

## IN-SITU CHARACTERIZATION OF THE SINTERING PROCESS THROUGH PROCESS-TEMPERATURE CONTROL RINGS

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### **Abstract**

*Process temperature control rings are recommended for checking the temperature of heat treatment processes a posteriori, the temperature reading being obtained from the shrinkage during the heat treatment process through data sheets supplied for each batch of rings. Here it is shown through dilatometric studies that in fact these rings are indicating not so much the sintering temperature but the „sintering intensity“. In addition to the isothermal temperature, also the soaking time and the heating/cooling rates play a major role while the atmosphere is less relevant. The temperature reading (‐reference temperature‐) agrees with the furnace temperature as e.g. indicated by thermocouples only at slow heating and cooling and rather long soaking times, conditions that are common in ceramic firing rather than in PM. In any case, however, the rings are excellent tools for checking the reproducibility of the sintering effect for PM precision parts as well as for assessing the sintering effect and the temperature distribution in furnaces and sintering boats.*

**Keywords:** *sintering, process control, in-situ control, temperature distribution*

### **INTRODUCTION**

For sintering of metals and ceramics, the sintering parameters, in particular temperature and time, are critical, and they have to be precisely adjusted and controlled accordingly especially in industrial practice [1, 2]. In the case of discontinuous, i.e. batch-type, furnaces, this control is comparatively easy, e.g. by putting thermocouples between the compacts to be sintered; since the compacts are not moved during sintering, there are no major technical problems. Thus, the very tricky sintering of high speed steel compacts has been performed successfully in vacuum, i.e. batchtype, furnaces [3].

For sintering of precision parts, which is usually done in continuous furnaces, the sintering conditions are adjusted through setting of the temperature control units and the transport speed of the parts or boats, e.g. belt speed in mesh belt furnaces or cycle time in walking beam furnaces. However, this gives the desired values for the parameters but not the real ones. i.e. the temperature-time profile really encountered by the parts that travel through the furnace. For belt furnaces with open ends, long thermocouples may be used; for walking beam furnaces and for all other types of furnaces that are equipped with locks in order to ensure proper atmosphere control, this measure is impractical. Recording boxes that travel through the furnaces together with the parts are commercially available (e.g. [4]), but for reasonable geometrical dimensions, i.e. such that fit into commercial furnaces, their maximum service temperature is limited, and they can be used for sintering of aluminium and bronze but not for sintering of ferrous products in walking beam furnaces.

For sintering of ceramic materials, Seger cones, invented by H. Seger in 1886, have been used for a very long time (e.g. [5]). These cones consist of ceramic materials with a specific softening temperature interval; different types of cones are available. For a firing run, several cones that soften at different temperatures within the relevant interval are added, and then the run is done. Afterwards the cones have been bent to varying degrees, and the effective temperature of the firing run can be given a posteriori.

A similar route is followed by the so-called Process Temperature Control Rings (PTCRs). These are ceramic rings that show very reproducible shrinkage behaviour over a wide temperature interval [6]. Such rings (occasionally also known as “Philips rings”, after the previous manufacturer) are available for varying temperature ranges, as shown in Fig.1 and Table 1. For sintering of ferrous components, from the supplier used here mainly the grades LTH (red, for mesh belt furnaces) and STH (green, for walking beam furnaces) can be regarded most useful for sintering of ferrous PM and MIM parts.



Fig.1. PTCRs new (back row) and used (foreground).

Tab.1. PTCR grades available for the respective temperature interval (obtained from M.E.Schupp GmbH, Aachen, Germany [6]).

