The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Foamic Characteristics of Porous Materials Using the Duckeum Gold and Silver Mine's Waste Slime

Hyung Seok Kim[1], Ji-Whan Ahn[1], Hyoung Ho Lee[2], Hwan Kim[2], Kyung Sun Choi[3], Kyuh Young Lee[3], Hong Lim Lee[3], Kyung Soo Kim[4]

[1] Institute of Geoscience & Mineral Resources, Taejon, 305-350, Korea
[2] School of Materials Science and Eng., Seoul national University, Seoul, 151-742, Korea
[3] Dept. of Ceramic Eng., Yonsei University, Seoul, 120-749, Korea
[4] Ministry of Construction & Transportation, kyonggi, 427-712, Korea

In this research, porous materials were made from mine's waste slime. As a temperature changes, a phase changes, a porosity, and a mechanical strength of porous materials were observed and measured. The process of pore-formation was observed by SEM according to the change of heat-treatment temperature and time. It turned out that the foaming reaction of mine's waste slime was resulted from liquid phase by decomposition of the sanidine and the muscovite-3T. When heat-treated at over 1200℃, it appeared high porosity. And, to activate the foaming reaction, an alkaline oxide concerned with liquid formation was added and its effects were examined.

1. Introduction

Environmental pollution is getting worse and worse because of fast changes of industry pattern and the great development of various industries. All over the world, the concern about the prevention of environmental pollution has been growing and many researches in environment have been done and the industry market related to it has expanded. Pollutants from many different industry fields are soot and smoke, dust, gas, nasty smell, waste water, sewage and excretions. And there are a lot of different kinds of pollutants and exhaust quantity has been steadily increasing. Therefore, equipments and parts which can remove and reduce pollutants are used and developed. Especially, in case of ceramic used for environmental products, there are two main uses. One is that it contributes to environment indirectly. Another is to purify and clear pollutants directly.

Since the porous ceramic was used for virus-filtering in 1887, it has been used in various ways to construction materials by using a fluid contact function, separation, and absorption, for insulations and sound-absorbing materials, living goods for moisture absorbents and deoderants, and environmental fields for exhaust gas purification filter. Recently, it is used for semiconductor, medicine, bio, environment, new material and high technology by accurately controlling a pore's physical and chemical properties. The application fields are expected to be a lot more. As the porous ceramic, there are porous silica, porous alumina for catalyzer, honeycomb, porous hollow sphere and porous glass.

Mine's waste slime, by-product remaining from gold and silver mine, contains many kinds of mineral contents. It is the substance with multi-ingredients and also generated a great deal from mining and a small amount of heavy metals such as Pb, Hg, and Fe, etc. Therefore it is necessary to be treated in a special way. Because several multi-mineral chemical compounds exist in mine's waste slime which has a mixed melting points by heat-treatment and its reaction happens in a complicated way. As a result of chemical reactions of mine's waste slime, it is known to create a large amount of foaming pores. And lately many researches have been doing to applicate pores for clearing and purifying pollutants and waste water. However the research is very rare to go to work out the reaction of many kinds of inorganic chemicals, pore-generating mechanism, pore size, control of porosity, mechanical strength, and their relationships.

Accordingly, in this research by using mine's waste slime remaining after mining, a porous catalyzer is made and its characteristics are examined according to the experiment variables influencing on manufacture ; heat-treatment conditions, increasing temperature speed, maintenance time, cooling time. Phase analysis of porous materials manufactured in various conditions, a pore size, its distribution and a compressive strength changing by different heat-treatment were observed and measured. To activate the foaming reaction, as additives Na_2O, K_2O and a 1:1 mixture of Na_2O and K_2O were added 2.5, 5, 7.5 and 10 wt% and mixed after dry ball-milling for 48 hours. The mixed powder was molded and the phase and the microstructure of test pieces that went through the heat treatment at 1100, 1125 and 1150℃ for 1, 5 and 10 hours, respectively, were analyzed and examined.

