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MECHANICAL MATERIAL PROPERTIES OF MARBLE AFFECTED BY HIGH TEMPERATURE CAUSED BY FIRE

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Abstract. *In Mediterranean Sea area, there exist a number of historical constructions using marble stones. Those marble stone constructions suffered sometimes serious damage by historical fires in their long histories. However, there have been insufficient knowledge and lack of information on the mechanical characteristics of marble stones affected by high temperature caused by historical fires. Such fire damage might reduce seismic safety of those marble constructions, as seismic activity is high in Mediterranean Sea area. As well as, it might cause serious issues to be solved for restoration of heritage marble structures.*

The scope of the present study is, as a fundamental research, to describe the mechanical material properties of marble stones used for constructions of ancient Greek temples, affected by high temperature caused by fire.

In the present research, heating tests of marble stone samples were conducted to study their material behaviors affected by high temperature. In these tests, the temperature for heating varied from 200°C to 1200°C with temperature interval of 200°C. Also, the duration of heating was 2 hours (constant temperature time) in consideration of historical fires. Ocular inspections of materials and measurement of weight were carried out. In addition, compression tests of the specimen were performed to evaluate mechanical properties affected by high temperature. These experimental results demonstrated that marble stones used for constructions of Greek temples are vulnerable to high temperature caused by fires. Damage by historical fires should be considered for restoration of Greek temples of marble stones.

1 INTRODUCTION

In Mediterranean Sea area, there exist a number of ancient constructions of marble. In their long history, those marble stone heritages sometimes suffered serious damage by historical fires. However, there have been insufficient knowledge and lack of information on the mechanical characteristics of marble affected by high temperature caused by fires. Sometimes, it might cause serious issues to be solved for their restoration projects. On the other hand, Mediterranean Sea area is a high-seismicity area in Europe, therefore, most of those heritage structures of marble have been subjected to earthquakes. This imposes necessity for assessment of the fire damage to structural seismic safety.

A number of studies on the thermo-mechanical performance of rocks and stones have been conducted in rock engineering field to construct structures for storage of oils and radioactive wastes.[1] As well as, thermal weathering of them has been studied for assessment of deterioration of rocks not only under natural climate conditions, but also under mountain fires.[2] Fundamental data of thermal properties were published in the scientific chronological tables in Japan.[3] However, most of those past studies and data dealt with granite, andesite, tuff, sandstone or the other popular rocks. Only a few studies have been performed on mechanical properties of marble. Hence, N. Sakai described the compressive tests of marble (Akiyoshi Marble in Japan) subjected to high temperature from the room temperature to 600°C [4], showing gradual reduction of strength with temperature. Paying attention that characteristics of marble depend on place where they were produced, furthermore, considering that mechanical properties of marble subjected to higher temperature caused by fire (800°C -1,000°C) have not been reported, it needs to study mechanical properties of marble affected by high temperature caused by fires. The scope of the present study is, as a fundamental research, to describe the mechanical properties of marble used for construction of ancient Greek temples, affected by high temperature caused by fires.

In the present paper, laboratory heating tests of marble samples were conducted to study their material behaviors affected by high temperature. Level (degree) of temperature and exposing duration were the parameters in the heating tests. As chemical change of marble materials might be caused by high temperature, mass variation of the specimens during heating was measured. Also, ocular inspection of the specimens was performed not only just after heating but also during cooling period. In fact, the state of the specimens exposed to high temperature was affected by absorbing phenomenon of moisture in the air during cooling time. As fundamental mechanical properties, compression tests of the specimens were conducted after cooling in the air.

2 LABORATORY TESTS

2.1 Heating Tests

In the present study, cylindrlical marble specimens of φ50[mm]×H100[mm] or φ50×H50[mm] were examined. Marble stones for those specimens were taken from Deonisos Marble quarry in the suburbs of Athens.

