A new composite ceramic coating composed of various minerals for exterior and interior concrete walls and its thermal insulation performance

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Abstract
Thermal insulating materials for building envelope are of great importance for saving the operational energy of buildings. The conventional thermal insulating board like polystyrene plate has problems of heat bridge effect, increasing the construction cost, and environmental infection. To resolve such problems, we invented a new composite material for coating the concrete wall, by mixing the sixteen kinds of mineral powders. Cement was added to the composite material while pouring the water, producing the colloidal solution. After three months for hardening of the coating layer, the composite ceramic was found to form on the wall. The test of thermal insulation and fireproof confirmed that the ceramic coating layer has a very low thermal conductance and no heat bridge effect. The thermal conductivity was estimated to be 0.008 W/(m·K) on average, and the heat transmission coefficient of the coated concrete wall was determined to be 0.416 W/(m²·K) at the wall thickness of 280 mm. By carrying out the numerical simulation of the heat transfer equation, the time lag and decrement factor were evaluated to be 10.9 h and 0.009, respectively. Through the economic assessments, the composite ceramic coating was revealed to save the construction cost by half.

Key words: Thermal insulating material, Ceramic coating, Concrete wall, Heat flow, Mineral

1. Introduction
Recently, green buildings have been drawing a great deal of attention worldwide in mitigation of global warming and climate change, due to massive energy consumption and severe environmental impact of building industry [1,2,6,8,5]. In fact, it is known that the building industry, which consists of many phases such as raw materials mining, building materials production, building construction, operation and demolition, is responsible for ~40% of global energy use and ~50% of world greenhouse gas emission [6]. In this context, green buildings can be represented by sustainability and ecological benignity: minimizing construction energy, reducing operation and maintenance resources (energy, water and materials), releasing less waste and carbon dioxide, while offering improved indoor environment quality, to ensure safety and comfort for healthy working and living conditions for its residents [7,8,9].

Among such several aspects of green buildings, the top priority should go to the minimization of energy consumption. Provided that the energy demand of buildings in their life cycle includes mostly embodied (10−20%) and operational (80−90%) energies [10,11,12], the primary attention should be paid to a decrease in the operational energy, which is variable and controllable in contrast to the embodied energy fixed after construction. Then, the building operation requires energy for space conditioning (heating, cooling and ventilation) and lighting, of which amount depends on the climatic condition of the region and comfort request of the resident. As we hope to improve the thermal comfort of room with an energy supply as low as possible, good thermal insulation between indoor and outdoor environments, resulting in a decrease in the indoor temperature swing, is one of the key points of operational energy saving. In this respect, it is of great importance to design and develop buildings with effective thermal conserving and/or insulating walls, since the heat flow through walls take larger part in heating/cooling load of the room than those through other envelope elements such as roof and floor [13,14].

Since the discovery of portland cement in 1824 by Joseph Aspdin, most of building walls are made of cement concrete, which is an artificial composite material made by mixing cement, supplementary cementing materials, aggregates (sand and small stones), chemical admixtures and water, and contains steel reinforcing bars inside to increase its toughness. When compared to traditional or natural building materials such as timber, mud and straw, the concrete wall is known to increase the heat flow due to higher thermal conductivity and larger mass density of concrete and moreover heat bridges formed by the steel bars. To enhance the thermal performance of the concrete wall and promote the green building construction with concrete, there has been extensive research effort for improving the thermal insulation performance of concrete itself, by altering constituent materials and optimizing the size and distribution of pore-particle microstructure [15,16,17]. Meanwhile, the thermal performance of concrete wall can be significantly enhanced by attaching heat insulating boards with a thickness of several
centimeters outside and/or inside the wall, using expanded perlite, polystyrene foamed plastics, silicate cotton, and silica aerogel. These conventional heat insulating boards have common characteristics of low thermal conductivity under 0.1 W/(m·K) and a great number of pores, which is beneficial in prohibiting the heat transfer by a conductive way [18, 19]. However, these materials have disadvantages of high production cost, complicated construction procedure, low durability and environmental impact, resulting in a sharp rise of total construction cost.

Another significant way for enhancing the thermal insulation performance of the concrete wall is to paint the wall with cool materials and/or coatings [19, 20, 21, 22, 23, 24, 25, 26, 27], which can remarkably reduce the construction cost due to relatively low costs of raw materials and a simplicity of procedure. Although the thickness is less than millimeters, these coatings can effectively prevent the heat transfer from the outside to the inside room and vice versa. Coatings with a specially designed thermal reflectance and an infrared emittance are recognized to have a both-sided function: they are more solar reflective to decrease the exterior wall surface temperature during the cooling period in summertime, while more absorptive to take the solar heat during the heating period in wintertime [25, 28]. Such thermal insulating effect is from the reflection, separation and radiation of solar light wave, that is, coating absorb solar and infrared radiation and dissipate partly the accumulated heat through convective and radiative processes into the atmosphere [28].