2. Experimental Procedures

2.1 Phase analysis and observation of microstructure

To observe a phase changes depends on heat-treatment conditions, raw powder was heat-treated at 1050, 1100, 1150,1200, 1250℃ for two hours, respectively and analyzed by XRD. To detect a small amount of heavy metals from raw powder, chemical leaching experiment for heavy metals was done.

To observe the micro-structure, the powder of mine's waste slime was set at the pressure of $50 kgf/cm^2$ and treated at 1200, 1250℃ for 10, 20, 30 min. 1,2,5 hours,

Table 1. Leaching Test Results of Heavy Metals in Mine's Waste Slime (ppm)

Element	Mn	Fe	Pb	Cd	Zn	As	Hg	Cr	Ni	Cu
Amounts	0	0.203	0.051	0	0.02	0.045	0.027	0	0	0

respectively and examined the fracture surface of sample by SEM.

To the composition with no additive and the ones with 2.5 and 5 wt% Na2O as an additive, their density, porosity and compressive strength after heat treatment on each condition were measured. Density and porosity were measured using the Archimedes법 and the Mercury Porosimetry. The UTM (Universal Test Machine) was used to measure the compressive strength, with 0.5mm/min crosshead speed.

2.2 Basic physical properties measurement

In each condition, a density, a porosity and a compressive strength of heat-treated samples were measured. Density and porosity was measured by the Archimedes' law. Compression strength was measured by using UTM(Universal Test Machine) at the speed of 0.5mm/min.

3. Result and Discussion

When heat-treated for two hours at 1050, 1100, 1150, 1200, 1250℃, raw powder of mine's waste slime appeared XRD result at Fig. 1. Raw powder turned out to be the substance which contains α-quartz, the muscovite-3T[(K,Na)(Al,Mg,Fe)$_2$(Si$_3$1A$_{l0,9}$) O$_{10}$(OH)$_2$]. At the result from the chemical leaching test, it turned out to contain a small amount of Fe, Pb, Zn, As, Hg shown as Table 1.

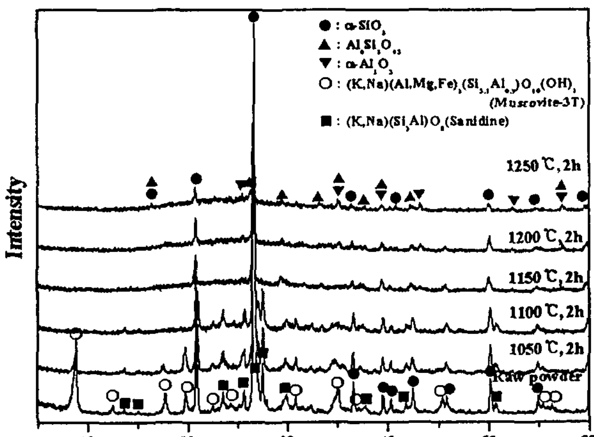

Fig. 1 XRD patterns of mining tailings sintered at different heating condition.

To investigate the foaming mechanism of mine's waste slime with this composition, the phase analysis and micro-structure were observed when heat-treated at 1050, 1100, 1150, 1200, 1250℃ for two hours, respectively. In the case of heat-treatment over 1150℃, a typical halo at XRD peak is clearly shown as a amorphous phase at around 20-30° . This amorphous phase was made by decomposing the sanidine and the muscovite-3T, reaction formula (1) and (2). According to the component ratio, a composition appears to be a group of Na_2O-K_2O-SiO_2 which is

possible to make a liquid-phase at over 750℃. α-Al_2O_3 was made with glass phase creation and decomposition and the mullite(3$Al_2O_3$2SiO_2) was made by reaction of Al_2O_3 and SiO_2 .