In these heating tests using a high speed electric furnace (See Fig.1), we heated specimens for 90 minutes until the internal temperature of specimens reached to setting temperature (preheating), then continued keeping the temperature for 30 minutes, 1 hour, 2 hours, or 4 hours at the temperature between 200°C and 1,200°C. Thermocouple was installed in the center of a cylindrical specimen to measure the internal temperature of the specimen. Temperature in the chamber of the furnace was also measured. It was considered that the temperature caused by historical fires of which source was woods could be estimated to be 800°C -1,000°C. In addition, when two specimens were heated by one heating case at the same time, a sheathed thermocouple (Type K. $\phi 3.2mm$) was installed to one of two specimens to confirm that the internal temperature of the specimens continued keeping temperature. Fig.3 shows the time for heating as the experimental condition.

After heating tests, weight of the specimen was measured by an electronic balance. Hence, while specimens were cooled down naturally in the air, photographs were periodically taken to record the change of aspect of specimens. After natural cooling in the air, we conducted the compression tests of a total of 17 marble specimens exposed to high temperatures, moreover, a total of 7 un-heated specimens to examine how heating temperature and heating time affected the mechanical characteristics of those marble stone samples. In this compression experiment using the universal-testing machine shown in Fig.2, a data-logger was used for the recording device. Strain induced in the specimen was measured in both directions of axis and of circumference.

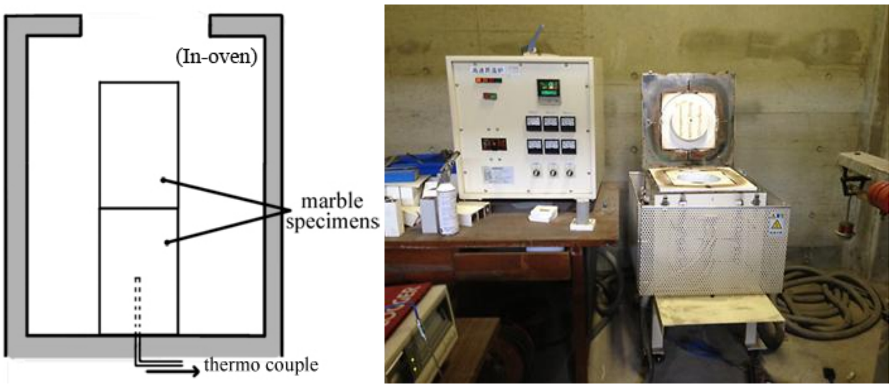


Figure 1: Electric furnace and specimen

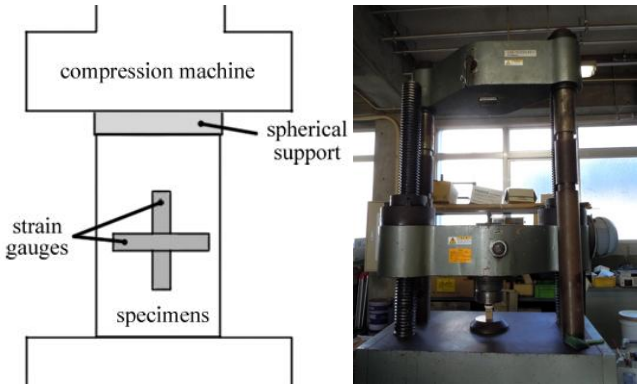


Figure 2: Compression test

Marble is a metamorphic rock composed of, commonly, calcite or dolomite, and the chemical formula for marble is $CaCO_3$. Eq.(1) is the chemical equation of the reaction in pyrolysis $CaCO_3$. $CaCO_3$ is changed into CaO as CO_2 evaporates. At this time, the weight of marble stones begins to decrease. Moreover, CaO absorbs moisture in the air, then it is changed into $Ca(OH)_2$ while giving off the heat of reaction. (See Eq.(2)) [5]

Therefore, we expected that water content is useful data for understanding weight decrease because of occurring chemical reaction. A total of 3 specimens of marble stones were examined by the Forced Air Flow Oven for understanding how many grams decreased by evaporating water content. Hence, the specimens were heated at 110°C for 24 hours, and compared the weight before and after drying by using an electric balance.

$$CaCO_3 \rightarrow CaO + CO_2 - 177.9[kJ/mol] \ [5] \tag{1}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2}$$

Table.1 shows the mass variation of specimens of marble stones caused by heating at 110°C. Negligible density variation less than 0.2% was found, which demonstrated no water content of the marble stones.

