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Application News

DTG-60 Simultaneous Thermogravimetric and Differential Thermal Analyzer
TMA-60 Thermomechanical Analyzer
DTG-FTIR Evolved Gas Analysis System

Analysis of Ceramic Molded Products by Thermal Analysis

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User Benefits

- The decomposition temperature of debinders which are necessary in ceramic production processes can be measured by using the DTG-60.
- Qualitative analysis of the gases evolved in ceramic production processes is possible by using the DTG-FTIR system.
- The production efficiency of ceramic production processes can be improved by utilizing thermal analysis data.

■ Introduction

Ceramics are one of the three major types of materials, together with metals and organic materials, and are widely used as materials for industrial products. Ceramics are made using inorganic solid powders, which are artificial materials, and are utilized in various fields such as electronic components and insulating materials. Ceramic products are manufactured through a series of processes that includes mixing materials such as alumina, zirconia, and silicon nitride and an organic binder, then, degreasing (debinding), and sintering. In the degreasing process, the compacted powder is heated to remove the binder, but this step takes time, which is a problem from the viewpoint of high energy consumption. Since suppressing energy consumption has a large impact on cost reduction and reduction of carbon dioxide (CO_2) generation, shortening the time required in the degreasing process (= improvement of production efficiency) is demanded. However, individual differences between operators and the difficulty of optimization are issues because the temperature patterns used in the degreasing process are decided based mainly on experience and intuition.

This Application News article introduces the thermal analysis data obtained with the Shimadzu DTG-60 Simultaneous Thermogravimetric and Differential Thermal Analyzer and TMA-60 Thermomechanical Analyzer (Fig. 1), as well as the DTG-FTIR evolved gas analysis system (Fig. 2), which can be used to improve production efficiency in the manufacture of ceramic products.

Fig. 1 Appearance of (Left) DTG-60 and (Right) TMA-60 Instruments

Fig. 2 Appearance of DTG-FTIR System

■ Effect of Atmosphere in Production of Ceramics

In many cases, the degreasing and sintering processes for oxide-based ceramics are conducted in air, but due to the rapid exothermic reaction associated with the oxidative decomposition of the binder, the decomposition gas of the binder that was evolved internally may cause deformation, cracks, or other defects in molded products if degreasing is done in the air. To prevent this, the temperature must be raised very gradually, but depending on the product, stable debinding treatment is possible by conducting degreasing in nitrogen rather than air. Therefore, the atmosphere and temperature conditions must be verified in order to improve production efficiency by removing the binder at high speed in a short time while avoiding deformation and cracks in the molded product [1].

■ Analysis by DTG-60

Decomposition behavior was measured using the DTG-60 to confirm the effect of the atmosphere gas on the decomposition reaction of the binder.

In this experiment, an injection-molded ceramic made using alumina as the raw material was introduced into a platinum cell and measured in an air atmosphere or nitrogen atmosphere. Table 1 shows the analysis conditions.

Table 1 DTG-60 Analysis Conditions

Instrument	: DTG-60
Heating rate	: 10 ˚C/min
Temperature range	: 30 ˚C - 600 ˚C
Sample weight	: 16 mg
Atmosphere	: Air, nitrogen

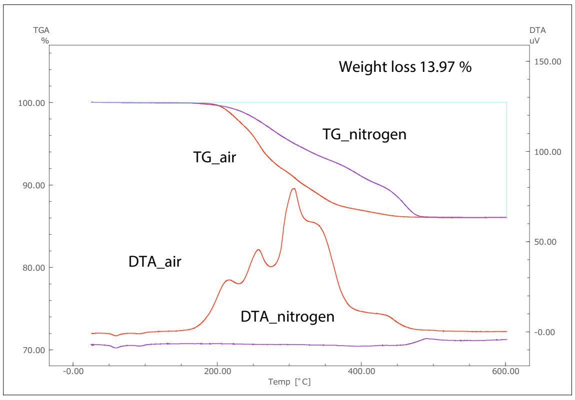

Fig. 3 TG-DTA Curves of Injection-Molded Ceramic in Air and in Nitrogen

Comparing the TG curves in nitrogen and air in Fig. 3, the decomposition starting temperature is lower in air and weight loss occurs rapidly. At the end of heating upon reaching 600 ˚C, a weight loss of approximately 14 %, which is equivalent to the amount of added binder, was obtained in both air and nitrogen, and completion of degreasing was confirmed.

When the DTA curves are compared, it can be understood that thermal runaway occurs easily under an air atmosphere, as a large exothermic peak due to oxidative decomposition of the binder was observed in degreasing in air. In contrast, under the nitrogen atmosphere, a small endothermic peak due to thermal decomposition was observed at around 400 ˚C.

■ Analysis by TMA-60

Looking at the TG-DTA curve in Fig. 3, there was no weight change in TG up to 150 ˚C, and only a small endothermic peak at around 50 ˚C was observed by DTA. To compare the dimensional change of these specimens, the same specimens as those used in the DTG-60 analysis were cut to a sample length of about 5 mm, and TMA measurements were carried out in air and in nitrogen. Table 2 shows the analysis conditions.