Designation	Temperature range [°C]	Colour
RTC – AQS	660 – 1100°C	Green
PTCR - ETH	850 – 1100°C	Light green
PTCR - LTH	970 – 1250°C	Pink
PTCR – STH	1130 – 1400°C	Green
PTCR – MTH	1340 – 1520°C	Yellow
PTCR - HTH	1450 – 1750°C	White

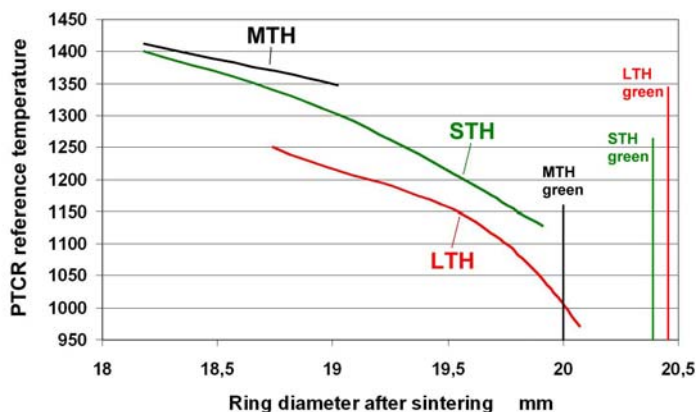


Fig.2. PTCRs: relationship shrinkage-temperature (M. E. Schupp data table).

It is stated by the manufacturer that from the shrinkage during the sintering/firing process the temperature attained can be determined, as given in Fig.2 (plotted following the table supplied with the rings; also the green dimensions are given). Here it should however be considered that the tables hold only for the respective batch of rings, therefore for each PTCR batch a separate table is supplied.

However, it must be considered that shrinkage of the rings is a sintering effect, and sintering is of course related at least to both temperature and time. I.e. absolute temperature reading can be attained from the PTCRs only for a given isothermal holding time, and, as will be shown below, for a given heating/cooling rate. Therefore the manufacturer uses the term “reference temperature” for what is in effect a “sintering intensity”, and a correction graph is supplied for estimating the time effect. If however the rings are used primarily for process control, i.e. for assessing the reliability and reproducibility of a sintering/firing process or for checking the temperature distribution in a furnace or a sintering boat, only the relative changes are relevant.

Generally, PTCRs can be regarded to be useful both for checking the “sintering intensity” – i.e. the temperature-time combination - of the sintering process in a given sintering equipment and also to give some idea of the effective temperature in the furnaces at a given temperature setting. For this purpose, in the present work the effect of the sintering parameters other than the temperature, i.e. time, heating rate and atmosphere, were determined.

## EXPERIMENTAL PROCEDURE

For the experiments described here, the grade STH (green) was used since it was regarded optimal for sintering in the range of 1220 to 1280°C, i.e. standard high temperature sintering as done in walking beam furnaces.

PTCRs were sintered in a pushrod dilatometer, although here the pushrod was removed, the dilatometer being used simply as a high precision programmable furnace. The rings were inserted lying flat on a ZrO<sub>2</sub> plate. For the first test series, heating and cooling rates were 10 K·min<sup>-1</sup>, and the temperature was set at 1230°C, the isothermal sintering time being accordingly varied. The atmosphere was rotary pump vacuum. In parallel, sintering runs were carried out also in a pushtype furnace (AHT-Silit) equipped with a Kanthal APM superalloy muffle, the atmosphere being flowing nitrogen. Here the rings were placed into a

steel boat, lying on  $\text{ZrO}_2$  plates once more, and pushed into the high temperature zone of the furnace where they rested for the given time; then they were pushed into the water-jacketed exit zone. In this case, with the “push-in-push-out” procedure, the heating and cooling rates were markedly higher (but still sufficiently low to avoid cracking, see below). In both cases, the dilatometer and the pushtype furnace, the temperature controller was connected to a thermocouple outside the working space (i.e. in the case of the dilatometer to the furnace control thermocouple and not the recording thermocouple close to the specimen). I.e. the temperatures given are those set at the controller.