The tested coating materials include cool materials, thermochromic materials [29, 30], and phase change materials [31, 32, 33]. In particular, inorganic mineral based coatings have been found to exhibit outstanding thermal insulation performance, together with other benefits of low cost and high stability against ultraviolet due to no organic stuff [34, 35, 36, 37]. In this respect, it is of great importance and urgency for viable green buildings to seek for innovative mineral based coating materials and to clarify the mechanism of thermal insulation performance based on experimental measurement of their material properties and numerical estimation of the heat flow feature (time lag and decrement factor) [38, 39, 40, 41].

In this work we aimed at developing a new kind of composite coating material with high thermal insulating and conserving performance, based on a variety of minerals originated exceptionally in DPR Korea. We described the preparation of the coating materials, their application procedure to the wall, and characterization of their material composition, thermal properties and ceramic feature on the concrete wall upon their coating. Based on the measured material parameters, the thermal performance of the ceramic coated wall was evaluated by numerically solving the one-dimensional heat transfer equation, determining a time lag and decrement factor of heat flux. We provided the most acceptable mechanism for the high thermal insulation of the wall with these thin ceramic coating.

2. Materials and methods

2.1. Materials

The composite material for coating was made of minerals and supplementary agents. The sixteen kinds of mineral based materials were used, including silicates, silica (quartz) sand, nickel-zinc ferrite, graphite, swelling clay, ultraanthracite ash etc. In particular, the use of GumGant adamelite that is special only from DPR Korea should be emphasized. These mineral reagents were pulverized to become ultrafine powders using a ball mill so that a continuous particle size distribution ranges from ~100 nm to 10 µm. It should be noted that a great number of pores with nano- and micro-meter sizes were included inside the reagents by the pulverization.

In addition, small amounts of supplementary agents were in use in this work; triethanolamine as a surface active agent, diethanolaminearyl ester sulphate or albumino-exudate, pulp waste liquor as an air entrained agent, hydroxyethyl cellulose (HEC) as a thickening agent, and tributyl ester phosphate or butanol as a defoaming agent.

The composite material was prepared by uniformly mixing the powders of mineral reagents and supplementary agents with the following mixing ratio; the metal oxides including SiO₂, Al₂O₃, Fe₂O₃, TiO₂, ZnO, etc.: 30~40 wt.% (weight), the GumGant adamelite: 15~20 wt.%, the surface active agent: 2~5 wt.%, the air entrained agent: 2~5 wt.%, the thickening agent: 1~2 wt.%, and the defoaming agent: 1~2 wt.%

2.2. Methods

2.2.1. Mixing and application

In order to apply the prepared composite material to the concrete wall, the potland cement (mark over 20 MPa) as a binder should be added into the composite material. Either a hand mixing stick or a machine mixer was used for the mixing work. Before the mixing with cement, it would be better to evenly stir the composite material in a container with the mixer. For the case of spraying or painting, water of 4~5 kg was poured into a container of cement of 2.5 kg while stirring for a while, and the composite material of 1 kg was added, followed by a careful stirring until arriving at homogenized color to become colloidal solution. For the case of putty making, the mixing ratio is different: composite 1 kg, cement 2 kg, water 1 kg.

![Figure 1: Execution ways of coating the composite material to the interior wall using the air-pump spray gun or brush.](image)

Before an execution of composite coating, the concrete wall should be covered well with cement mortar plaster of 20~25 mm thickness. After hardening the plaster surface, the colloidal solution should be broadly sprayed on the wall over two times using the air-pump spray gun within two hours after its preparation. If no spray gun, the solution should be painted over two times by using the brush with drawing a large circle and straining the surface, as depicted in Fig.1. The thickness of coating
layer should be 1~2 mm. It takes about two hours for the composite coating layer to sufficiently dry. To prevent a surface drying and accelerate the hardening after the execution, water should be sprinkled three times at an interval of two hours.

2.2.2. Characterization methods

The crystal structures of the mineral-based raw materials and the prepared composite coating material were determined from powder X-ray diffraction (XRD) measurements using a CuKα (1.54051 Å) radiation source from a Smartlab X-ray diffractometer (Rigaku, Japan), which involves a software to measure the precise 2θ positions and the full-width at half-maxima of the diffraction peaks. The analysis of elements and oxide components was performed using an energy dispersive X-ray (EDX) spectrometer (Model: ZSX Primus III+, Rigaku, Japan). To study the surface morphology of the coated surface, scanning electron microscopy (SEM) was analyzed using a machine of ZSM-6610A (JEOL, Japan), which integrates an energy dispersive spectrometer (EDS) for the elemental analysis or chemical characterization of the samples.

To estimate the fireproofness of the composite coating material, the interior wall was heated using a torch lamp while measuring temperatures of around points by using a forward-looking infrared (FLIR) thermometer (Model: FLIR I7; measurement range: −20 to 250 °C).

