

OPTIMIZATION OF FIRING PARAMETERS FOR CERAMIC WARES BY THERMAL ANALYSIS

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Abstract

Aesthetic and utilitarian properties of traditional ceramic wares as well as engineering properties of modern advanced ceramics are attained by maintaining an optimum temperature-time-atmosphere relationship, called firing schedule, in the kiln. The contribution of modern thermal analysis (TA) techniques such as TG/DTG, TG/EGA, TG/MS, DTA, DSC, TDA, etc. in 1) optimizing production steps by raw material quality control, by studying binder burn out, product densification, 2) in simulating appropriate preheating, firing and cooling schedules as well as 3) in developing shorter firing cycles has been extensively reported in recent literature. The paper will first discuss theoretical curves and energy required for ceramic firing and present from the literature selected examples of applications of thermal analysis in ceramic technology.

Keywords: ceramics, firing, thermal analysis

Introduction

The science and technology of producing quality ceramic wares is extremely complex due to vast diversity of products, their geometry and size, complex realities of kinetics, thermodynamics and practicalities of firing. The nomenclature 'ceramic body' and 'ceramic ware' is loosely used, the raw product or the 'green body' turns into 'ware' – the final product – after heat hardening.

Of all the processing steps in ceramic manufacturing, the most important is the firing process which is the least well understood and is still susceptible to myth, empirical art, tradition and rules of thumb. Precise and controlled thermal treatment play the crucial role in producing quality ceramic wares and developing advanced ceramics. Temperature, time and kiln atmosphere all influence the properties of fired ceramic wares. Each different type of ceramic product requires its own special well-balanced firing process involving a number of time-dependent processing steps which are functions of both temperature and its rate of change. Some of the important steps are the heating up rate which depends on the thermal conductivity, moisture and gas evolution during drying and mineral decomposition, phase transformations such as $\alpha \rightarrow \beta$ quartz, low viscosity liquid phase formation and solid state reactions as a function of temperature profile during sintering. The soaking time at maximum temperature depends on the rate of dissolution of crystalline components while controlled cooling is essential to prevent thermal stress being induced in the ware.

Theoretical firing curves and reaction enthalpy

The credit for deriving a theoretical firing schedule based on volume change of the body and allowing for other factors that affect firing goes to Munier [1]. The total firing time of the theoretical curve is dependent on the type of the body, density of setting, thickness of the ware and the kiln cross section.

The theoretical energy required for ceramic firing was investigated by Hennicke [2] who worked out the time-dependent basic reaction heat balance of clay-ceramic materials. Table 1 shows the reaction enthalpy for a porcelain firing charge. Different clay reactions have heat of reaction in the range of 0.2 to 0.8 MJ kg⁻¹, for tiles the energy consumption for drying and firing lie in the range of 1.7 to 3.3 MJ kg⁻¹. Precise enthalpy and specific heat measurements can be used to calculate the energy consumption during heating and to establish a practical energy balance by thermal analysis.

Table 1 Reaction enthalpy for a porcelain firing charge

Porcelain: 50 kaolinite – 25 quartz – 25 feldspar		
Charge: feldspar 26.87, quartz 26.87, kaolinite 53.74		
Loss on ignition: 6.96%		
Product: mullite 25%, quartz 10%, glassy phase 65%		
	kJ kg ⁻¹	
	Endothermic	Exothermic
	(+)	(-)
1	Kaolinite decomposition	420
2	Crystallization of a) corundum	-89
	b) quartz	-50
3	Mullite formation	-1
4	Quartz dissolution	56
	Melting feldspar	129
	Corundum dissolution	27
	632	-140
	Reaction enthalpy	492 kJ kg ⁻¹

The most energy intensive step is almost invariably raising the body to the firing temperature, which is in the range of 928 kJ kg⁻¹ for 1000°C temperature rise. Cooper [3] developed the concept of 'activated time' and 'equivalent time' as function of increasing temperature from Arrhenius 'activation energy', and translated the firing curve into an activated time curve. Further, superimposing the isothermal rate curves for densification of pure Al₂O₃ as function of rising temperature, Cooper transformed temperature profiles into equivalent times at top temperatures and brought out the pronounced importance of 'dwell time' at 'peak' temperatures. Fig-