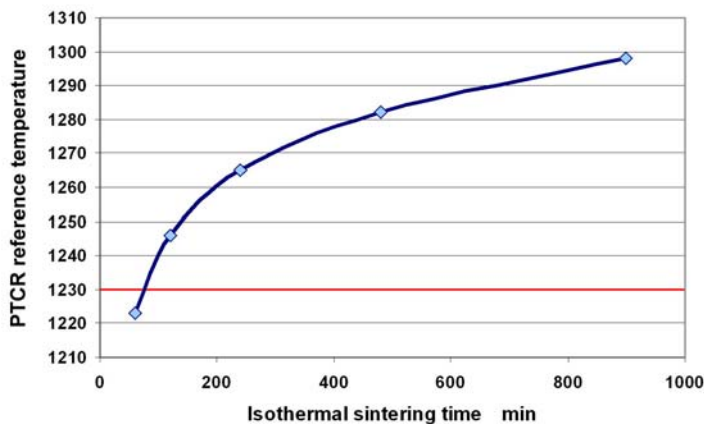
The diameter of all the rings was measured using a digital micrometer with special support, also obtained from the supplier of the PTCRs [6], which gave readings to 0.01 mm; in parallel also a slide rule with a resolution of 0.02 mm was used, which yielded virtually the same results as the micrometer. The advantage of the slide rule is that the ring diameter can be measured for the top and the bottom end of the ring; therefore, conical distortion during sintering could be identified if occurring. For each ring, two diameters were measured taken at  $90^\circ$  angle to each other. In order to assess the effect of the sintering parameters other than the temperature, from the diameters measured after sintering the “reference temperature” was taken, i.e. that temperature that corresponded to the measured dimensional change according to the tables supplied by the manufacturer for each batch of PTCRs.

### EFFECT OF ISOTHERMAL SINTERING TIME

The relationships between isothermal sintering time at  $1230^\circ\text{C}$  and reference temperature as obtained for dilatometer and pushtype furnace, respectively, are given in Fig.3a and 3b. As can be seen, for both regimes the temperature reading tends to increase with longer isothermal sintering times. In both cases a well defined logarithmic relationship between reading and time is found, indicating the typical shrinkage behaviour of a sintered system. This stands out still more clearly if a logarithmic x-axis is taken; here the result is a relatively straight line for both furnaces.

These results clearly show that the reference temperature given by the PTCRs is in fact not a reading for the temperature but for the “sintering intensity”, i.e. a combination at least of temperature and time. This is similar to the parameters known from creep studies such as e.g. the Larson-Miller parameter, defined as  $\text{LMP} = T \cdot (C + \log t)$ ,  $T$  being the temperature in K and  $t$  the time in hrs, the constant  $C$  is commonly set at 20 [7]. It is well known that creep and sintering are closely related processes [8], and therefore the applicability of the Larson-Miller parameter for both is not surprising, either.

The effective furnace temperature, i.e. that temperature that is measured in parallel either through thermocouples (in the dilatometer) or pyrometrically (in the pusher furnace) agrees with the temperature reading obtained through the PTCRs only at a certain isothermal sintering time. This “critical” sintering time however is different for the sintering aggregates used, being about 76 min in the dilatometer and about 145 min in the pushtype furnace, which indicates that in addition to temperature and time there are further parameters affecting the shrinkage of the rings. Of course, in practice a “temperature” in furnace A is usually not identical to that in furnace B (nor is the sintering effect), despite identical settings and even readings, but also other parameters should not be ignored; in particular the heating and cooling rates differed very pronouncedly between dilatometer and pushtype furnace.