On the basis of the above-mentioned results, it should be recognized that the chemical reaction of $CaCO_3$ and the weight variation of the specimens could be observed at the same time in heating tests at high temperatures.

Fig.4 shows the relation between heating temperature with time and mass variation. In this figure, “In-specimen temp.” denotes the temperature at the center of specimen, respectively. The irregular variation shown at 1,000°C was caused by an experimental problem, therefore, should be neglected. In the present heating test, reduction of weight was initiated at 750°C. This indicated that the chemical reaction expressed by Eq. (1) started in the specimen at this temperature. Such reduction of the density was caused by the chemical reaction described by Eq. (1), when the specimen exhausted CO_2. In addition, soon after having set the higher temperature from750°C, the mass of specimen decreased remarkably.

Fig.5 and Fig.6 show the mass variation of specimens after the heating tests at temperature between 200°C and 1,200°C. Mass variation at between 200°C and 600°C was less than 0.2%, indicating no density reduction was caused at the range between 200°C and 600°C. However, the remarkable mass variation of specimens was found after the heating at between 750°C and 1,200°C. The weight of specimens just after the heating at 800°C became less than 97% of the initial one even if there found a little difference in mass caused by the heating time. Moreover, the weight of the specimens heated at 1,000°C and 1,200°C was reduced to be less than 60%. Shown in Fig. 6, the weight of the specimens heated at 800°C was recovered during the cooling time in the air, as the specimens absorbed moisture in the air. This phenomenon can be interpreted by exhaustion of CO_2 expressed by Eq. (2).

Apparent deterioration of the specimens at heating temperature of higher than 700°C was remarkably observed (See Fig.7 and 8). By heating the specimen over 700°C, such deterioration of the specimens were corresponding to the density reduction that was caused by chemical reaction given by Eq. (1). Moreover, deterioration of specimens significantly proceeded during exposing to the air after heating. For the test case of heating temperature at 800°C for 2 hours, a thin surface layer (thickness = 1-2mm) of the specimen was first exfoliated along the axis. Next, distortion was gradually caused at the inner part of the specimen and extended to whole. Furthermore, the surface layer of the specimen was separated at several parts of the specimen. During exposing to the air, the strength of the specimen was getting lower and finally reached to collapse, while cracks were developed.

Table 1: Results of measurement of the water content

	Before → After	Water Content [%]
Specimen A	487.5[g] → 487.6[g]	0.00
Specimen B	544.3[g] → 544.2[g]	0.00
Specimen C	524.6[g] → 524.5[g]	0.00

