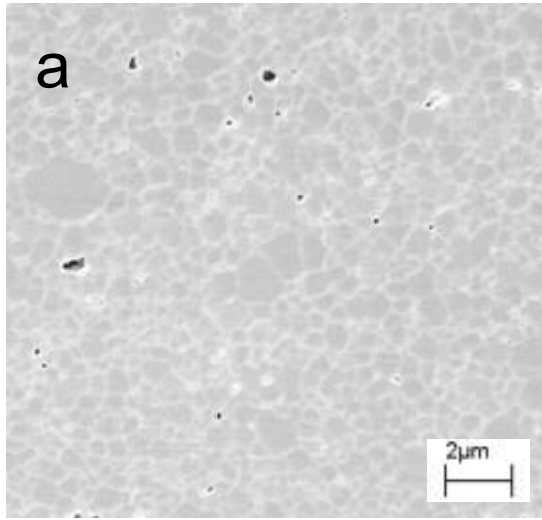


Fig 3

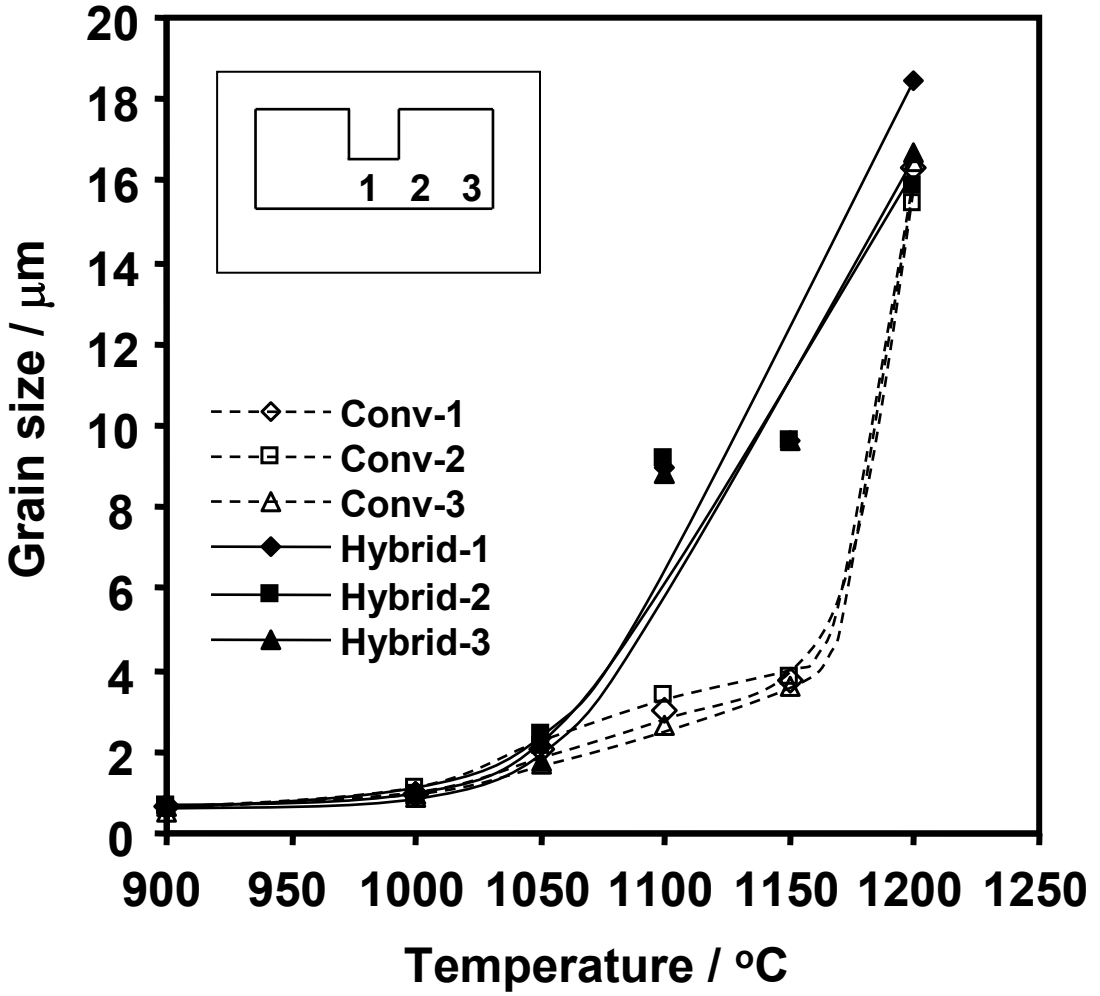


Fig 4

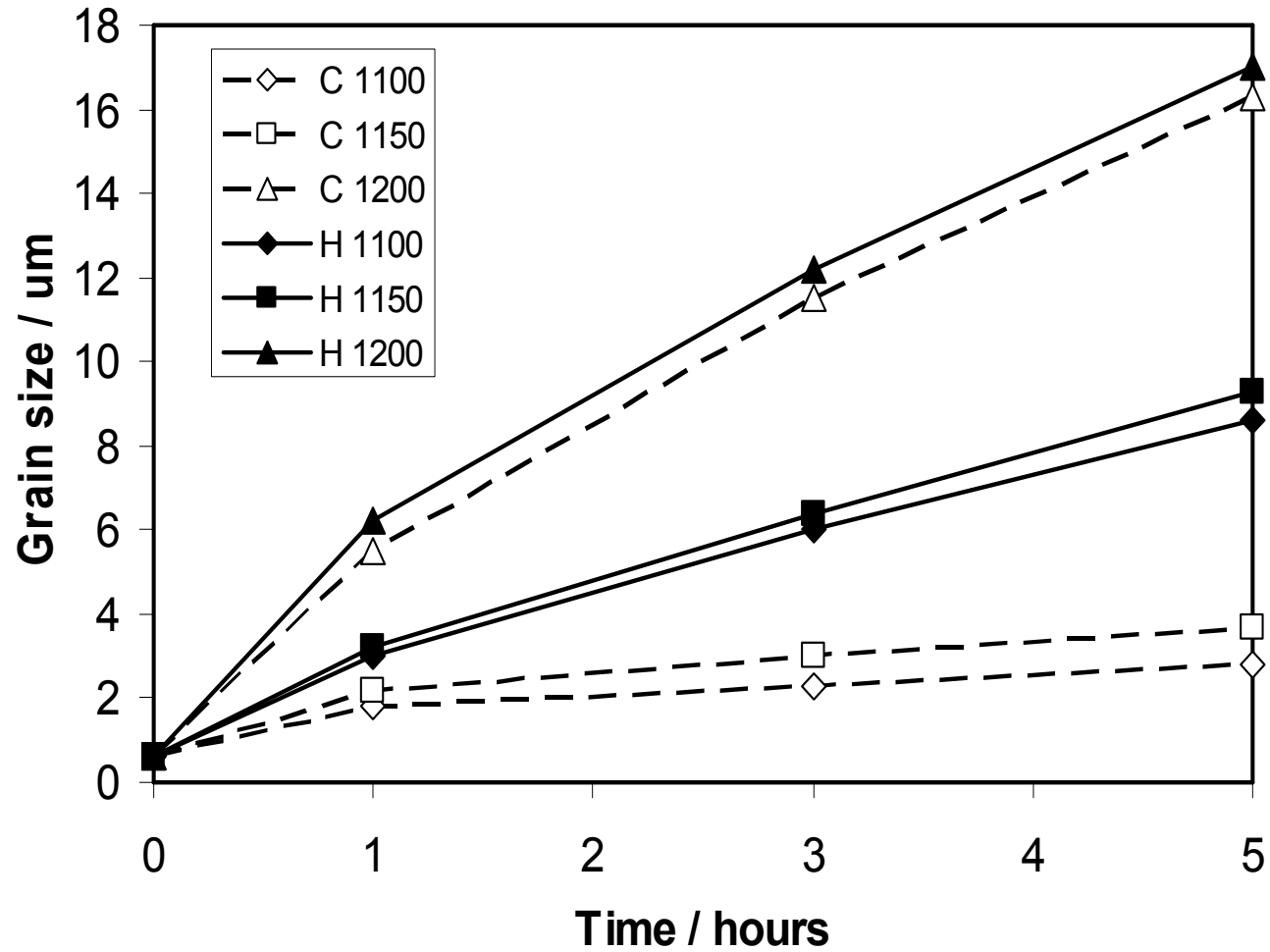


Fig 5

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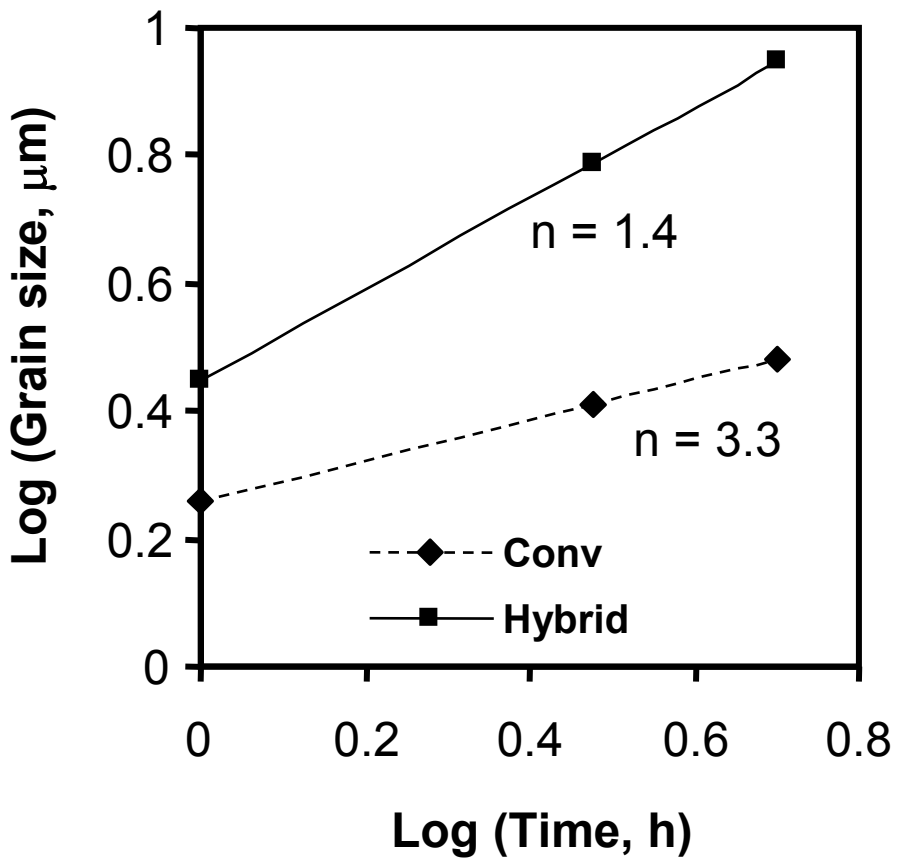


Fig 6

Annealing temperature / °C	Start of anneal soak period $\Delta T / ^\circ\text{C}$		End of anneal soak period $\Delta T / ^\circ\text{C}$	
	Conv	Hybrid	Conv	Hybrid
900	15	13	5	0
1000	16	14	4	0
1050	16	14	5	1
