# Supersonically sprayed thermal barrier layers using clay micro-particles

Do-Yeon Kim<sup>†,1</sup>, Jong-Gun Lee<sup>†,1</sup>, Bhavana Joshi<sup>1</sup>, Jong-Hyuk Lee<sup>1</sup>, Salem S. Al-Deyab<sup>2</sup>, Ho Gyu Yoon<sup>3</sup>, Dae Ryook Yang<sup>4</sup>, Alexander Yarin<sup>1,5</sup>, Sam S. Yoon<sup>1\*</sup>

 <sup>1</sup>School of Mechanical Eng., Korea University, Seoul 136-713, Korea
<sup>2</sup>Petrochem. Research Chair, Department of Chemical, King Saud Univ., Riyadh 11451, Saudi Arabia.
<sup>3</sup>School of Materials Science & Eng., Korea University, Seoul 136-713, Korea
<sup>4</sup>Department of Chemical & Biological Eng., Korea University, Seoul 136-713, Korea
<sup>5</sup> Department of Mechanical & Industrial Eng., University of Illinois at Chicago, 842 W. Taylor St., Chicago 60607, USA

# Abstract

Several clays were supersonically sprayed onto flexible substrates to form highly thermally and electrically insulating materials which could be wrapped onto protected surfaces. Of these clays, montmorillonite revealed the best thermal insulating properties.

Keywords: Thermal barrier coating, Supersonic spray, Clay, Thermal insulation

Corresponding author: ayarin@uic.edu, skyoon@korea.ac.kr

#### Introduction

Thermal barrier coatings (TBC) are widely used in gas turbines and power generators to increase their efficiency by thermally insulating metal components in the hot section (Evans et al., 2001). These coatings are advantageous because of their ability to endure at high thermal gradients. Lowering temperature of metal substrate prolongs the life of the component by protecting it against environmental attack, creep fracture, or fatigue. For turbines and high-temperature engine parts, only Ni-based super alloys can be used, and the temperature of hot gas in engines exceeded the melting point of these alloys (Schulz et al., 2003). Demand for TBC materials with better thermal insulation is growing. TBC are also used to insulate electric cables with metals cores such as copper shield with plastic jackets made of various polymers for electrical insulation. These jackets may melt because of heat or fire. Thus, a TBC is needed between the core and the plastic jacket, and also for the outer encapsulation, as reported by Woodland *et al.* (1967) and Elliot (1970).

There are two ways to improve thermal insulation: increasing the insulation layer thickness and/or searching for new materials with lower thermal conductivity and diffusivity. A variety of materials have been investigated as potential candidates for TBC. Several ceramic coatings such as  $Al_2O_3$ ,  $TiO_2$ , yttria-stabilized zirconia (YSZ),  $ZrO_2$  have exhibited the best performance in terms of insulation and have been well studied. Selection of TBC materials depends on some requirements : (1) high melting point, (2) no phase change between room temperature and operation temperature, (3) low thermal conductivity and diffusivity, (4) chemical inertness, (5) similar thermal expansion as that of metallic substrate, (6) good adherence to the metallic substrate, and (7) low sintering rate of the porous microstructure (Cao et al., 2004).

Plasma spray is commonly used for depositing TBC, and mainly ceramics such as  $Al_2O_3$ , YSZ, and ZrO<sub>2</sub> have been reportedly deposited (Schulz et al., 2003) (Curry et al.,

2011). The cold spray technique is used for deposition of the above-mentioned ceramics (Lee et al., 2005) and thermally grown oxides (TGO) for bond coatings (Li et al., 2010).

The cold spraying technique facilitates acceleration of coating particles up to supersonic speeds. This coating method is rapid and scalable, which will thereby enable large-scale roll-to-roll manufacturing, as shown in **Figure 1**. The sprayed particles have high kinetic energy such that they flatten on impact and adhere strongly to the substrate(Kim et al., 2015). In this work, supersonic spray method have been used for deposition of thermal barrier coatings from clay and clay minerals such as bentonite, kaolinite, and montmorillonite respectively. Clays show good thermal insulation (Dogar Cetin et al., 2014; Pelot et al., 2015) and comparably low thermal conductivity and diffusivity, cf. **Table 1**. Clays are attractive coating materials because of their abundance in nature and low toxicity. Clays have been compounded in nanocomposites with some polymers using the sol-gel (Meera et al., 2012) and layer-by-layer (Lin et al., 2008) methods. However, to the best of our knowledge, clays have never been spray-deposited as a thermal barrier coating, even though spraying of clays holds great potential for preparation of commercially viable thermal and electrical insulation films.

Material	Thermal Conductivity [W/m-K]	Thermal diffusivity [m <sup>2</sup> /s]
Kaolinite	2.6	$1.01 \times 10^{-6}$
(Brigaud and Vasseur, 1989)		
Bentonite	1.3	$5.71 \times 10^{-7}$
(M. Plotze et al., 2007)		
Montmorillonite	0.48	$2.51 \times 10^{-7}$
(BLITZ, 2011)		

Table 1. Thermal conductivity and thermal diffusivity of clay and clay minerals.

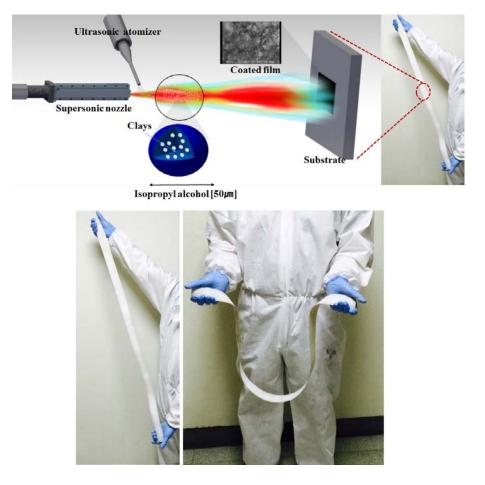


Figure 1. Supersonic spray schematic (top) and large-scale flexible insulating tape coated with montmorillonite that can wrap around multiple copper cables as a thermal barrier/protection layer.