(K, Na)(Si$_3$Al)O$_8$ →(SiO_2 - Al_2O_3)system + glass **(1)**

(K, Na)(Al, Mg, Fe)$_2$ (Si$_3$,1A$_{l0,9}$)O$_{10}$ (OH)$_2$ (SiO_2-Al_2O_3)system+glass+H_2(g) **(2)**

In a phase analysis after heat-treatment, the substance with alkali or alkaline earth, an ingredient of sanidine and muscovite-3T was not detected. Therefore, it is thought that almost all substances are consumed as the liquid-phase is created. On the other hand, at the result of micro-structure examination, a pore-creation was hardly shown at 1150℃. And it turned out that a quantity of pore was just a little. But, over 1200℃, the foaming reaction happened very actively. A temperature is expected to lower by adding alkali oxide either Na_2O or K_2O in a starting material and by changing the component ratio of each substance because liquid-phase is possible at over 750℃ from the phase equilibrium.

To evaluate application possibilities as a porous material, the basic physical properties were measured. The heat-treatment temperature was arranged at 1200 and 1250℃, which the liquid-phase happens actively. At each temperature, it was treated to examine the degree of foaming progress for 10, 20, 30min. 1, 2, 5 hours, respectively. Density, porosity and compressive strength, and micro-structure were shown at Table 2 and Figs. 2 and 3, respectively.

Table 2 Density and Mechanical Strength Changes of Sintered Body according to Heat Treatment Conditions

Heat Treatement (℃)	Maintenance Time(min)	Density (g/cm^3)	Compressive Strength (kgf/cm^3)
1200	10	2.37	1006
	20	1.96	474
	30	1.85	431
	60	1.78	276
	120	1.66	200
1250	10	1.48	184
	20	1.25	136
	30	1.20	128
	60	1.07	113
	120	1.02	109
	300	0.85	64

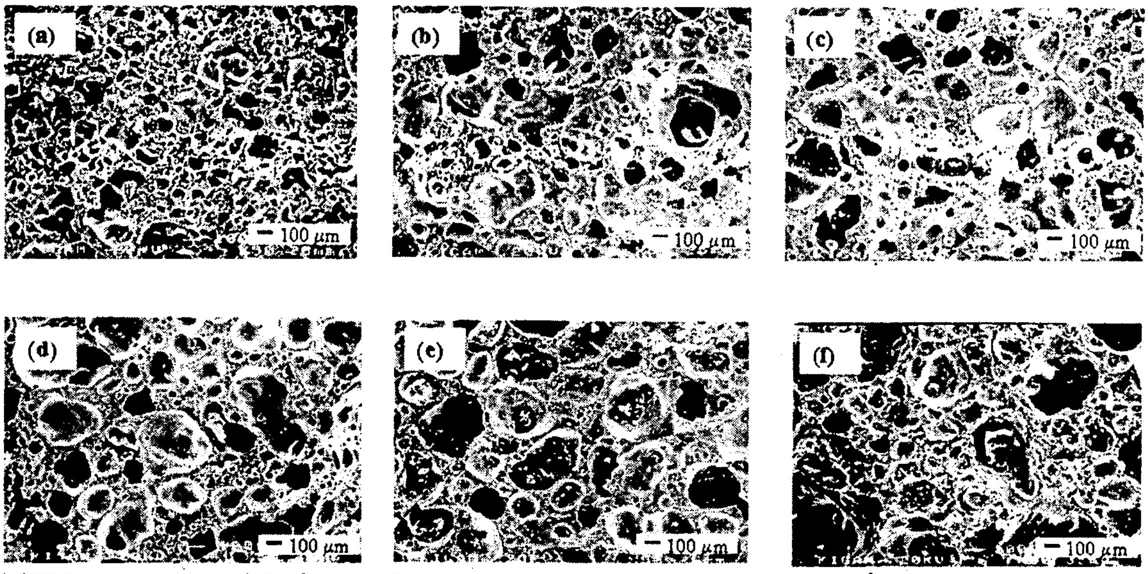

Fig. 2 SEM photographs of the fractured surface of mining tailings sintered at 1250℃ with different heating time. (a) 10min (b) 20min (c) 30min (d) 1hr (e) 2hrs (f) 5hrs

