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Study on the Growth of Monoclinic VO_2 Phase Applicable for Thermochromic Ceramic Tile

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ABSTRACT

Vanadium dioxide (VO_2) of monoclinic phase exhibits Metal Insulator Phase Transition (MIPT) phenomenon involving a sharp change in electrical and optical properties at 68°C. Solution-based process is applied to form uniform VO_2 coating layer on ceramic tiles. This can selectively block the near-infrared light to possibly reduce the energy loss and prevent dew condensation caused by the temperature difference. Heat treatment conditions including temperature and dwell time were examined to obtain a monoclinic VO_2 single phase. Both rutile and monoclinic VO_2 phases were observed from in the tiles post-annealed below 700°C. Desired monoclinic VO_2 single phase was grown in the tiles heat treated at 750°C. Nano facets of irregular size were observed in the monoclinic VO_2 phase involving the phase-transition. Grain growth of monoclinic VO_2 phase was observed as a function of dwell time at 750°C.

Key words : Thermochromic, Vanadium oxide, MIPT, Infrared block, Ceramic tile

1. Introduction

Thermochromic refers to the reversible color change in a substance realized at a particular temperature when heated or cooled. Currently, Thermochromic materials are commercially used in several areas such as temperature recording medium, optical sensor, laser display, etc., and many studies are being conducted as organic and inorganic compounds, polymers, and a smart window based on sol-gel. To use the Thermochromic materials for purpose of infrared block rays in actual life, optical characteristics are required where transmittance of infrared rays is sharply lowered near ambient temperature. Substances exhibiting the behavior where Thermochromic characteristics are drastically changed as a phase transition phenomenon at the threshold temperature include VO_2, Ti_2O_3, Fe_2O_3, NiO_3, NbO_2, etc.

While vanadium exists as oxides in a stable form such as VO, VO_2, V_2O_3, V_3O_5, V_2O_5 depending on oxygen contents,[1-4] and changes in Thermochromic characteristics may be ascertained through a change in electrical conductivity of vanadium oxides, substances showing the largest change around the phase transition temperature among vanadium oxides are VO and V_2O_3 having a difference in electrical conductivity in the order of 10^5 and VO_2 in the order of 10^3.[5] However, since VO and V_2O_3 have very lower phase transition temperatures compared with ambient temperature, it is not easy to control the phase transition temperatures to be close to ambient temperature. Since VO_2 has a phase transition temperature of 68°C which is closest to the ambient temperature as compared with other substances having Thermochromic characteristics, temperature control toward the ambient temperature is easy and may be considered as the most suitable substance for temperature-sensitive variable type of infrared block among substances having suitable Thermochromic characteristics.[6-9)]

VO_2 exists in a total of 7 types of polymorphism including Monoclinic(VO_2(M)), Tetragonal Rutile(VO_2(B)), Orthorhombic(VO_2(O)), Triclinic as well as 3 unstable phases of VO_2(A), VO_2(B) and VO_2(C).[10-13] While VO_2 exists as VO_2(M) phase below 68°C, and as VO_2(R) above 68°C, since distances between twisted vanadium atoms in the VO_2(M) phase become equal to each other.[14-16] Since the VO_2(M) phase below 68°C has a high electrical resistance value exhibiting the characteristics of an insulator, it is referred to as an insulator phase and transmits visible light and infrared rays. On th other hand, since electrical conductivities are exponentially increased in the VO_2(R) phase as compared with the VO_2(M) phase so as to have very low electrical resistance values and exhibit characteristics of a metal, it is called a metal phase and shows characteristics of transmitting visible light while blocking infrared ray.[11-13] Such reversible phase transition phenomenon at 68°C[17] is called Metal-Insulator Phase Transition (MIPT) (Fig. 1), showing a drastic change in specific resistance in the phase transition section.[18] At the MIPT temperature, the two phases exhibit a difference of about 60% in transmittance, indicating that they have optical characteristics capable of executing functions as a practical Thermochromic sub-