Table 2 TMA-60 Analysis Conditions

Instrument	: TMA-60
Heating rate	: 10 °C/min
Temperature range	: 25 °C - 600 °C
Atmosphere	: Air, nitrogen
Load	: 3 g

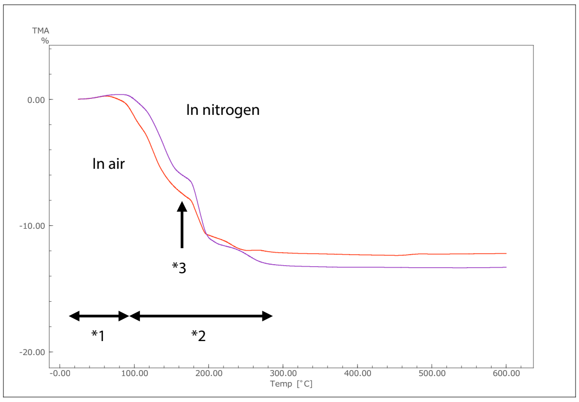

Fig. 4 TMA Curves of Injection-Molded Ceramics in Air and in Nitrogen

From the TMA curves in Fig. 4, expansion (*1 in Fig. 4) occurs until at around 60 °C in air and around 80 °C in nitrogen, and is followed by multistage contraction (*2 in Fig. 4). Differences in this contraction behavior were observed in air and nitrogen. Furthermore, particularly rapid contraction occurred at around 200 °C (*3 in Fig. 4), where decomposition of the binder began, and no dimensional change was observed when the temperature exceeded 400 °C.

■ Analysis by DTG-FTIR

The molded ceramic specimen was placed in the platinum cell and measured under an air atmosphere. Table 3 shows the analysis conditions.

Table 3 DTG-FTIR Analysis Conditions

Instrument	: DTG-FTIR
Heating rate	: 20 °C/min
Temperature range	: 30 °C - 600 °C
Atmosphere	: Air
Resolution	: 8 cm^{-1}
Interval	: 30 sec
Accumulation	: 10 times

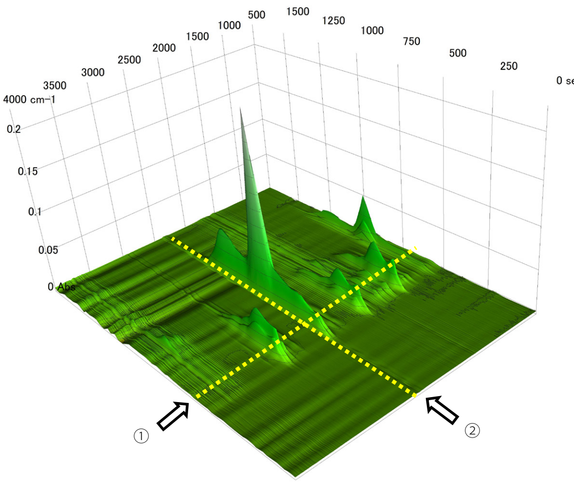

Fig. 5 3D Display of IR Spectrum in Air

From the IR spectrum at 690 sec extracted from the position of arrow ① in Fig. 5, it can be estimated that evolution of decyl methacrylate occurred (Fig. 6). Fig. 7 shows an IR chromatogram in which the change in absorption at around 2361 cm^{-1} (arrow ② in Fig. 5), which is the absorption wavenumber of CO_2, is plotted against the temperature axis. This figure indicates that evolution of carbon dioxide begins gradually from about 220 °C, reaches a peak at around 360 °C, and then occurs again at around 440 °C.

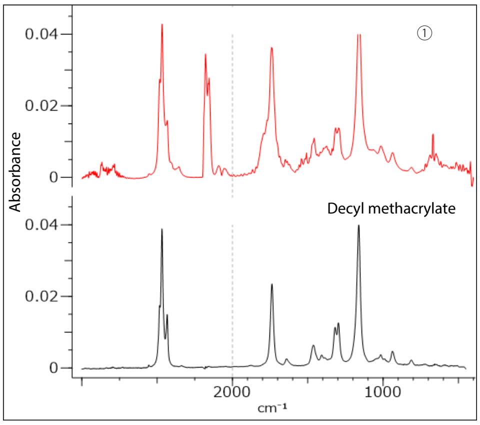

Fig. 6 Spectrum Extracted from ① and
Standard Spectrum of Decyl Methacrylate

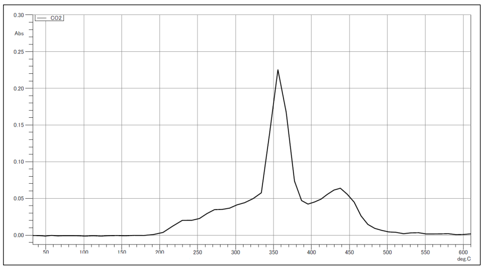

Fig. 7 IR Chromatogram of ②

■ Conclusion

To improve the production efficiency of ceramics, it is necessary to combine the atmosphere gas species and optimize the temperature pattern of the degreasing process so as to minimize the binder removal time while also preventing cracking. Verification of the binder decomposition behavior by the TG-DTA, confirmation of dimensional changes by the TMA, and qualitative analysis of the evolved gas and clarification of the gas evolution process by the DTG-FTIR using the instruments introduced in this article are considered to be an effective method for this type of optimization. Since these methods do not require complicated sample preparation and can be carried out in a comparatively short time, it is an extremely useful approach in study of the manufacturing conditions for ceramics.

The author wishes to express her heartfelt appreciation to all those concerned at the Kyoto Municipal Institute of Industrial Technology and Culture (Local Incorporated Administrative Agency), which participated in this joint research project, for their generous cooperation in the preparation of this Application News article, including provision of the specimens, instructions concerning the analysis conditions, and other assistance.

<References>

1) Tomohiro Wada and Taiki Horino, Development of Atmospheric Gas Technology for Dewax and Sintering in Fine Ceramics Products, TAIYO NIPPON SANSO Technical Report No.29 (2010)

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01-00629-EN First Edition: Jan. 2024

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