In order to measure the thermal conductivity of the composite coating material, we prepared a series of concrete block samples with fully coated surfaces of 2 mm thickness. The surface dimension of the concrete block sample is 400×400 mm, and the thicknesses are 58, 170, 240, 318, 370, 400 mm. The sample was placed on the heating plate, which was in the indoor environment at a constant temperature of 20±2 °C. While heating the plate by electricity until the temperature of the plate arrived at 100 °C, the temperatures of bottom and upper surfaces were measured by using a digital surface thermometer (Model: HL-200, Anritsu, Japan; measurement range: −200 ~ 1200 °C). When the temperatures of both surfaces became constant, the heat flow was measured through a heat flow meter equipped with a sensor (Model: HIT-MH2, Showa Denko K.K., Japan; measurement range: 0 ~ 400 W/m², operation temperature: −30 ~ 60 °C) settled on the upper surface. The experimental setup is shown in Fig. 2.

The thermal conductivity of material can be determined by measuring the heat flow and the temperature difference between the bottom and upper surfaces using the following equation,

$$q = \frac{\lambda}{\delta}(T_b - T_u)$$  \hspace{1cm} (1)

where $q$ is the heat flow through the wall, $\lambda$ is the thermal conductivity of the wall material, $\delta$ is the thickness of the wall, and $T_b$ and $T_u$ are the temperatures of the bottom and upper surfaces, respectively. For the case of multilayer wall consisted of coating layer and concrete layer, the total thermal resistance $R$ is estimated to be a sum of every layer thermal resistances,

$$R = R_i + R_c,$$ \hspace{1cm} (2)

$$R = \frac{\delta}{\lambda} = \frac{\Delta T}{q} = \frac{\delta}{\lambda_i} + \frac{\delta}{\lambda_c}$$ \hspace{1cm} (3)

where suffixes “i” and “c” stand for thermal insulating and for concrete, respectively, and $\Delta T = T_b - T_u$. The thickness of the whole layer should be $\delta = \delta_i + 2\delta_i$ in this work. Then, the thermal conductivity of the thermal insulating coating layer is obtained as follows,

$$\lambda_i = 2\delta_i \left[ \frac{\Delta T}{q} - \frac{\delta_i}{\lambda_c} \right]^{-1}$$ \hspace{1cm} (4)

2.2.3. Computational method for heat flux fluctuation

The fluctuation of outdoor temperature due to the solar-air temperature variation in a day can induce the indoor temperature fluctuation by the heat flux propagation through the wall. Provided that the heat transfer in the wall is assumed to be onedimensional, the governing equation for the temperature $T(x, t)$ as a function of distance ($x$) and time ($t$) is as follows [38, 39],

$$\rho C_p \frac{\partial T(x, t)}{\partial t} = \lambda \frac{\partial^2 T(x, t)}{\partial x^2}$$ \hspace{1cm} (5)

where $\rho$ and $C_p$ are the mass density and specific heat of the wall constituent material, respectively.

As the variation of distance is set to be from $x = 0$ for the exterior wall surface to $x = \delta$ for the interior wall surface, the following convection boundary conditions should be satisfied on both sides of the wall,

$$\lambda \left( \frac{\partial T(x, t)}{\partial x} \right)_{x=0} = h_e [T_{sa}(t) - T(x, t)_{x=0}]$$ \hspace{1cm} (6)

$$\lambda \left( \frac{\partial T(x, t)}{\partial x} \right)_{x=\delta} = h_i [T(x, t)_{x=\delta} - T_{in}]$$ \hspace{1cm} (7)

where $h_e$ and $h_i$ are the heat transfer coefficients on the exterior and interior surfaces of the wall, respectively. $T_{sa}$ is the indoor temperature, which is assumed to be a constant, leading to the normal convection boundary condition on the interior surface. $T_{sa}(t)$ is the so-called sol-air temperature, which is often assumed to be a sinusoidal function of time with a period of $P = 24$ h as follows [38, 39],

$$T_{sa}(t) = \frac{T_{max} - T_{min}}{2} \sin \left( \frac{2\pi t}{P} - \frac{\pi}{2} \right) + \frac{T_{max} - T_{min}}{2} + T_{min}$$ \hspace{1cm} (8)

Figure 2: Experimental setup to measure thermal conductivity of the composite coating layer using the coated concrete block.
Table 1: First and second major oxides and detected crystallites included in the sixteen kinds of raw materials, identified by EDX and XRD analysis.