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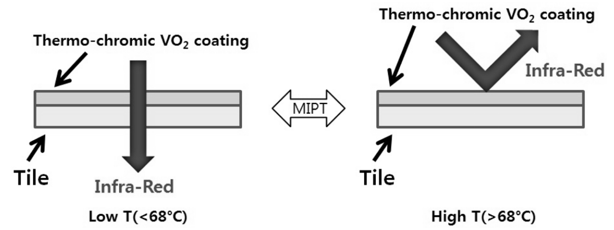

Fig. 1. Thermochromic properties according to MIPT.

stance for blocking infrared ray.[19)]

In the present study, experiments involving application of VO_2 having Thermochromic characteristics to exterior finishing tiles were implemented with the purpose of saving energy for buildings. To obtain reversible colors and switching efficiencies of ultraviolet protection provided by the change in optical characteristics, Monoclinic VO_2 single phase should be formed first, and the reversible phase transition should be made to occur at the threshold temperature. For this purpose, VO_2 coating layer was formed on tiles for buildings with glazing of a glaze material to establish optimum heat treatment conditions for formation of the Monoclinic VO_2 single phase.

2. Experimental Procedure

To prepare the glaze for white porcelain tiles to be used as a Substrate, powders with mixing in the weight ratio of feldspar 56.12%, quartzite 13.44%, limestone 19.6%, kaolin 10.84% and distilled water were mixed in the weight ratio of 1 : 1 to be ball-milled for 24 h for mixing. Glazing of the mixed glaze onto the biscuit firing white porcelain tiles was followed by sintering held at 1250°C for 1 h in an oxidizing atmosphere. Surfaces of the sintered tiles were cleansed by ethanol.

To prepare the solution for Spin-coating, Vanadium oxyacetylacetone($VO(acac)_2$, 98.0%, SIGMA Aldrich) was used as a VO_2 precursor material. $VO(acac)_2$ and methanol(DAEJUNG) were mixed at a concentration of 0.125mol/L for 1 h at ambient temperature using the ultrasonic wave. After dropping 0.1 mL of the prepared solution onto the white porcelain tiles (1×1 cm^2) and Spin-coating at 1500 RPM, it was completely dried a 70°C for 30 minutes. The dried tiles were annealed at 550°C for 30 minutes following temperature rise at a rate of 10°C per minute in a nitrogen atmosphere for calcination and crystallization of organic compositions, and then subjected to Post annealing between 600°C ~ 750°C in an oxidizing atmosphere for growth and stabilization. To analyze crystallographic changes of VO_2 phase as a function of temperatures, it was post annealed between 600°C ~ 750°C, and was subsequently heat treated for 2 ~ 8 at annealing temperatures for growth of VO_2(M) single phase to affirm the phase changes as a function of dwell times.

Crystalline phases were analyzed using XRD(X-ray diffraction, D-max-2500, Rigaku, Japan), with measurements made at 40 kV, 100mA up to 20 ~ 70° at a rising rate of 10°/min. The VO_2 crystal shapes grown as a function of diversified heat treatment conditions were observed using a Scanning Electron Microscope(JSM-6701F, JEOL, Japan).

3. Results and Discussion

3.1. Formation of VO_2 crystalline phases as a function of heat treatment temperatures.

To analyze the crystalline phases appearing due to a glaze layer, crystalline phases were analyzed after heat treating the tiles having no coating of VO_2 solution under the same conditions as those for growing VO_2(M). Fig. 2 is an XRD pattern of the tile. According to the figure, there were no peaks showing a crystalline phase other than the broad diffraction peak corresponding to an amorphous phase. This shows that the crystalline phases appearing in the heat treated tiles after coating of VO_2 solution are unrelated to the glaze layer.