At the above two heat-treatment temperature, the density of heat-treated body was decreased as heat-treatment time got longer, however, its porosity was increased. Therefore it is well known that the foaming reaction was progressing continuously. But in case of heat treatment at 1250℃, there were over 100㎛-sized pores because the foaming reaction already happened actively. Though it satisfies the basic element of a high porosity in practical uses of porous materials, it has a very weak point in a specific surface. So it is not proper to use it.

At 1200℃, the foaming reaction occurs actively at the beginning. Next, the reaction speed becomes slower, and then created pores are combined each other. Thus the number of pores decreases and their sizes get larger as time passes by. The result of compression strength measurement was shown at Table 2. When a sample was heat-treated at 1200℃ for a short time, its strength turned

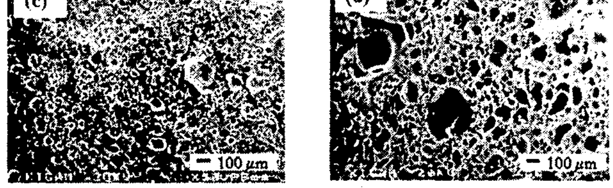

Fig.3 SEM photographs of the fractured surface of mining tailings sintered at 1200℃ with different heating time. (a) 10min (b) 20min (c)20min (d) 2hrs

out to be over 400kgf/㎠. However the mechanical strength of samples heat - treated at 1200 ℃ for a long time and at 1250℃ represent below 276kgf/㎠. This is because large pores

3.2. The Effects of Additives

As it was found that the foaming reaction was mainly caused by the liquid formation of Na_2O-K_2O-SiO_2 system, Na_2O, K_2O and a 1:1 Na_2O/K_2O mixture were added to waste mine slime powder, 2.5, 5, 7.5 and 10 wt%, respectively, to facilitate the foaming reaction and reduce the foaming temperature. As the result of forming the mixed powder and conducting heat treatment at 1100, 1125, 1150, 1175 and 1200℃, the addition of K_2O and a 1:1 Na_2O/K_2O mixture caused a weaker foaming reaction than that of Na_2O. When Na_2O was added, the test piece showed a tendency to have a sharp foaming reaction at over 1125℃, irrespective of the added amount. However, the composition with the addition of more than 7.5 wt% Na_2O and the one with heat treatment at 1175℃ or higher couldn't maintain the structure because of excessive liquid formation and the growth of pores. Fig. 4 and Fig. 5 show the XRD results of the test pieces with 2.5 and 5 wt% addition, respectively, after heat treatment at 1100, 1125 and 1150℃ for 10 hours. The overall constituents were similar to those of the waste slime with no additives.

Because the materials with the composition which includes Na were not detected, most of them are thought to contribute to the liquid formation. Furthermore, with the increase in the added amount of Na_2O and the temperature for heat treatment, the intensity of halo which has amorphous phase was raised. For the compositions with the addition of 2.5 and 5 wt% Na_2O which had the most excellent foamic characteristics, the physical properties of a test piece after heat treatment were measured and shown in Table 3. The temperature for heat treatment which has similar porosity was about 100℃

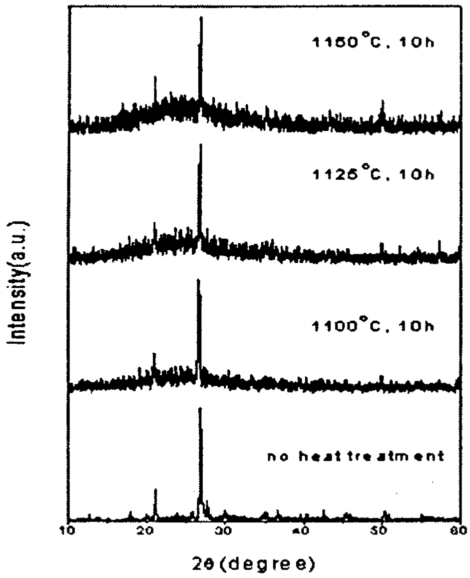

Fig. 4 XRD patterns of 2.5 wt% Na2O added mining tailings sintered at different heating conditions.