| Raw material number | First Oxide wt.% | Second Oxide wt.% | Detected crystallites                      |
|---------------------|------------------|-------------------|--------------------------------------------|
| 1                   | SiO₂             | Al₂O₃             | Quartz                                     |
| 2                   | SiO₂             | Al₂O₃             | Quartz, Meixnerite, Hematite, K-mica        |
| 3                   | SiO₂             | Al₂O₃             | Quartz                                     |
| 4                   | SiO₂             | SO₃               | Silicate                                    |
| 5                   | SiO₂             | Al₂O₃             | Quartz, K-mica                              |
| 6                   | Fe₂O₃            | SO₃               | Quartz, Periclase, Zn-Ti oxide, K-Zn silicate|
| 7                   | SiO₂             | Al₂O₃             | Quartz, Mn sulfide                          |
| 8                   | Al₂O₃            | SO₃               | Zn silicate, Corundum                       |
| 9                   | SiO₂             | SO₃               | Quartz, Hendricksite, Dolomite, Calcite, Hematite, K-mica |
| 10                  | Fe₂O₃            | SiO₂              | Quartz, Meixnerite, Hematite                |
| 11                  | CuO              | SiO₂              | Quartz, Meixnerite, Hematite                |
| 12                  | NiO              | SiO₂              | Quartz, Meixnerite, Hematite                |
| 13                  | Fe₂O₃            | SiO₂              | Quartz, Meixnerite, Hematite                |
| 14                  | MgO              | SiO₂              | Muscovite, Quartz, Chlorartinitic           |
| 15                  | MgO              | SiO₂              | Muscovite, Quartz, Chlorartinitic           |
| 16                  | SiO₂             | MgO               | Muscovite, Quartz, Chlorartinitic, Dorfmanite, Lannonite |

where $T_{\text{max}}$ and $T_{\text{min}}$ are the maximum and minimum outdoor temperature, respectively. This describes that on the exterior wall surface the time-periodic boundary condition is presented since the heat flow includes the periodic solar radiation and the convection through the exterior wall surface.

The initial condition of the heat transfer equation (Eq. 5) is assumed to be a linear function of distance as follows [39],

$$T(x, t)_{t=0} = T_{\text{min}} + \frac{T_{\text{in}} - T_{\text{min}}}{\delta} \cdot x$$  \hspace{1cm} (9)

The thermal insulation performance of the wall and thus the thermal comfort of the room can be evaluated by the time lag ($\phi$) and the decrement factor ($f$), defined as follows,

$$\phi = t(T_{\text{max}}^i) - t(T_{\text{max}}^e)$$  \hspace{1cm} (10)
$$f = \frac{A_i}{A_e} = \frac{T_{\text{max}}^i - T_{\text{min}}^i}{T_{\text{max}}^e - T_{\text{min}}^e}$$  \hspace{1cm} (11)

where $t(T_{\text{max}}^i)$ and $t(T_{\text{max}}^e)$ are the time in hours when the interior and exterior wall surface temperature are at their maximums, respectively. In the second equation, $A_i$ and $A_e$ are the amplitudes of the heat waves on the interior and exterior wall surfaces, respectively. Since the time lag represents the time taken for propagating the heat flux through the wall and the decrement factor is the amplitude ratio between the indoor and the outdoor heat waves, more thermal comfort favors the longer time lag and the smaller decrement factor.

This equation can be numerically solved by finite difference method, using the central difference in space and the backward difference (fully implicit method) in time, as implemented in COMSOL Multiphysics version 4.2. We treated both the pure cement concrete wall and the concrete wall coated by the composite material on its both sides. The thickness of the cement concrete wall was set to be $\delta = 280$ mm and the thickness of coating layer is set to be 1 mm. The space grid size and the time step were set to be 0.1 mm and 20 s, respectively.

Figure 3: XRD patterns of typical reagent raw materials of (a) No. 1 and (b) No. 2.
3. Result and Discussion

3.1. Material characteristics

We performed the X-ray diffraction and energy dispersive X-ray analysis of all the sixteen kinds of raw mineral materials to identify the crystalline characteristics with the included elements and oxide components. Table 1 shows the first and second major oxides and crystal forms included in all the sixteen kinds of raw materials. Fig. 3 shows the XRD patterns of typical reagent raw materials of No. 1 and No. 2. In these raw materials, the major oxides were found to be SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CuO, NiO, MgO and SO$_3$, which exist in the crystal forms of quartz, meixnerite, hematite, silicate, mica, corundum, cuprite, hendricksite, dolomite, calcite, borate, muscovite, kalinite, chloraritinite, etc. In addition, graphite, sulfide and carbide, which do not contain oxygen element, were also identified.

To see oxide components in more detail, we show the EDX analysis results for the typical reagent raw materials of No. 1 and No. 2 in Table 2. For the sake of simplicity, the only oxide components included in the composite coating material powder, which do not contain oxygen element, were also identified. It should be noted that in the rest of raw materials these oxides were also observed but with different content. (See Supplementary data for XRD and EDX results for all the raw materials.)

![Figure 4: EDS spectrum of composite coating material obtained by drying colloidal solution.](image)

Figure 4: EDS spectrum of composite coating material obtained by drying colloidal solution.