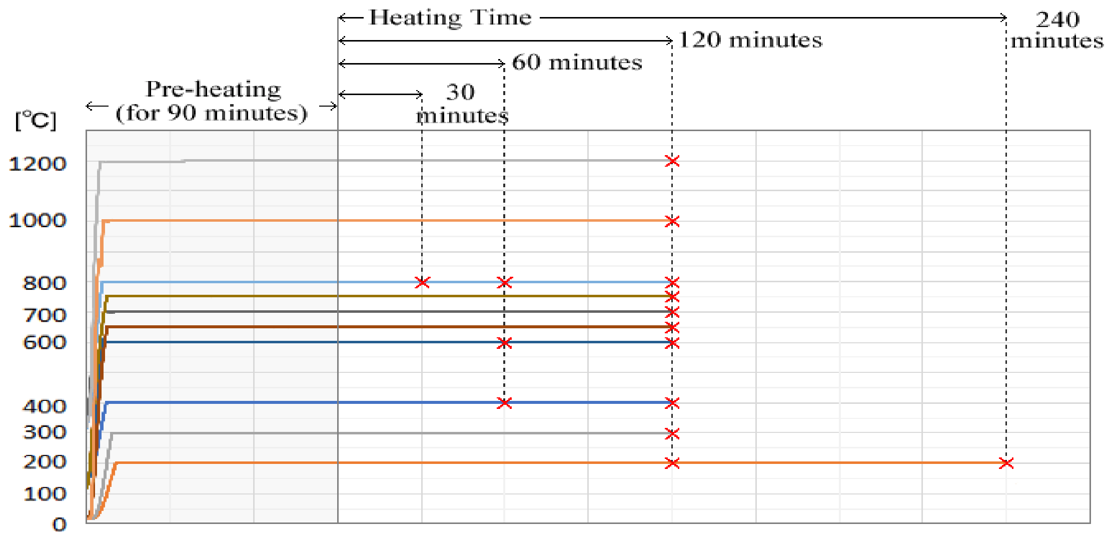


Figure 3: Controlled Temperature of heating tests

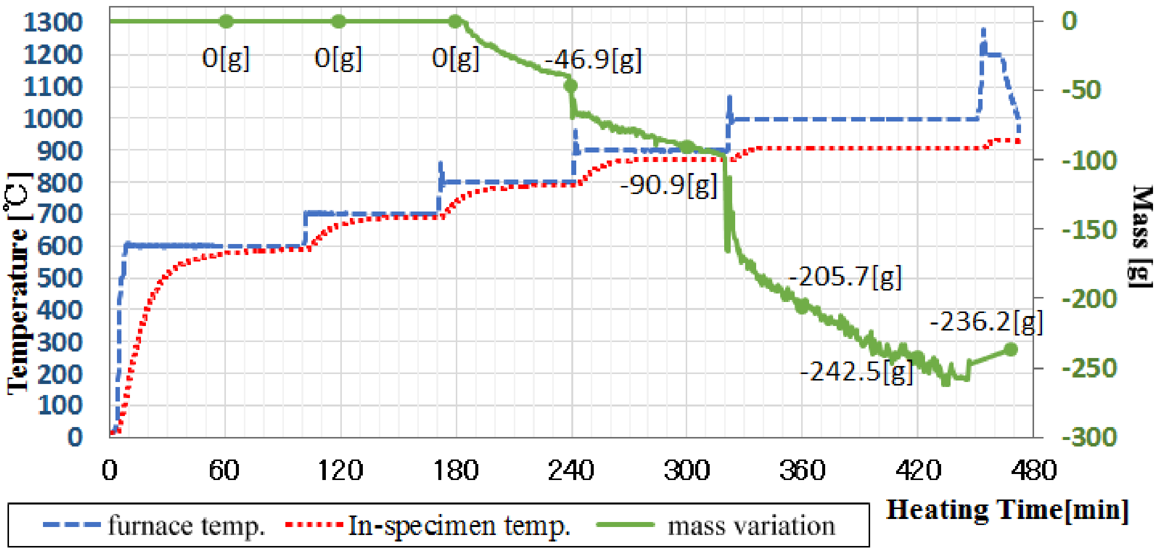


Figure 4: Mass variation with time in step heating test by raising 100°C.

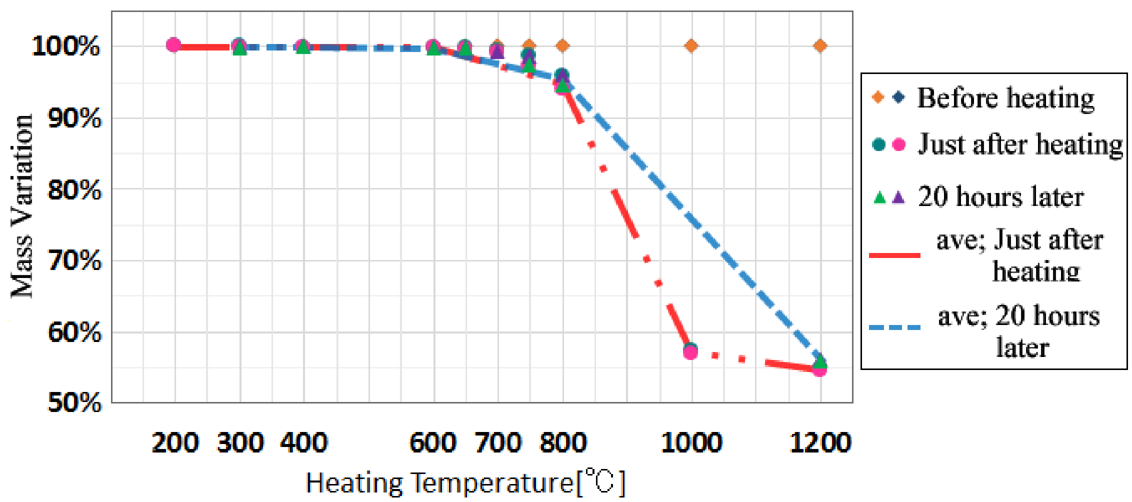


Figure 5: Relation heating temperature and mass variation with Constant Temperature Tests.