(a) dilatometer, vacuum

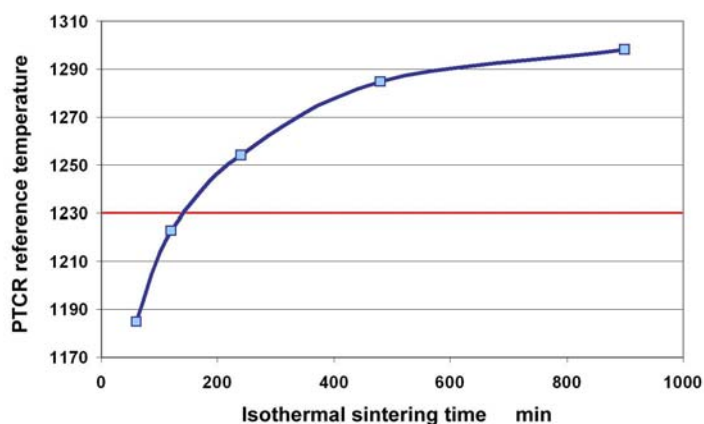
(b) pushtype furnace, N<sub>2</sub>

Fig.3. PTCR reference temperature for sintering at 1230°C set temperature (indicated as red line) for different lengths of time.

If the graphs obtained for the dilatometer and the pushtype furnace, respectively, are plotted side by side (Fig.4) it stands out clearly that at shorter sintering times the pushtype furnace results in lower temperature reading than the dilatometer while at long times the results are virtually identical. This discrepancy indicates that there is some influence of the heating / cooling rate which in the dilatometer is decidedly lower than in the pushtype furnace, resulting at least in longer times at high temperatures. In both cases, plotting the PTCR reference temperature against the Larson-Miller parameter yields a fairly straight line, that for the pushtype furnace being slightly bent at high LMP (Fig.5).

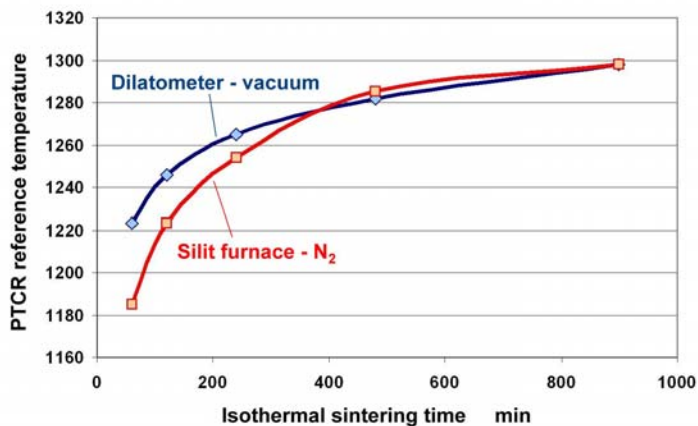


Fig.4. PTCT reference temperature in the dilatometer/vacuum and pushtype furnace/N<sub>2</sub>. Set temperature 1230°C, various times.