![Figure 5: XRD pattern of the composite material coated to concrete wall.](image)

Figure 5: XRD pattern of the composite material coated to concrete wall.

| Oxide wt.% | Oxide wt.% | Oxide wt.% |
|------------|------------|------------|
| SiO$_2$    | 56.71      | SiO$_2$    | 57.52      | SiO$_2$    | 37.31      |
| Al$_2$O$_3$| 22.93      | Al$_2$O$_3$| 16.14      | CaO        | 35.10      |
| SO$_3$     | 8.54       | Fe$_2$O$_3$| 8.78       | Al$_2$O$_3$| 8.66       |
| Fe$_2$O$_3$| 6.89       | SO$_3$     | 7.91       | Fe$_2$O$_3$| 7.53       |
| K$_2$O     | 2.02       | CaO        | 3.55       | SO$_3$     | 5.19       |
| CaO        | 0.91       | K$_2$O     | 2.83       | K$_2$O     | 2.49       |
| MgO        | 0.77       | MgO        | 1.34       | MgO        | 2.22       |
| TiO$_2$    | 0.66       | V$_2$O$_5$ | 0.62       | TiO$_2$    | 0.77       |
| Na$_2$O    | 0.28       | TiO$_2$    | 0.38       | ZnO        | 0.36       |
| P$_2$O$_5$ | 0.10       | P$_2$O$_5$ | 0.24       | MnO        | 0.20       |
|            |            | Na$_2$O    | 0.17       | P$_2$O$_5$ | 0.13       |
| ZnO        | 0.11       |            |            |            |            |

We then performed the analysis of elements and oxide components included in the composite coating material powder, which was obtained by mixing all the sixteen raw materials with a certain ratio, the organic supplementary agents, cement, and water, and by drying the colloidal solution in air for 24 h. Fig. 4 shows the EDS spectrum of the composite coating material and Table 3 presents the corresponding elemental and oxide analysis. The major oxides were also found to be SiO$_2$ (57.21%), Al$_2$O$_3$ (20.49%) and Fe$_2$O$_3$ (8.94%). It can be readily accepted that when applying the colloidal solution including the composite material to the concrete wall, complex processes such as chemical reactions between the composite and concrete will occur. Therefore, we prepared a piece of the concrete wall sample coated with the composite coating material of ~ 2 mm thickness, which was sufficiently hardened during one year after application. Then, a small amount of applied composite coating material power was collected by carefully scratching the coated surface, and analyzed by XRD and EDX spectrometer. Fig. 5 shows the XRD pattern of the composite coating material and Table 3 lists the included oxides identified by EDX analysis. From the XRD pattern, it turned out that the applied composite coating material contains several kinds of crystallites such as calcite, quartz, muscovite and dolomite, which may originate from the raw materials or may be newly formed by the chemical reactions. In Table 3, the calcium oxide (CaO) is found to be major oxide (35.1%) unlike in the dried composite material as well as the raw mineral materials, which can be thought to originate from the cement or cement concrete without doubt. It should be noted that other oxides such as TiO$_2$, ZnO and MnO were also found.

3.2. Surface morphology and ceramic formation

The morphologies of concrete wall surface coated with the developed composite coating material were studied to get an insightful understanding of the material processes, which can be
Table 3: EDS analysis result of composite coating material powder obtained by drying colloidal solution.

| Element | Energy (keV) | Mass% | Sigma | Mol% | Oxide Mass% | Cation |
|---------|--------------|-------|-------|------|-------------|--------|
| O       | 0.525        | 47.48 |       |      |             |        |
| Si      | 1.739        | 26.74 | 0.31  | 67.66| SiO₂        | 48.216 |
| Al      | 1.486        | 10.85 | 0.16  | 20.49| Al₂O₃       | 18.6957|
| Fe Kor | 6.398        | 6.25  | 0.12  | 8.94 | Fe₂O₃       | 13.9959|
| K       | 3.312        | 3.01  | 0.07  | 2.73 | K₂O         | 6.7228 |
| Ca      | 3.690        | 2.12  | 0.07  | 3.76 | CaO         | 5.3793 |
| S       | 2.307        | 1.30  | 0.09  | 2.89 | SO₃         | 2.6856 |
| Mg      | 1.253        | 0.91  | 0.07  | 2.67 | MgO         | 1.3114 |
| Na      | 1.041        | 0.71  | 0.06  | 1.10 | Na₂O        | 1.1442 |
| Ti      | 4.508        | 0.62  | 0.06  | 0.92 | TiO₂        | 1.3488 |
| Total   | 100.00       | 100.00|       |      |             |        |

Figure 6: Photographs of appearances for ceramic coating formed on the concrete wall, taken after peeling the organic outdoor paint off. To see the inside morphology, a hole with a radius of ~15 mm and a depth of ~5 mm was dug by chiseling with a hammer.

The formation of ceramic on the concrete wall during the hardening period of the composite coating material was also evidenced in the interior wall, as shown in Fig. 7. A small house was built to test the thermal insulation performance of the composite coating layer. The interior wall was not painted or covered, and also the sufficient time for hardening the composite coating layer was provided. The surface seems to be smooth with a brown color, and moreover contains a good developed network of fine cracks. It looks like a Korean traditional ceramic named “Koryo celadon”.