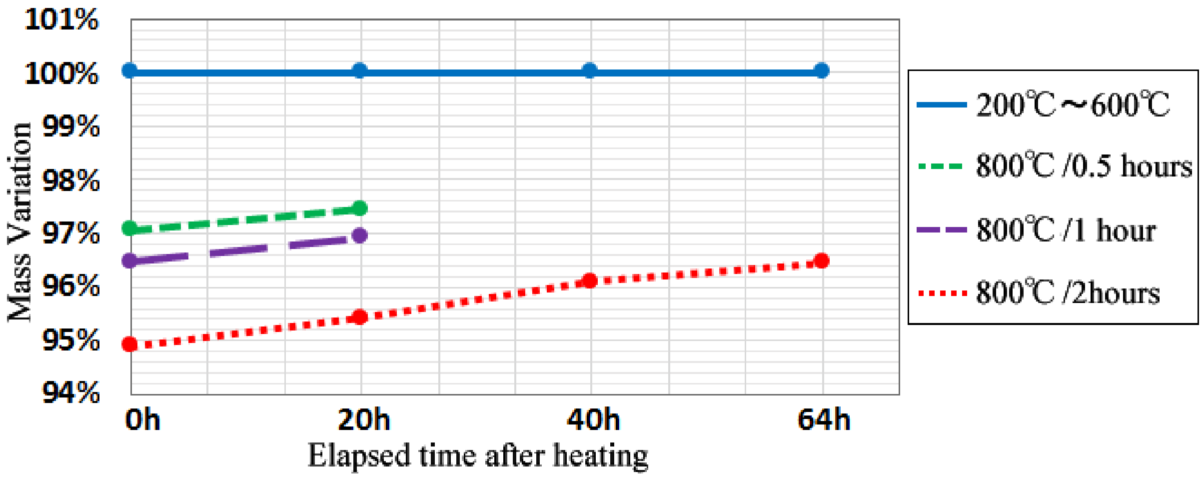


Figure 6: Relation elapsed time after heating and mass variation

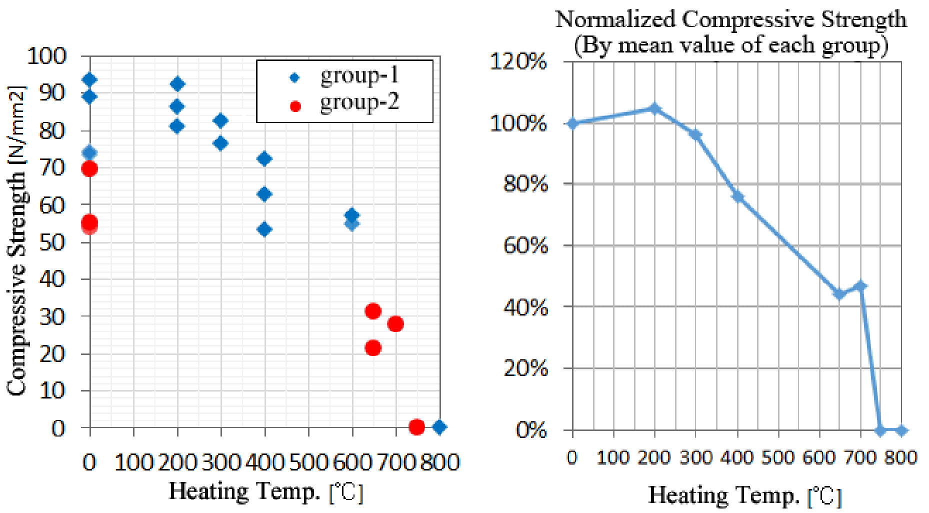
Figure 7: Deterioration of specimen with time. (After 60 hours from the end of heating at 700°C for two hours)