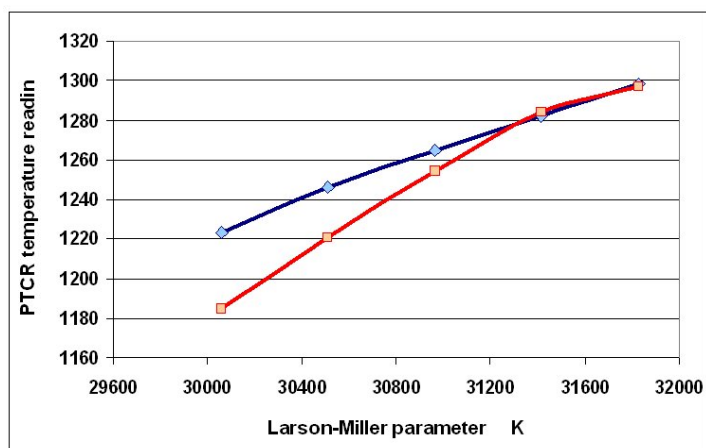


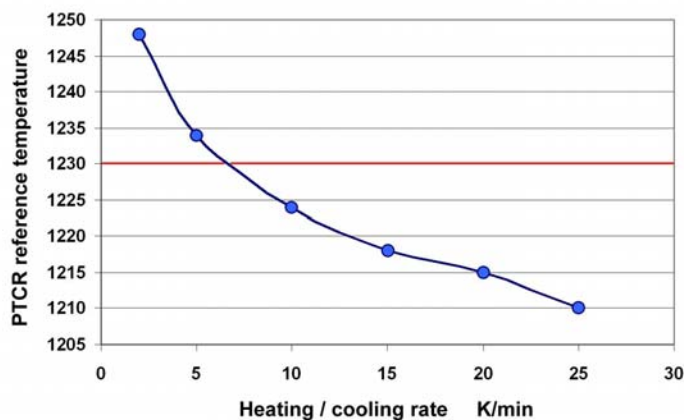
Fig.5. As Fig.3, PTCT reference temperature as a function of the Larson-Miller parameter (for the LMP: T in K, t in s).

### EFFECT OF THE HEATING/COOLING RATE

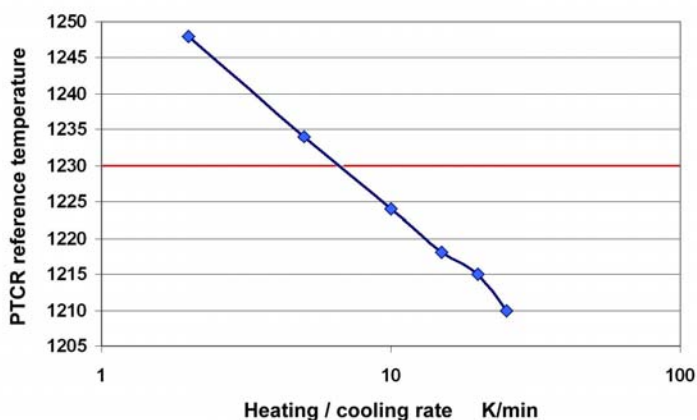
Therefore, sintering runs were carried out with varying heating/cooling rates. The tests were done in the dilatometer as described above, but the temperature and time were set at 1230°C and 60 min isothermal, respectively, while the heating and cooling rates were varied between 2 and 25 K·min<sup>-1</sup> (the latter being the maximum tolerable for the Al<sub>2</sub>O<sub>3</sub> measuring system of the dilatometer to safely avoid thermal shock). The resulting temperature readings are plotted in Fig.6. Here it stands out clearly that, as expected, faster heating results in lower PTCT reference temperatures, which can be attributed to longer exposure to high temperatures in the case of slower heating and cooling. It must be considered here that at e.g. 1250°C temperature and 60 min isothermal time, the time above 1100°C is 72 min for 25 K·min<sup>-1</sup> heating/cooling rate while for 2 K·min<sup>-1</sup> it is in fact 210 min! Since the PTCRs are employed primarily for firing of ceramics, mostly in large

chamber furnaces, in which case heating and cooling rates have to be traditionally low to ensure even temperature distribution and avoid thermal shock effects, it is not surprising that the temperature readings for standard PM sintering conditions are too low; in the continuous furnaces commonly used in PM production simply higher heating and especially cooling rates are used.

The time effect is also corroborated by the fact that also here, the relationship between heating/cooling rate and PTCR reference temperature is fairly linear if a logarithmic x-axis is taken, as clearly visible from Fig.6b. This relationship is well in agreement to that shown in Fig.3.



(a) linear x-axis



(b) logarithmic x-axis

Fig.6. PTCR reference temperature reading for different heating/cooling rates.  
Dilatometer/vacuum, set temperature 1230°C, 60 min isothermal.

For practical purposes there is however a limit for the heating rate: Since the rings contain organic binders that evaporate and decompose during the heating procedure, forming gaseous compounds, cracking may occur at too fast heating, as illustrated in Fig.7.

This is not a problem for industrial use since the heating rates are usually rather low; it should however be considered when using the PTCRs for laboratory sintering runs.



Fig.7. Cracked PTCR after sintering with high heating rate in laboratory furnace.