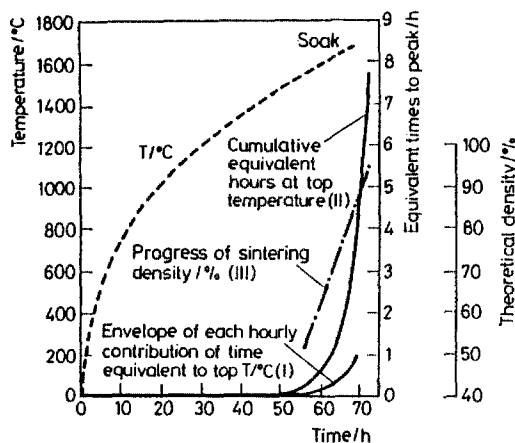


Fig. 1 Development of final sintering curve from cumulative equivalent hours to peak

ure 1 reproduces an actual time temperature profile of a kiln firing alumina bodies as given by Cooper. Examination of curves I and II demonstrates that the 68 h to reach soak temperature are equivalent to only 3 1/2 h at peak for the same densification.

Optimum firing schedule using pyrometric cones

The progress of firing within the kiln is best followed by Heat Work Recorders or Thermoscopes, called Pyrometric Cones (PC) made out of the same raw materials as those used to manufacture most conventional ceramics. These are made into slender, truncated pyramids inclined 8° from the vertical and act on the principle of 'fusion with deformation'. Spaced amongst the ware, the PCs can be observed through a spy hole. With increasing temperature, portion of the cone begins to soften, melt and its tip bends down due to gravity. The deformation temperature of the cone varies with heating rate and its amount is a measure of the heat work which is the combined effect of temperature and time on the body.

The first standard and regularly placed series of pyrometric cones was introduced by Seger in 1886 in UK and Seger cone numbers, and in the US, Orton cones became well established temperature indicators.

Thermal analysis and its application in ceramic technology

Thermal analysis is best suited to simulate pyroprocessing of minerals in the laboratory. A combination of thermal analysis techniques such as TG/DTG, TG/EGA, TG/MS, DTA, DSC, TDA etc. provides itself to be the best practical tool for monitoring and optimizing production processes, for elimination of firing defects, for problem solving, quality control, research and development, beginning with characterization and quality of raw materials. Materials microstructure defines

the decisive effects of the chemico-thermal reactions which are the basic prerequisites for achieving an optimum firing cycle.

One of the main characteristics of ceramic firing is the drastic reduction in volume; dilatometry or thermo-mechanical analysis is thus very helpful to study the progress of densification during linear heating, isothermal as well as rate controlled sintering. Dilatometry also detects qualitatively and quantitatively the thermally induced dimensional variation and determines the coefficient of linear expansion of the sintered product. The first differential dilatometer was developed in 1963 to control expansion mismatch between ceramic components being considered for gas turbine heat exchangers.

It is obviously not possible to cover the exhaustive application of combination of thermal analysis techniques with continuously developing advanced instrumentation to large number of ceramic products, both classical and advanced, to arrive at optimum processing conditions. Thus, typical examples of applications in few selected fields and products such as raw materials, shrinkage, binder burn out effect, etc. ultimately leading to establishing optimum firing curve and its contribution to modern kiln design are discussed in this presentation.

Firing of kaolin: Figure 2 reproduces thermal analysis of kaolin by TG-DTA method [4]. Dehydration at low temperature, followed by dehydroxylation between 450 and 750°C corresponds to the formation of meta-kaolin. The DTA signal between 950 and 1000°C shows exothermic effect due to transformation of meta-kaolin to alumina and mullite.