To analyze crystallographic changes of the VO_2 coating layer as a function of het treatment temperatures, the XRD results measured after heat treatment in the range of 600-750°C at an interval of 50°C are arranged in Fig. 3. In the tiles post annealed at 600°C, 650°C, 700°C, respectively, for 4 h in an oxidizing atmosphere after heat treatment at 550°C for 30 minutes in a nitrogen atmosphere, Monoclinic crystalline phase of VO_2(M) and the metastable phase of VO_2(B) crystalline phase without causing MIPT at 25.12° (110) were present in a mixture at diffraction angles of 27.83°(011), 37°(211).(Fig. 3(a) - (c)) In the tiles post annealed at 750°C, diffraction peaks corresponding to the stable single-phase Monoclinic VO_2 finally appeared.(Fig. 3(d))

The starting substance of $VO(acac)_2$ had pyrolysis and crystallization of organic components realized in the First annealing process in a nitrogen atmosphere, and the crystallized phase realized growth and stabilization of the phase

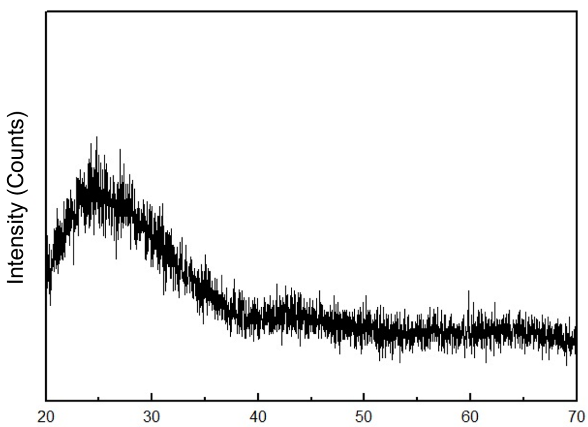

Fig. 2. X-ray diffraction pattern of a ceramic tile without VO_2 coating; heat treated at 550°C for 30 min in N_2 and then at 750°C for 4 h in ambient atmosphere.

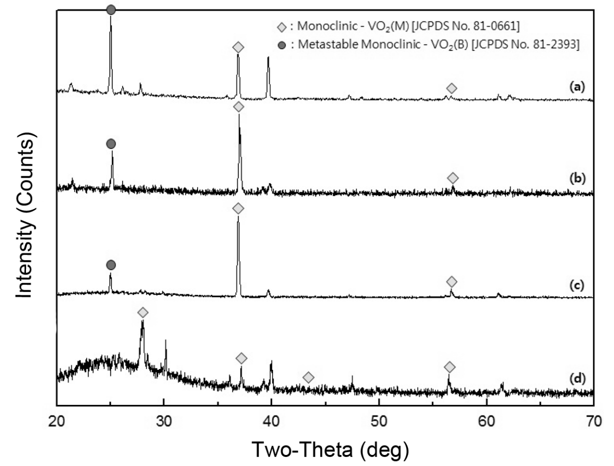

Fig. 3. X-ray diffraction pattern of ceramic tiles with VO_2 coating; heat treated at 550°C for 30min in N_2 and then at (a) 600°C, (b) 650°C, (c) 700°C and (d) 750°C respectively for 4 h in ambient atmosphere.

during post annealing process in an oxidizing atmosphere. To grow the desired single VO_2(M) phase, precise control of heat treatment conditions was required to allow transformation to V_2O_5 which was the most stable form of vanadium oxide. Growth of the Monoclinic single phase was affirmed to depend on dwell times in the First annealing process and heat treatment temperatures in the post annealing process. Through growth of the metastable VO_2(B) phase, the corresponding heat treatment temperatures were affirmed not to be suitable temperatures, and 750°C forming the VO_2(M) single phase was affirmed to be the most suitable heat treatment temperature.