### EFFECT OF THE ATMOSPHERE

Since the PTCR reading is a shrinkage effect caused by sintering mechanisms, also the atmosphere may play a significant role. The manufacturer recommends using in oxidizing atmosphere and states that in inert or reducing atmosphere carbon may remain in the rings and affect shrinkage. To study the effects of the atmosphere, sintering runs were carried out in the dilatometer as described above, and the atmosphere was varied between rotary pump vacuum, air, and static nitrogen. The results of the temperature reading are shown in Fig.8.

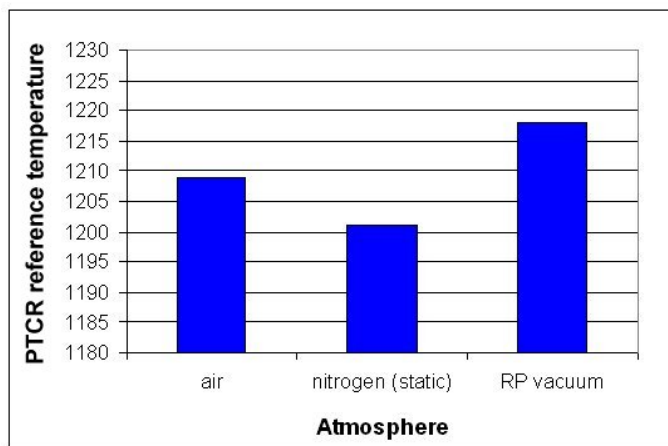


Fig.8. PTCR temperature reading for different atmospheres. Dilatometer,  $10\text{ K}\cdot\text{min}^{-1}$ , set  $1230^{\circ}\text{C}$  60 min.



Evidently there is some effect of the atmosphere on the PTCR reference temperature indicated; vacuum results in the highest temperature reading and nitrogen in the lowest while air is in between. The reason for this may be at least in part be linked to the presence of the organic binder phase in the “green” (= unsintered) PTCRs. This organic binder is removed in the first stage of the sintering process but it can be assumed that in vacuum – which is a dynamic atmosphere, gases generated being continuously pumped off - binder removal is more complete than in the static nitrogen in which the gas space of the dilatometer is closed.

In the case of air, the atmosphere is also static but since the box covering the recording unit of the dilatometer was left open there was a better chance for gas transport; furthermore, it can be expected – as suggested by the manufacturer - that the organic compounds in this case are not only evaporated but also burnt by reaction with the oxygen of the atmosphere. In any case the differences observed are in the range of 20°C maximum between vacuum and nitrogen and therefore cannot be regarded excessive; i.e. the effect of remaining carbon, if any, is at best marginal to negligible.

The atmospheres tested so far can be regarded as inert towards the ceramic base material of the rings. Hydrogen or  $N_2-H_2$  mixes, in contrast, might exert reducing effects and therefore are particularly interesting; however these atmospheres cannot be used in the dilatometer due to the sensitivity of the Pt thermocouples. Therefore, sintering runs were done in  $N_2-10\%H_2$  atmosphere, which is a common composition, using the same pushtype furnace as described above; here, also the temperature readings as a function of boat arrangement were studied as well as the temperature distribution inside the boat.

## USING THE PTCRs FOR ASSESSING TEMPERATURE DISTRIBUTION IN A FURNACE

For the sintering runs in the pushtype furnace, different boat arrangements were used (Fig.9). Steel boats were used both as single open boats (Fig.9b, c) and as closed boxes consisting of two boats of slightly varying size, similar to the usual arrangement for getter boxes (Fig.9d, e). In all cases, fused alumina (corundum) granulate (in a layer about 5 mm thick) was filled into the boat, and PTCRs were placed onto that layer in 3 positions within the boat (see Fig.9a, b). In part the boat was then completely filled with  $Al_2O_3$  granulate, in order to increase the thermal mass.

The boats were pushed into the furnace as described above, and the sintering temperature was set uniformly at 1250°C at the controller; the isothermal sintering time (period between push-in and push out) being 60 min. The atmosphere was flowing  $N_2-10\%H_2$  with about 2 l/min flow rate. After sintering the diameter of the rings was measured both at the top and the bottom, to identify any conicity. The results are given in Table 2.

