Improvement of Precision in Oxygen and Nitrogen Analysis of Raw Ceramic Powders

—Introduction of a Press Machine to Seal the Flux Capsule—

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セラミックス原料の酸素・窒素分析における精度改善

—プレス機を利用したフラックスカプセル封入—

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In the analysis of oxygen and nitrogen in raw ceramic powders by the inert gas fusion method, differences in the sampling procedure carried out by separate individuals is thought to be a primary factor in the reproducibility. We introduced a press machine for sealing nickel capsules in the sample molding process and confirmed that it was effective in decreasing these differences. Sample molding using a press machine requires pressures above 14.7 kPa. As a result of the helium purging test, it was clarified that some pressed 0.5 g capsules gave high blank values for residual air inside pressed capsules.

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1. Introduction

Ceramic materials have many uses. It is therefore important to check the purity, or level of impurity, of raw ceramic powders. Currently, the elemental analysis of ceramic powder is performed not only by chemical analysis but also by instrumental analysis which is becoming more common. Oxygen and nitrogen analyzers based on the inert gas fusion method are capable of determining average mass ratios (mass%, ppm) of oxygen and nitrogen in these ceramic powders in a short time.¹⁾⁻⁶⁾ For this instrumental method, the completeness of melting or thermal decomposition of the sample ceramic powder is important. Generally, we use flux to analyze such materials because their decomposition temperatures are very high. Flux, i.e., the bath material and accelerator, is used to promote decomposition or reduction.²⁾ We usually weigh an appropriate amount of a ceramic powder into a nickel capsule which has a low blank value and good ability to promote reduction or decomposition. Thus the capsule also becomes the flux. Up to now, the sample ceramic powder was weighed into a nickel capsule, which was then sealed by pinching using two pliers (this method will henceforth be called as hand molding). However, human skill is thought to have a significant effect on the precision of the analysis by this method. In order to solve these problems, we developed a press machine for nickel capsule molding and applied it to oxygen and nitrogen analysis (this method will henceforth be called as press machine molding).

2. Experimental

The oxygen and nitrogen analyzer employed was EMGA-650 from Horiba Ltd. It is able to simultaneously detect carbon oxide and nitrogen generated from the melted or decomposed sample materials in inert gas (helium), by means of infrared absorption and thermal conductivity, respectively. The details of the measurement procedure have been presented elsewhere.¹⁾⁻⁶⁾ We used Si_3N_4 (Denka Silicon Nitride, with the nickel capsule and a 0.5 g tin pellet as flux) as the model sample. Generally, Si_3N_4 should be preserved in a desiccator, after drying for 2h at

Fig. 1. Cross section of the molding component of the press machine.

110°C.⁴⁾ For hand molding, 0.3 and 0.5 g nickel capsules were prepared, while those for press machine molding weighed 0.35 and 0.55 g. The latter are henceforth expressed as 0.3 and 0.5 g for simplicity. The nickel capsule for press machine molding consisted of a cap and a cup, while that for hand molding, consisted only of a cup. One measurement required 35 mg of Si_3N_4 , a 0.5 g tin pellet and the nickel capsule. For press machine molding, the prototype press machine was EX-95 from Micronix Ltd. Figure 1 shows a cross section of the molding component of the press machine. In addition, a second press machine (Riken Seiki Co., Ltd., hydraulic press machine) was used to measure the press pressure. The CuteVac (Hitachi Ltd.) vacuum pump was used for degassing. Because date precision was more important than the accuracy in this study, we simply compared all the data without calibration.

3. Results and discussion

3.1 Optimum pressure for press machine molding

First of all, in order to determine the pressure to be used, we checked the effect of the press pressure on nitrogen and oxygen measurements of a model sample Si_3N_4 . The press pressure was varied from 4.9 to 24.5 kPa in 4.9 kPa intervals. The results are shown in Table 1. For reference, hand

Table 1. Data for Press Machine Molding and Hand Molding. Relationship between the Press Pressure and Measured Value

		Hand		Press machine				
		skilled	unskilled**	4.9kPa	9.8kPa	14.7kPa	19.6kPa	24.5kPa
Oxygen	X bar	0.783	0.800	0.780	0.798	0.810	0.795	0.804
	/mass %	σ_{n-1}	0.005	0.007	0.005	0.005	0.003	0.006
	CV%	<u>0.58</u>	1.05	0.94	<u>0.67</u>	<u>0.64</u>	<u>0.43</u>	<u>0.76</u>
	Range	0.018	0.027	0.027	0.017	0.018	0.011	0.018
Nitrogen	X bar	34.79	34.97	34.41	34.69	34.75	34.80	34.69
	/mass %	σ_{n-1}	0.09	0.16	0.11	0.08	0.10	0.08
	CV%	<u>0.26</u>	0.50	0.48	0.31	<u>0.23</u>	<u>0.28</u>	<u>0.24</u>
	Range	0.28	0.41	0.49	0.27	0.28	0.33	0.26
n		10	10	5	5	5	5	5
time/sec*		~30	~140	~15	~15	~15	~15	~15

0.3g Ni capsule with Si₃N₄.