As shown in Fig. 5 and Tables 2 and 3, the similar oxides (SiO₂, Al₂O₃, Fe₂O₃, etc.) and crystallites (quartz, muscovite, calcite, dolomite) with the traditional ceramic were identified. However, it is not clear whether these ceramic crystallites were created by chemical reaction or simply came from the raw materials, which also include similar oxides and crystallites. Nevertheless, it should be emphasized that the ceramic formation on the concrete wall occurred in the atmospheric condition (room temperature and no pressing) in contrast to the traditional ceramic production requiring high temperature of over 1000 °C in a specially designed room. Recent advances in ceramics demonstrate that using the nanostructured materials and innovative techniques such as sol-gel method high strength porous ceramic can be synthesized at such low temperature [42]. In recent years, there have been reported several research work for ceramic thermal insulation coating [24, 37]. In this work, the important point is that the hardening time should be long enough (at least three months) to mimic natural process of ceramic formation from the nanostructured composite materials. Therefore, it can be regarded that the ceramic formation would be a result of gradual chemical reaction between the composite material and the cement concrete with a presence of water.

Fig. 8 shows the SEM micrograph of the coating surface of
the interior wall. The even distribution of micro or nanometer sized grains were observed, confirming the polycrystalline characteristics of ceramic. Table 4 presents the result of EDS analysis of the grain corresponding to the (001) point indicated in Fig. 8. It is quite different from the above EDX analysis to find large amount of carbon element, which might be come from dolomite and/or calcite.

3.3. Fireproofness and thermal conductivity

To estimate the thermal insulation performance of the composite coating ceramic, we measured its fireproofness and thermal conductance. The small houses, one of which was coated with the composite coating ceramic and another was insulated using the polystyrene foamed plastics, were built and used for testing, as already shown in Fig. 7. The interior walls were heated using the torch lamp while measuring the temperatures of center and around points by using the FLIR thermometer. Fig. 9 shows the measuring process and the corresponding FLIR images. The temperatures at the points apart from the heating center with the same distance were measured to be $\sim$38 °C for the case of composite coating ceramic wall and to be $\sim$73 °C for the case of polystyrene foamed plastics wall, indicating the better fireproofness and much lower thermal conduc-

tance of the composite coating ceramic wall compared to the polystyrene attached wall.

![Figure 8: SEM image of concrete wall coated with the composite ceramic.](image1)

Table 4: EDS analysis result of grain corresponding to the (001) point indicated in Fig. 8.

| Element | Energy (keV) | Mass% | Sigma | Mol% |
|---------|-------------|-------|-------|------|
| C K     | 0.277       | 35.11 | 0.20  | 49.02|
| O K     | 0.525       | 33.06 | 0.29  | 34.66|
| Si K    | 1.739       | 12.68 | 0.10  | 7.57 |
| Ca K    | 3.690       | 10.58 | 0.09  | 4.43 |
| Al K    | 1.486       | 3.28  | 0.05  | 2.04 |
| Fe K    | 6.398       | 6.91  | 0.07  | 0.69 |
| K K     | 3.312       | 1.39  | 0.04  | 0.60 |
| Mg K    | 1.253       | 0.76  | 0.03  | 0.52 |
| Na K    | 1.041       | 0.36  | 0.03  | 0.26 |
| S K     | 2.307       | 0.26  | 0.02  | 0.14 |
| Ti K    | 4.508       | 0.19  | 0.03  | 0.07 |
| Cl K    | 2.621       | 0.05  | 0.02  | 0.02 |
| Total   | 100.00      | 100.00|       |      |

Next, we measured the heat bridge effect in the same testing houses. Fig. 10 shows the FLIR images at the corner point of the wall, which includes the heat bridge, and at the point 300 mm away from the corner. The measure was performed on the interior wall surface of the testing houses. The temperature difference between the heat bridge point and the inside point was found to be negligible for the case of the composite coating ceramic wall (0.6 °C) while to be distinctive for the case of polystyrene foamed plastics insulated wall (1.4 °C). This indicates that the composite coating ceramic can effectively prevent the heat transfer through the heat bridge, while the polystyrene plastics are not effective for preventing the heat bridge effect.

![Figure 9: Photographs for heating the interior wall using the torch lamp and FLIR images for temperatures at the center and around points in (a) composite ceramic coating wall and (b) polystyrene foamed plastics insulated wall.](image2)

![Figure 10: FLIR images for temperatures at the corner point (left panel) and the point 300 mm away from the corner (right panel) in (a) composite ceramic coating wall and (b) polystyrene foamed plastics insulated wall.](image3)

From the above experimental measurement, the thermal conductivity of the composite coating ceramic can be expected to be quite low. In order to check the reliability of the equipment
to measure the thermal conductivity, we first checked whether the known thermal conductivity of the standard sample (white slag) could be reproduced. Then, the thermal conductivity of pure cement concrete was also measured for checking the reliability and for using in estimation of the thermal conductivity of the composite ceramic coating layer by Eq. 4. As increasing the thickness of concrete block coated with the composite ceramic, the heat flow was measured to estimate the effective thermal conductivities of the whole block and the composite ceramic coating material.