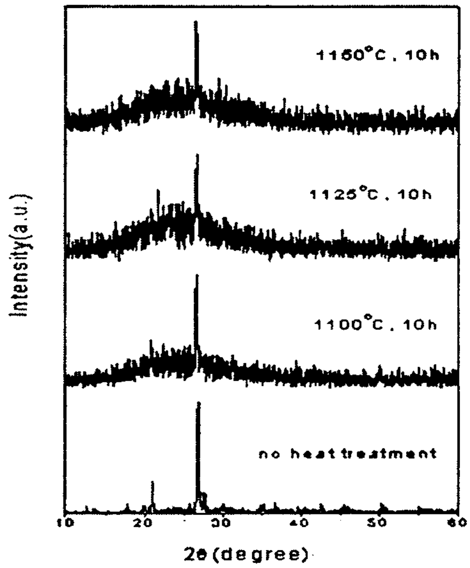

Fig. 5 XRD patterns of 5 wt% Na2O added mining tailings sintered at different heating conditions.

Table 3 Density and Mechanical Strength Changes of Na2O added Specimens According to Heat Treatment Conditions

Wt.% of added Na_2O	Heat Treatment Temp.(℃)	Maintenance Time(h)	Density (g/cm^3)	Compression Strength (kgf/cm^2)
2.5	1125	1	1.81	-
		5	1.10	219
		10	0.85	106
	1150	1	0.93	200
		5	0.58	41
		10	0.53	19.5
5	1125	1	1.45	-
		5	1.38	203
		10	0.99	74
	1150	1	0.97	139
		5	0.63	50
		10	0.57	37

lower than that of the one with no additive. If it had similar density, the test piece with Na_2O addition had a relatively higher degree of compressive strength than the one with no additive, which shows that the addition of Na2O gives a favorable effect on the foaming reaction and the mechanical properties. Theses are explicable in terms of the fine structure of the test pieces with Na_2O addition shown in Fig 6 and fig 7. If no additive was added, as mentioned above, some pores grew unusually and deteriorated the mechanical strength by acting as a destructive agent. On the other hand, if Na_2O was added, as shown in the fine structures of Figs. 6 and 7, pores with relatively regular size that had strong resistance to destruction were formed.

To examine the characteristics of the pores generated by foaming, the Mercury Porosimetry analysis of test pieces with the addition of 2.5 and 5 wt% Na_2O was made and its results were shown in Table 4. While the average size of pores and the bulk density of both test pieces were measured to have similar results, the apparent density and the measured porosity showed great differences. This means that most pores generated by foaming are open pores when 2.5 wt% Na_2O is added and closed pores with the addition of 5 wt% Na_2O. As shown in Fig. 7, it's thought that this is because in case of the addition of 5 wt% Na_2O, more excessively generated amorphous phase contributed to the formation of network structure of porous material. Therefore, if the kinds of additives, the added amount, the conditions of heat treatment, etc. are adjusted, it would be possible to control the properties of pores generated by foaming.