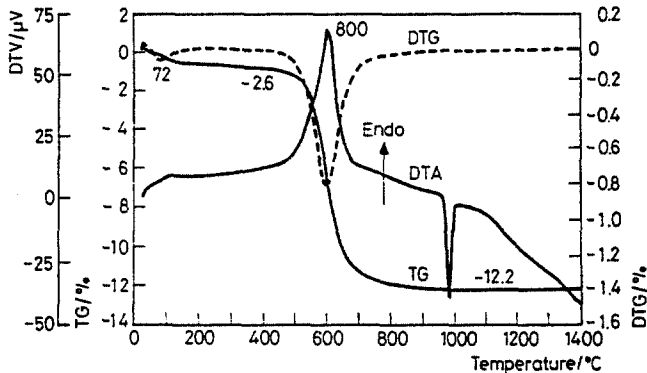


Fig. 2 Thermal analysis of kaolin (TG-DTA method)

Irreversible thermal expansion of a whiteware body can be investigated by the technique of percent linear change (PLC) and its differential coefficient of expansion (DCE) [5]. A glassy phase begins to form above 900°C and shrinkage becomes pronounced. As gas pressure in the pores within the body equals the force causing densification, shrinkage stops. On further heating the body expands. Its properties, density, strength etc. are generally optimum in the region of maximum shrinkage, which is also affected by moisture.

Binder(carbon) burn out influences the dimensional stability, surface and micro-structure defects of the finished product. Hairline cracks in finished alumina prod-

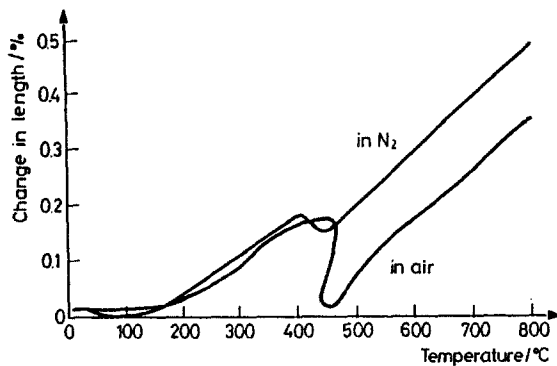


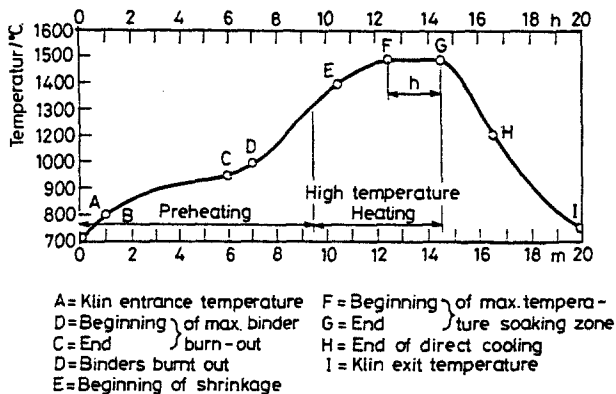
Fig. 3 Binder burn out in nitrogen and in air

ucts due to binder burn out can be examined by simultaneous TG/DTA and TDA on raw alumina/binder powder in air and in nitrogen. In air, exothermic binder oxidation occurs very suddenly; in nitrogen the reaction is actually endothermic as the binder only decomposes (Fig. 3) [6]. A reduction in the amount of oxygen below 8% in the binder burn off zone in the kiln eliminated the majority of the cracking.

Rate controlled sintering: This is used to achieve high densification of functional ceramics while avoiding cracking, by maintaining a linear rate of sintering, that is a linear rate in shrinkage rather than a linear rate of heating, by modifying the temperature profile of the kiln and adjusting the sintering rate.

Ferrites and electro-ceramics: The sintering-temperature curve and atmosphere curves for soft and hard ferrites, semi-conductors are shown in Figs 4 and 5 respectively [7]. The sintering temperature is sub-divided into steps with different time-temperature ratio in all kiln types. The atmosphere in the kiln is regulated according to respective ware to be sintered, with the important conditions shown in Fig. 5.