Surface microstructures of tiles heat treated at different temperatures were observed with a scanning electron microscope and are shown in Fig. 4. On surfaces of the tile post annealed at 600°C (Fig. 4(a)), Nano needles shape reported as a metastable VO_2(B) phase have been observed.[20-25] $VO(acac)_2$ employed as a precursor consisted of bundles having the shape of a rectangular parallelepiped. When mixed with a methanol solution using ultrasonic wave, it was dissolved and dispersed by methanol which had infiltrated between $VO(avac)_2$ bundles. The dispersed $VO(acac)_2$ crystals are known to form a Nano needles phase by growing longitudinally through heat treatment.[20]

In the tile post annealed at 700°C (Fig. 4(c)), grain growth of Nano needles phases could be observed, and Nano facets with a irregular and continuous spherical shape due to the grain growth resulting from increased heat treatment temperatures could be affirmed in the tile post annealed at 750°C where VO_2(M) single phase was grown (Fig. 4(d)).

Vanadium dioxide grown on the tiles was affirmed to have polymorphism as a function of heat treatment temperatures and the corresponding inherent shapes. Thus, heat treatment temperatures were affirmed to be an important factor for type, size of crystalline phases as well as shape control.

3.2. Changes in crystalline phases and microstructures a function of dwell times.

To analyze crystallographic changes as a function of dwell times, XRD measurement results for VO_2 tiles post annealed at 750°C with formation of VO_2(M) phase for 2 ~ 8 h are shown in Fig. 5. Under all heat treatment conditions irrespective of dwell times, clear diffraction peaks corresponding to the Monoclinic VO_2(M) crystalline phase were affirmed at diffraction angles of 27.83°(011), 37°(211), 42.11°(212). Also, as the heat treatment temperatures were increased, gradual extinction of SiO_2 phase near 30° could be affirmed, excluding the stable VO_2(M) crystalline phase. Formation of the stable VO_2(B) crystalline phase and changes in the diffraction pattern as a function of dwell times could not be affirmed. Hence, the control of dwell times were affirmed not to have any effects in maintaining the VO_2(M) single

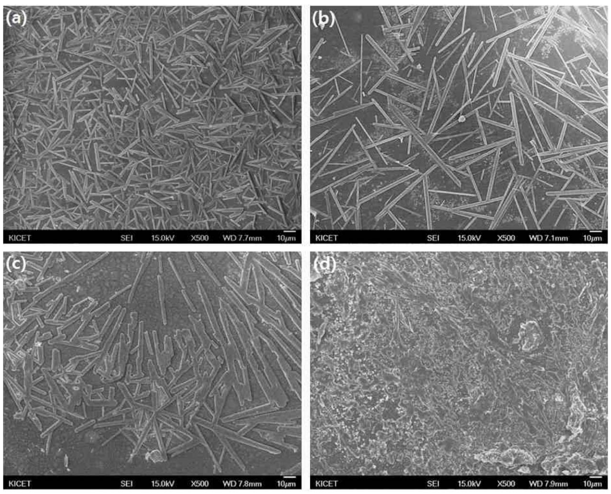

Fig. 4. Micrographs of VO_2 coated ceramic tiles; heat treated at 550°C for 30min in N_2 and then at (a) 600°C, (b) 650°C, (c) 700°C and (d) 750°C respectively for 4 h in ambient atmosphere.

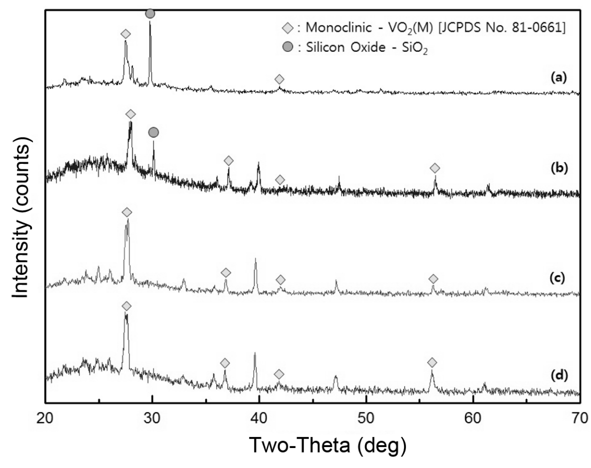

Fig. 5. X-ray diffraction patterns of VO_2 coated ceramic tiles; heat treated at 550°C for 30 min in N_2 and then 750°C for (a) 2 h, (b) 4 h, (c) 6h and (d) 8h respectively in ambient atmosphere.