Table 4 Mercury Porosimetry Results of 2.5 and 5 wt.% Na_2O added speciments(heating treatment condition ; 1125℃ for 5h)

Wt.% of added Na_2O	Total pore area (m^2/g)	Average pore diameter (㎛)	Bulk density (g/cm^3)	Apparen t density (g/cm^3)	Porosity (open pore) (%)
2.5	246.953	7.3	1.10	2.16	49.33
5	25.710	8.0	1.38	1.49	7.14

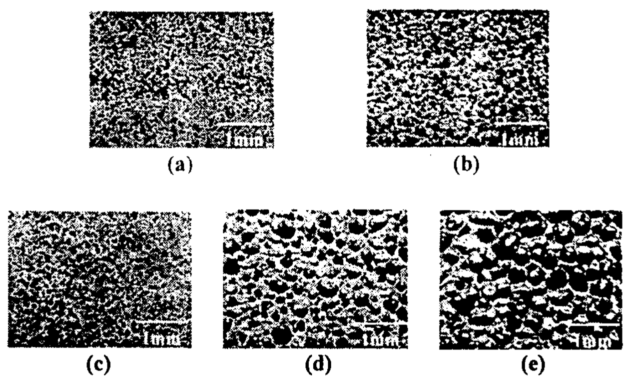

Fig. 6. Photographs of the fractured surface of 2.5 wt% Na_2O added mining tailings with different heating conditions.
(a) 1125℃, 5h (b) 1125℃, 10h (c) 1150℃, 1h
(b) (d) 1150℃, 5h (e) 1150℃, 10h

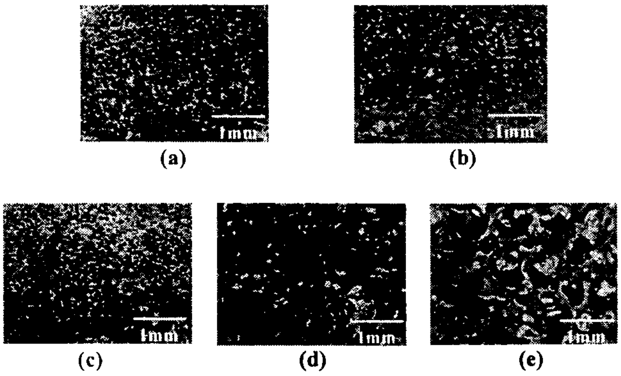

Fig. 7. Photographs of the fractured surface of 5 wt% Na_2O added mining tailings with different heating conditions.
(a) 1125℃, 5h (b) 1125℃, 10h (c) 1150℃, 1h
(b) (d) 1150℃, 5h (e) 1150℃, 10h

4. Conclusion

The results from examining the foaming mechanism of mine's waste slime. are as follows

1. The main cause of foaming reaction is that liquid phase was made by decomposition of the sanidine and the muscobite-3T. This reaction of creating the liquid phase actively happened at 1200℃.
2. Foaming reaction was activated at 1200℃ and it was getting more active at the beginning, however, its reaction was remarkably getting slower after a certain time passed by.
3. When heat-treated at 1200℃ for two hours and at 1250℃, They turned out to have a high porosity because of maximizing the activation of foaming reaction. But some pores are grown too large, which causes to deteriorate the physical properties.
4. When heat-treated mine's waste slime, as the temperature gets higher and time gets longer, Density and compressive strength reduced and porosity and its size increased
5. 5. By the addition of Na_2O, the foaming reaction was facilitated and the foaming temperature was reduced about 100℃.

References

[1] H. Jeong, D. S. Jeong "Manufacture and Application of Ceramic Filter for waste water purification", *Ceramist,* 3(6), 5-10(2000)

[2] J. Yang, "Ceramic for Air Purification",*Ceramist*, 3(6) 21-38(2000)

[3] A. S. Michaels "New Vistas for Membrane Technology", *J. Mater Sci.*, 10, 81(1985)

[4] I. M. Lachman, H. D. Bagley and M. Lewis, *Am Ceram.Soc. Bull.*, 60(2), 202(1981)

[5] M. Kawase, Nomura and Majima, "An Anaerobic Fixed Bed Reactor with Porous Ceramic Carrier", *Wat. Sci. Tech.*, 21,77(1989).

[6] H. Rawson, Properties and Application of Glass Elsevier Scientific Pub., N.Y. 1980.