Figure 8: Surface layer of specimen exfoliated. (After 120 hours from the end of heating at 800°C for two hours)

2.2 Compression Tests

Fig.9 shows the relation between heating temperature and strength of the marble specimens. Hence, we ulilized two groups of samples for the laboratory tests, therefore, their production date and souce rocks were different between the two groups. This caused a difference in compressive strength at normal temperature between two groups of samples.(See Fig.9(a)), therefore, the strength was normalized by the mean compressive strength of the normal temperature in every group. Fig. 9(b) shows the normalized residual compressive strength of the specimens after cooling them in the air. The overall behavior of material strength affected by the high temperature was summarized as follows ; 1) The strength began to decrease at the temperature of 400°C. 2) The strength was reduced to be 0 by heating over the temperature of 750°C. 3) The strength was reduced remarkably between 600°C and 800°C. Furthermore, a series of the tests showed a little effect of the heating duration on the strength, demonstrating that 2 hours was appropriate for heating time.

Fig.10, 11 and 12 present the specimens after the compressive tests of the specimens of heating at and, respectively, in order to show the fracture mode. Most of the specimens showed shear failure mode regardless of degree of temperature, shown in these photos. However, there found a difference in failure characteristics between the heated and un-heated specimens as follows. The heated specimens suffered circumference cracks before compressive tests, which caused separation between inner cylindrical part and outer surface deteriorated layer, shown in Fig.13. As the outer deteriorated surface was rather weaker, the inner part undertook most of the compressive load and was cracked with fracture mode corresponding to shear failure. On the other hand, the vertical crack was caused, which brock the specimen into some pieces for the un-heated specimens.



a) Residual Strength

b) Heating temperature and strength

Figure 9: Relation between heating temperature and strength

Figure 10: Failure mode
(un-heated specimen)

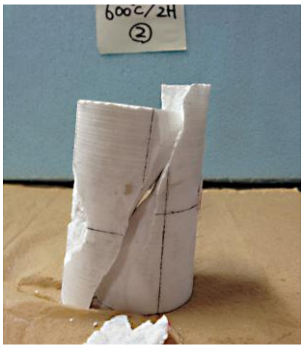


Figure 11: Failure mode
(heated specimen at 600°C)

Figure 12: Detail of failure mode
(heated specimen at 400°C)

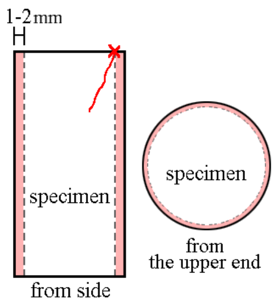


Figure 13: Mechanism of heated specimens

3 CONCLUSING REMARKS

To study the fire resistant performance of the marble stones utilized for construction of ancient Greek Temples, the heating tests were conducted with parameters of heating temperature and duration. The range of heating temperature in the present study was from 200°C to 1,200°C. The regular duration of heating time was 120min, while 30min and 60min heating tests were also performed to ensure the effect of heating time. After heating tests, the compression tests were carried out. The fundamental characteristics of the specimens affected by high temperature were as follows;

1) The strength of the specimens was not affected by heating at temperature lower than 300°C. The reduction of compressive strength began at around 400°C. Such reduction of strength was caused remarkably at over 650°C. The strength of the specimen after heating at 650°C was reduced by 60% of the un-heated one. The strength of the specimens heated at temperature over800°C reached 0 and fractured.
2) The weight of the specimens began to decrease at around 650°C. This reduction of weight can be explained by thermal decomposition reaction of marble material. Note that heating temperature having caused such reduction of density was corresponding to the temperature of remarkable reduction of the compressive strength mentioned above.
3) Progressive deterioration phenomenon of the specimens heated by higher temperature than 650°C -700°C was found during cooling time in the air. This phenomenon can be explained by absorption of moisture in the air. This deterioration must cause reduction of mechanical properties.

Consider that the temperature of historical fires of which source was wood was 800°C - 1,000°C, this research presents fundamental knowledge on the fire damage to marble stones used for construction of ancient Greek temples.

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