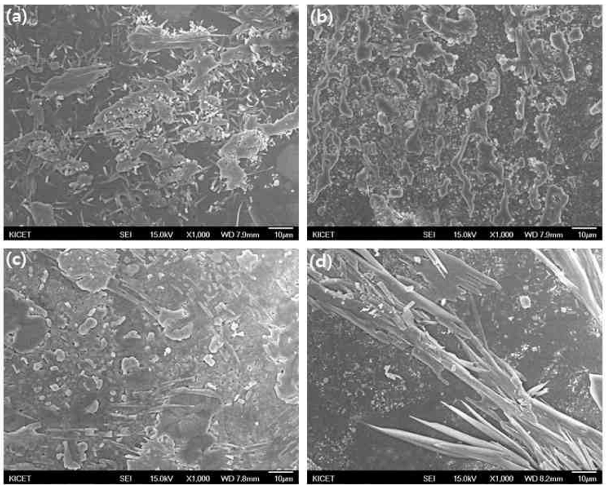

Fig. 6. Micrographs of VO_2 coated ceramic tiles; heat treated at 550°C for 30 min in N_2 and then 750°C for (a) 2 h (b) 4 h (c) 6 h and (d) 8 h respectively in ambient atmosphere.

phase other than improving crystallinity of the phase.

Scanning electron microscope observation results for the VO_2(M) tiles post annealed for different dwell times are shown in Fig. 6. According to the given figure, Nano needles of the locally remaining metastable VO_2(B) phase could be observed in the tile post annealed for 2 h (Fig. 6(a)). Simultaneously with complete extinction of Nano needles in the tile post annealed for 4 h (Fig. 6(b)), the shape of Nano facets corresponding to the VO_2(M) phase was observed, while Grain growth of the phase could be affirmed due to an improved crystallinity as a function of dwell times in the tiles post annealed for more than 6 h. (Fig. 6(c), (d)) Thus, the fact was affirmed that appropriate dwell times acted as a factor for extinction of the metastable phase, size of the phase and shape control.

4. Conclusions

In the present study, after a solution was prepared by mixing Vanadium oxyacetylacetone as a precursor and methanol, it was spin coated onto glassy white porcelain tiles. The coated tiles were then heat treated in a diversified temperature range and time band to establish optimum heat treatment conditions to obtain the VO_2(M) single phase as a substance required to cause MIPT at ambient temperature.

According to the results of heat treatment for 4 h by changing temperatures between 600°C-750°C in an oxidizing atmosphere after heat treatment at 550°C for 30 minutes in a nitrogen atmosphere, an optimum heat treatment condition was obtained in the tile heat treated at 750°C where the metastable phase of VO_2(B) crystalline phase was completely extinct and the single phase of VO_2(M) was grown.

Through surface observations using a scanning electron microscope, the shape of Nano needles corresponding to the metastable VO_2(B) was observed from the tiles post annealed at 600°C, 650°C, 700°C, while the Nano facets of VO_2(M) phase were observed at 750°C.

Changes in dwell times at 750°C did not cause formation of the metastable VO_2(B) crystalline phase nor changes in diffraction patterns. According to the results of observing morphology of the tiles after changing the dwell times between 2 ~ 8 h, grain growth in Nano facets shape could be observed with an increase in the times. Consequently, heat treatment conditions were affirmed to act as an important mechanism for the control of type, shape and size of the crystalline phase.

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