Table 5 shows the result of the measurement. For the standard testing sample (white slag) with a dimension of (120 × 200 × 45) mm, the thermal conductivity was determined to be 0.102 W/(m-K), which is in good agreement with the known value of 0.120 W/(m-K), indicating the reliability of the measurement in this work. The thermal conductivity of concrete block itself with a dimension of (400×400×55) mm and a mass density of 1780 kg/m³ was determined to be 1.12 W/(m-K), which is within the accepted range of 0.9 ~ 1.3 W/(m-K) for the general concrete block (ρ = 1700 ~ 2300 kg/m³). The effective thermal conductivity of the whole coated concrete block, where the thickness of coating layer was δ_e = 2 mm, was found to gradually decrease from 0.376 to 0.097 W/(m-K) as increasing the thickness, producing the average value of 0.169 W/(m-K) comparable to the value of the white slag. Accordingly, the value of the composite ceramic material was determined to be ~0.008 W/(m-K) on an average, which is remarkably low compared with the conventional material for thermal insulation.

Based on the effective thermal conductivities, we determined the heat transmission coefficient of the concrete wall coated with the composite ceramic K, defined as a reverse of thermal resistance as follows,

\[
\frac{1}{K} = R = \frac{1}{h_e} + \frac{\delta}{\lambda} + \frac{1}{h_i}\]  

where the surface heat transfer coefficients were set to be \( h_e = 23.2\) W/(m²-K) for the exterior wall and \( h_i = 8.7\) W/(m²-K) for the interior wall, respectively. Fig. 11 shows the heat transmission coefficient of the concrete wall coated with the composite ceramic layer as a power function of wall thickness to be \( K(\delta) = 690.6 \cdot \delta^{-1.3159} \) (W/(m²-K)), which gives the optimal value of \( K = 0.416\) W/(m²-K) for the case of thickness \( \delta = 280\) mm.

3.4. Time lag and decrement factor

Using the thermophysical properties of concrete wall and coating materials, we determined the thermal insulation performance of the walls by conducting the simulations described in subsection 2.2.2. The temperature parameters were set to be \( T_{\text{max}} = 29 ^\circ\text{C} \) and \( T_{\text{min}} = 21 ^\circ\text{C} \) in the sol-air temperature function (Eq. 8) according to the climate condition in the city of Pyongyang (DPR Korea) in the summer season (August), and \( T_{\text{in}} = 25 ^\circ\text{C} \) as the comfort indoor temperature in summer. The time lag (\( \phi \)) and decrement factor (\( f \)), as defined by Eqs. 10 and 11 were determined from the simulated temperature wave for the concrete wall and the concrete wall coated with the composite ceramic material. The thicknesses of the concrete wall and the composite ceramic coating layer were set to be \( \delta = 280\) mm and \( \delta_e = 1\) mm. For the case of coated concrete wall, the both exterior and interior wall were coated, and thus the thickness of the wall should be 282 mm. The determined material parameters were used: \( \rho = 1780\) kg/m³, \( C_p = 840\) J/(kg-K), \( \lambda = 1.12\) W/(m-K) for the cement concrete material, and \( \rho = 860\) kg/m³, \( C_p = 750\) J/(kg-K), \( \lambda = 0.008\) W/(m-K) for the composite ceramic coating material.

Fig. 12 shows the time variation of the temperatures in 48 hours, i.e. the temperature vibrations, at the different points of the wall: exterior, center, interior for the uncoated wall, while in addition coating layer points for the coated wall. For the case of the uncoated concrete wall, the time lag and decrement factor were determined to be \( \phi \approx 7.5\) h and \( f \approx 0.083\),
Figure 12: The temporal variation of temperatures in (a) concrete wall and (c) concrete wall coated with the composite ceramic. (b) Enlargement for interior wall temperature variation. Ext. and int. mean exterior and interior.

which are acceptable when compared with the previous calculations [38, 39]. It turned out that the thermal insulation performance of the concrete wall could be remarkably improved upon coating both exterior and interior walls with the composite ceramic on the condition that the used thermophysical parameters of the composite coating material are trustworthy. The time lag became longer to be $\phi \approx 10.9$ h, whereas the decrement factor became smaller to be $f \approx 0.009$.

Fig. 13 shows the spatial variation of the temperatures in the walls every four hours during a day. It is found that the temperature variation can be largely reduced by passing the coating layer. As shown in the insets of Fig. 13(b), the outdoor temperature variation could be reduced remarkably by the exterior wall coating layer of only 1 mm thickness, leading to much smoother variation through the inside wall compared with the uncoated wall. Moreover, after passing through the interior wall coating layer, the temperature could get close to the indoor temperature of 25 °C, as expected by very small decrement factor of 0.009. Therefore, it could be said that coating on both sides of wall is more beneficial than only one side coating.