Underline shows that CV is within 0.9% for oxygen or 0.3% for nitrogen.

CV%=100 σ_{n-1} /Xbar

* Sample weighing time is not included.

**Sealed by a beginner

molding results are also shown. The data precision is an important parameter here and is usually represented by the standard deviation (σ_{n-1}) or coefficient of variation (CV). The precision of the measured data for EMGA-650 is within 1.5%CV for oxygen and 0.5% for nitrogen, so those data which are within 0.9%CV for oxygen or 0.3%CV for nitrogen are underlined in Table 1. These results clearly show that press machine molding requires pressures above 14.7 kPa. The mean values (X bar) for both press machine molding and skilled hand molding are not significantly different. Table 1 shows press machine molding and both skilled and unskilled hand molding results. There is an obvious difference in precision and time between skilled and unskilled hand molding. However, the data for press machine molding are almost equal to those for a skilled hand molding, although press machine molding is faster and easier to perform. The level of skill will depend on the amount of experience of the worker. "Unskilled" here implies a beginner or a person not accustomed handling two pliers together. Unskilled data in Table 1 were obtained by a beginner.

3.2 Effect of press machine molding in blank measurement

EMGA-650 performs a relative measurement and therefore requires calibration. Calibration is normally performed between a blank and a span standard. However, some ceramics contain either nitrogen or oxygen as the main component, while others contain them as low-level impurities. Consequently, the blank value becomes very important. Table 2 shows the blank values of the nickel capsule, containing no sample, pressed by press machine molding and by hand molding. All blank values are in mass ppm. No meaningful difference can be seen between 0.5 g for hand molding and 0.3 g for press machine molding. However, for the case of 0.5 g in press machine molding, an especially large difference in the nitrogen value occurred, compared to 0.5 g in hand molding. The other nitrogen blank values are <about 10 mass ppm, so it is clear that the 57 mass ppm value from the 0.5 g nickel capsule in press machine molding is extraordinary. The precision was also poor. It is possible to attribute the difference to the contamination of air pressed into the capsule. In order to confirm this

Table 2. Blank Values of Ni Capsules and Effect of Degas/Purge

		Hand	unpressed*		Press machine				
			(without molding)		degas				purge
capsule weight		0.5g	0.5B	0.5BP	0.3g	0.5g	0.5g	0.5g	
Oxygen	X bar	73	81	87	91	109	89	78	
/mass ppm	σn-1	7			9	12	12	17	
Nitrogen	X bar	5	5	5	8	57	25	6	
/mass ppm	σn-1	2			2	34	10	2	
n		10	3	3	10	10	10	10	

Degassing time was about 5 min.

Purging time was about 5 min, flow volume was about 0.5l/min.

* 0.5B 0.5g Ni capsule for hand molding.

0.5BP 0.5g Ni capsule for press machine molding.

hypothesis, nickel capsules were pressed by press machine molding with degassing or with helium purging. The results are shown in Table 2. Although both the blank value and the precision were improved by degassing for 5 min, these values were still not as good as in hand molding. There are two possible explanations. One is that the capsules were not degassed completely, and the other is the leakage of air into the sealed capsule due to imperfect sealing and the pressure difference between the inside and outside of the capsule. The results of helium purging, on the other hand, show no meaningful differences in the blank value or precision compared to hand molding. The flow rate of helium was about 0.5 l/min and the purge time was about 5 min. These results clearly show that residual air inside the pressed nickel capsule is the cause of the unusually high blank values. The precision was poor because the exact amount of residual air trapped inside the capsule was not constant. The finding that residual air affected the nitrogen data more than the oxygen data is consistent with the fact that nitrogen concentration in air is approximately four times greater than that of oxygen. Press machine molding was hardly sensitive to the presence of residual air, except in the blank measurement, because the pressed nickel capsule was actually full of ceramic powder, whereby there was little space for residual air. Incidentally, the optimum pressure for press machine molding, as discussed in the previous section, would also be related to the amount of residual air.

Although helium purging was able to eliminate the influence of residual air, there is a simpler method of preventing air from contaminating the capsule. We confirmed that it was sufficient to measure an unpressed cap together with a pressed cup as the blank (it is possible to perform the measurements without pressing the cups, but some cups

tend to get stuck in the hopper). By this treatment, air was not trapped in the capsule.

The lower the nitrogen concentration of a sample, the greater the influence of residual air on the precision. It is expected, based on Table 2, that the influence of residual air on nitrogen values over a few thousand mass ppm is negligible.

4. Conclusions

It was clarified that the high blank values and poor precision that occurred when using the press machine were attributable to residual air trapped inside the nickel capsule. The effect of the residual air could be significantly removed by measuring an unpressed cap together with a pressed cup. The use of the press machine reduces the time required to seal the capsule, reduces the amount of labor required, and eliminates the effect of the level of skill of the worker.

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