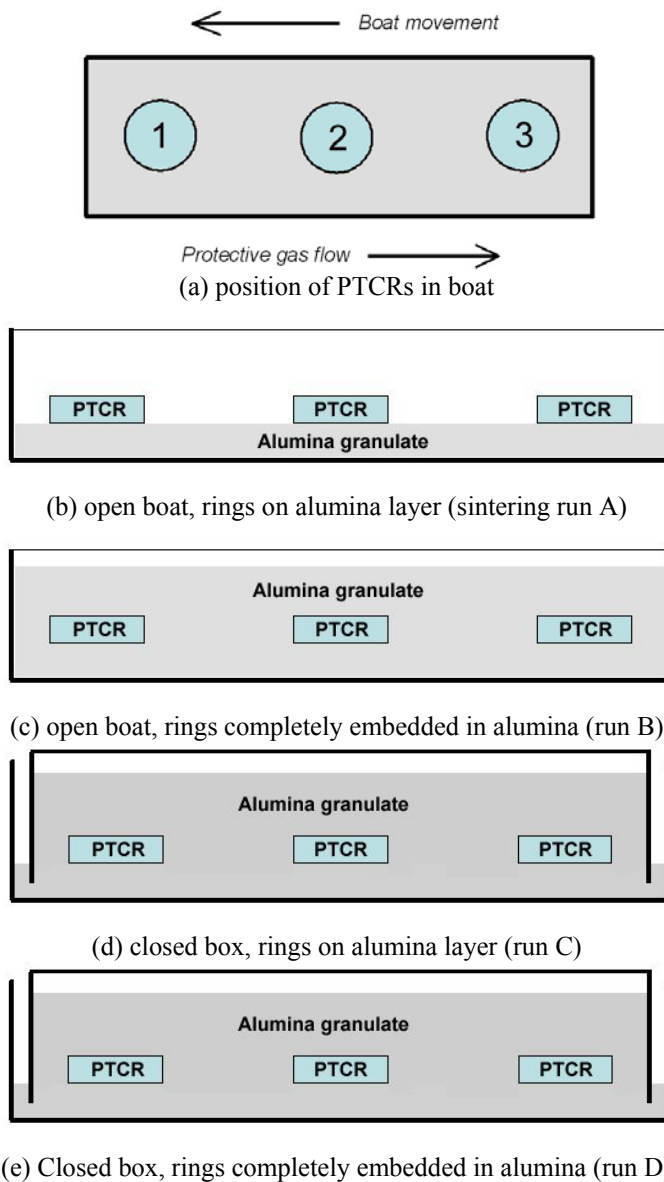


Fig.9. Boat arrangements for sintering and position of PTCRs in sintering boats.

Tab.2. PTCR reference temperatures (readings) for runs in pushtype furnace using varying boat assemblies. Set temperature 1250°C, 60 min isothermal, N<sub>2</sub>-10%H<sub>2</sub>.

Sintering run	Assembly	Al <sub>2</sub> O <sub>3</sub> filling	Ring pos.	T <sub>ref</sub> (mean)	T <sub>ref</sub> (top)	T <sub>ref</sub> (bottom)	T <sub>top</sub> - T <sub>bottom</sub>
A	boat	N	1	1192	1192	1191	+1
			2	1195	1196	1193	+3
			3	1193	1194	1191	+3
B	boat	Y	1	1181	1177	1185	-8
			2	1186	1187	1185	+2
			3	1184	1182	1185	-3
C	box	N	1	1191	1190	1191	-1
			2	1191	1189	1192	-3
			3	1190	1188	1192	-4
D	box	Y	1	1192	1190	1193	-3
			2	1192	1192	1192	0
			3	1191	1190	1192	-2

Generally it can be stated that the conicity of the rings is marginal, and there is no clear trend, except maybe a very slight tendency to higher shrinkage at the bottom. The differences in the readings should however not be overestimated when considering the precision limits of the slide rule used, since 0.02 mm, the resolution of the slide rule, are equivalent to a temperature difference of 4°C, i.e. against this background the results are surprisingly well reproducible. In any case, measuring with a precision slide rule and a micrometer, respectively, can be regarded as equivalent.