1100	16	13	3	1
1150	18	14	4	1
1200	19	14	4	1

$\Delta T = T_s - T_c$ where T_s and T_c are the surface and centre temperatures respectively.

Table 1.

Annealing temperature / °C	Grain growth exponent, n	
	Conventional heating	Hybrid heating
1100	3.3 ± 0.1	1.4 ± 0.1
1150	3.3 ± 0.1	1.4 ± 0.1
1200	1.6 ± 0.2	1.5 ± 0.2

Table 2.

Annealing conditions		Relative density / %					
		Conventional heating			Hybrid heating		
		Before annealing	After annealing	Δ	Before annealing	After annealing	Δ
900°C	5 hs	98.4	98.9	0.5	98.5	98.8	0.3
1000°C	5 hs	98.7	98.7	0	98.9	99.2	0.3
1050°C	5 hs	98.7	98.7	0	98.8	98.8	0
1100°C	1 h	98.9	98.9	0	98.9	98.9	0
	3 hs	98.9	98.9	0	98.9	98.9	0
	5 hs	98.9	98.9	0	98.9	98.4	-0.5
1150°C	1 h	98.9	98.9	0	98.9	98.7	-0.2
	3 hs	98.9	98.4	-0.5	98.9	98.3	-0.6
	5 hs	98.9	98.2	-0.7	98.9	97.9	-1.0
1200°C	1 h	98.9	98.0	-0.9	98.9	98.3	-0.6
	3 hs	98.9	97.6	-1.3	98.9	97.9	-1.0
	5 hs	98.9	97.5	-1.9	98.9	98.3	-0.6

Table 3.