Finally, we discuss a possible mechanism of such excellent thermal insulation performance of the concrete wall coated with the composite ceramic composed of various minerals. It is directly related with the formation of the dense ceramic layer due to the chemical reaction of composite coating material with the cement in the presence of water, which is thought to be a kind of natural process. This ceramic layer makes it possible to form a fully closed system consisted of the coating and the concrete layers, which contains lots of nano- and micro-size pores in its inside, leading to the low thermal conductance of the wall. It should be noted that reflection, absorption and radiation of solar light especially in the infrared region by the composite material are also a considerable factor of good thermal insulation. Therefore, we have a further research plan to precisely measure the reflectivity, absorptivity and emissivity of this composite ceramic material.

3.5. Environmental and economic assessments

The use of composite coating material was seen as environmentally benign for the following reasons; first, it is composed of various minerals, second, it is not an organic but purely inorganic material, third, it does not contain any toxic element, and fourth, it could not be easily decomposed under the external action such as moisture, solar light including ultraviolet rays, and temperature variation. In addition to the thermal insulation, we observed other distinct effects such as waterproof, soundproof and antibiosis, which enhance the significance of using the composite coating material in the context of green building. In particular, when the interior wall was coated with this composite ceramic, the room exhibited the antibacterial ef-
fects: for example, vegetables inside it can be reserved as fresh for several days in summer. This antibiosis effect can be expected due to the inclusion of nanosized TiO₂, CuO and ZnO, especially the GumGant adamelite that has a novel function of curing patient. However, such effects should also be measured quantitatively in the close future.

The replacement of the conventional thermal insulation material like polystyrene foam plastics by the composite coating brings a great profit in economic aspect; it makes it possible to remove several kinds of complex construction procedures, leading to not only economy in building materials, expenditures, and labor but also reduction of building construction period. For a construction of 1000 m² wall surface using the conventional foamed plastic plate, the following materials could be required; foamed plastic plate of 1010 m², cement of 19800 kg, sand of 109400 kg, calcium carbonate of 1500 kg, talcum powder of 892 kg, acryl outdoor paint of 400 kg, acryl indoor paint of 576 kg, acrylmetacryl plastic waterproof of 1300 kg, polyvinyl alcohol of 146 kg, mortar waterproof liquid of 250 kg, (9×9) mm iron metal lath of 1050 m², tholes of 7000, abrasive paper sheets of 100, and nonwoven scrim of 1024 m². When using the composite coating material, however, only the coating material of 1170 kg, cement of 7940 kg, acryl outdoor paint of 200 kg and acryl indoor paint of 288 kg were required. Then, the cost of building materials can be reduced by half.

4. Conclusions

The composite coating material for the concrete exterior and interior walls was prepared by pulverizing the sixteen kinds of minerals and mixing them in the designed ratio with a small amount of organic supplementary agents. Some of these minerals were only from DPR Korea, and contain a variety of crystallites including quartz, mica, muscovite, dolomite, calcite, etc. In order to apply to the wall, the composite coating material was mixed with the cement by using water, resulting in the colloidal solution. By spraying or brushing, the colloidal solution was coated to the surface of the wall, and it took over three months for the coating layer to harden.

It was found through the XRD and EDX analysis that the composite material coated on the wall surface contains several kinds of crystallites such as calcite, muscovite, quartz and dolomite. The investigation of surface morphology indicates the formation of ceramic on both the exterior and interior sides of wall, which can be a result by the chemical reaction between the composite material and the cement during the hardening period. The SEM micrograph of the interior wall coated surface revealed the even distribution of micro- and nano-sized grains, indicating the ceramic characteristics of polycrystalline solid.

The test of thermal insulation performance was performed using the built small houses, indicating a good fireproofness of the composite ceramic layer and none of heat bridge effect. Using a series of the concrete block, the effective thermal conductivity of the coated concrete wall was measured to be 0.169 W/(m·K), which is comparable to the value of the white slag (0.120 W/(m·K)). From these values, the thermal conductivity of the composite coating material was determined to be quite low as 0.008 W/(m·K) on average, and the heat transmission coefficient of the concrete wall as a power function of wall thickness was determined to be \( K(\delta) = 690.6 \cdot \delta^{-1.315} \) (W/(m²·K)). The numerical solution of the one-dimensional heat transfer equation yielded the time lag and decrement factor as 10.9 h and 0.009 for the coated concrete wall, indicating an enhancement of the thermal insulation performance when compared with those for the uncoated concrete wall (7.5 h and 0.083). By the economic assessments, the construction cost was revealed to be saved by half when replacing the conventional polystyrene plate by the composite coating layer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at URL.

Notes

Declarations of interest: none.

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