Comparing the rings from positions A, B and C for the individual runs shows that also here clear differences are absent i.e. there is no gradient in the effective sintering intensity along the sintering boat; cooling effects by the flowing atmosphere as well as significant radiation losses at the ends compared to the center thus can be excluded, which also means that the effect of sintering is virtually the same for all specimens within the boat or box.

When taking the absolute readings for the PTCR reference temperature, it stands out clearly that the agreement with the previous runs in the pushtype furnace (Fig.3b) is excellent; in the prior case about 1190°C have been recorded in N<sub>2</sub> atmosphere, and in the present case roughly the same readings are obtained.

Comparison between the boat assemblies is graphically presented in Fig.9, showing the mean reference temperatures for all rings from a given run; here it is evident that in all cases the “reference temperatures” are between 1190 and 1195°C, the only exception being the variant “B”, with readings between 1182 and 1185°C. This indicates that in the case of an open boat completely filled with alumina granulate, heat transfer is slightly slower; surprisingly this does not hold for a completely filled closed box (which however contains markedly less alumina due to the smaller size of the upper boat). The rings used in the run with ferromanganese were slightly discoloured, apparently as a consequence of Mn vapour reacting with the rings (see also [9]); however, the reference temperatures recorded are virtually identical to those of the parallel run without ferromanganese. This indicates that the temperature recording by the rings is reliable also in presence of Mn vapour in the atmosphere.

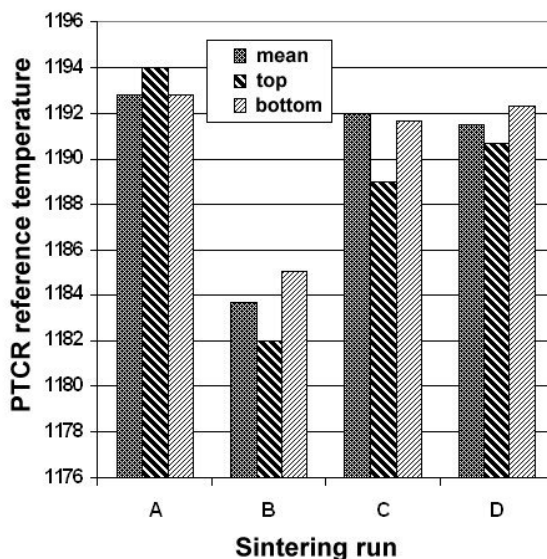


Fig.10. PTCR reference temperatures for different sintering boat assemblies as shown in Fig.9.

## CONCLUSIONS

Process temperature control rings can be used to advantage for checking the sintering procedures in powder metallurgy. However it must be considered that the result is in fact shrinkage of the rings which effect does not only depend on the isothermal temperature but also at least on the time; here, the Larson-Miller parameter, which is well established in creep testing, seems to be well suited to assess the “sintering intensity”. Also the heating and cooling rates are effective since slower heating and/or cooling extends the time at high temperatures. The effect of the sintering atmosphere is less pronounced but has to be considered if precise temperature control is necessary. Using the rings for assessing the sintering procedures in a laboratory furnace showed that there are only very slight differences between different boat assemblies and loadings; too fast heating should however be avoided since cracking might occur. In any case, the rings exhibit a very regular and reproducible shrinkage; they are thus well suited for checking the reproducibility of a given sintering process. Furthermore, they are a useful tool for defining the temperature distribution in a sintering furnace or sintering boat as well as assessing the effect e.g. of varying furnace loadings. This is particularly relevant for sintering processes in which the effective sintering temperature and time are not directly accessible.

## Acknowledgment

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