Porcelain: High quality glost firing of porcelain requires an extremely controlled sintering atmosphere. A reducing atmosphere at 1420°C ensures that ferric iron



- | | |
|---------------------------------------|--|
| A = Kiln entrance temperature | F = Beginning of max. temperature soaking zone |
| D = Beginning of max. binder burn-out | G = End of max. temperature soaking zone |
| C = End of binder burn-out | H = End of direct cooling |
| D = Binders burnt out | I = Kiln exit temperature |
| E = Beginning of shrinkage | |

Fig. 4 Sintering temperature curve for ferrites

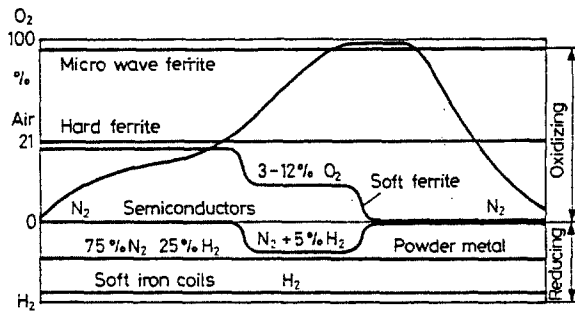


Fig. 5 Atmosphere curves for ferrites

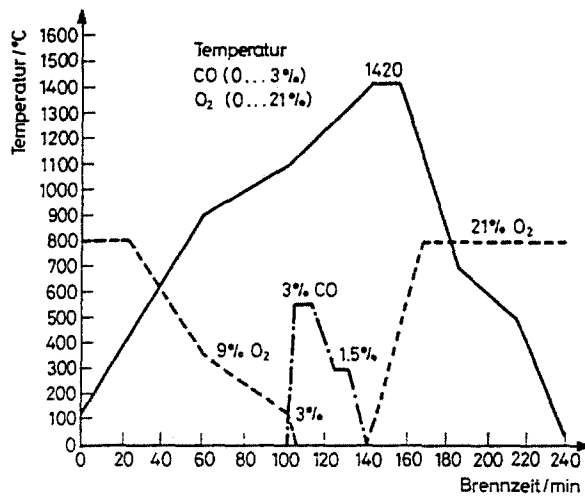


Fig. 6 Time-temperature-atmosphere profile for fast firing of porcelain

is converted into the ferrous stage to impart to the fired body the desired blue lustrous color [8]. The time-temperature-atmosphere profile for glost firing of porcelain is given in Fig. 6 [8]. By thermal analysis, boundaries for different atmospheres – oxidizing, reducing, and neutral – can be exactly determined.

Fast firing: With clean fuels like LPG and natural gas, fast firing for porcelain was introduced in 1970 for decoration firing and from the eighties for the glost firing. Fine grain stoneware and vitreous china are also suitable for fast firing. Reduction in firing time has been possible due to progress in kiln engineering leading to optimum energy balance. A comparison of present-day firing times for ceramic products with those 25 years earlier in Table 2 [9] brings out the value of thermal analysis in achieving short cycle times. Introduction of shorter firing cycles made the establishment of an optimum firing more complex and requiring precise switching and regulating techniques. Firing time of tableware was shortened by 5–10 times; 40–90 min for decorating and 3–5 h for glost firing in continuous kilns and upto 2 cycles/24 h in periodic kilns. For modern whiteware products the fast firing offers much potential in the way of maximum cost effectiveness.

Table 2 Comparison of firing times: then and now

	Wall-tiles	Floor-tiles	Split-tiles	Sanitary wares	Porcelain	Roof-tiles
1970	70 h (50 h biscuit 20 h glost)	36 h	50 h	32 h	58 h (26 h biscuit, 32 h glost)	60 h
1995	30 min (single firing)	40 min (single firing)	4 h	8 h	6 h (double firing)	3.5 h
Time saved	99%	98%	92%	75%	90%	94%

Conclusion

Detailed knowledge of the thermal behaviour of the ceramic raw materials as also of the final products is an indispensable prerequisite for optimal firing. Material and process engineering cannot be separated. Well coordinated kiln design with optimal firing curves adapted to the known thermal properties of the raw materials and body composition yield shorter firing cycles and lower specific energy consumption.

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