# 2. Experimental

Films of clay such as bentonite and clay minerals like kaolinite, and montmorillonite, have been fabricated using supersonic spray. All the mineral powders were purchased from Sigma Aldrich and were used as is. The basic setup of a supersonic spray consists of a gas tank, syringe pump, nozzle, and x-y motor stage. The details of the setup were published elsewhere (Kim et al., 2014). Each mineral powder (3 g) was mixed separately with 1.8 g nylon and 30 mL isopropyl alcohol (IPA) to make colloidal sols. The sols were supplied with a flow rate of 3 mL/min and fed into a supersonic air jet issued at a pressure of 4 bar. The sold were atomized and formed sprays, which were deposited onto a substrate located at a distance of 90 mm from the nozzle.

To evaluate the thermal insulation properties of the deposited clay films, a test was performed as depicted in the schematic shown in **Figure 2**. A Cu plate was positioned onto a pre-heated hotplate kept at a fixed temperature of 300 °C. In the first experiment, temperature was measured with a thermocouple at the back side of the Cu plate as a function of time (**Figure 2a**). In the following set of experiments (**Figure 2b**), a Cu plate was coated with an insulation layer (IL) using clay and the temperature was measured above the Cu plate placed on top of this clay after the entire sandwich was positioned onto a pre-heated hotplate kept at a fixed temperature.

The difference in the temperature of the heater and the Cu plate above the coating was measured using a chromel-alumel thermocouple (Type K). An infrared camera (FLIR system, Inc. FLIR-E63900) was utilized for visualizing the temperature field. In addition, the coatings were characterized using scanning electron microscopy (SEM, Hitachi S-5000) at 10 kV to reveal their structural morphology.

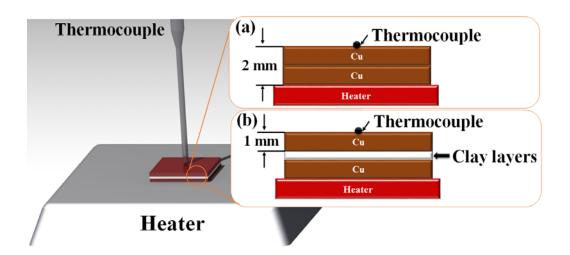


Figure 2. Schematic of the experimental arrangement used to study the thermal insulation capability: (a) measurements with pure copper, (b) measurements of the coated insulation layer.

# **3.** Results and Discussion

The SEM image in **Figure 3** demonstrates the morphology of different clay powders: kaolinite in panel (a), bentonite in panel (b), and montmorillonite in panel (c). These clay sizes are in the range of few microns.

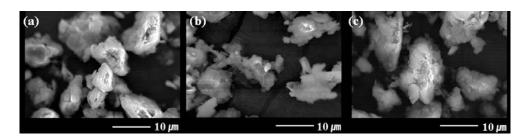


Figure 3. SEM image (a) kaolinite, (b) bentonite, (c) montmorillonite powder.

It is desirable that clay films would be not only thermal but also electric insulators, so that metal cables are protected from electrical shortcuts. After coating the clays with supersonic spray, the electric resistivity of a coated Cu plate was measured. A high resistance of 30 G $\Omega$  under a supplied voltage of 1050 V was measured due to the presence of the deposited layer, as shown in **Figure 4a**. **Figure 4b** illustrates its flexibility. No delamination of the deposited clay layers from the substrate was observed even after 1000 bending cycles, with the bent sample diameter of 2 mm.

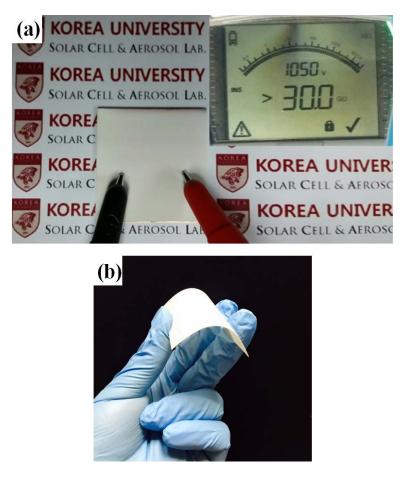


Figure 4. The clay coatings show: (a) high electrical insulation, (b) high flexibility.

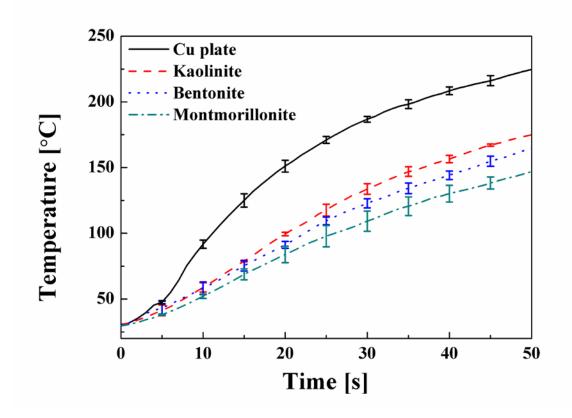


Figure 5. Thermal response of a single copper plate and of sandwiches of two copper plates with a 500-µm thick clay films in between at 300 °C temperature of the hotplate.

Temperature of a single copper plate and of sandwiches of two copper plates with a 500- $\mu$ m thick clay films in between measured as shown in **Figure 2 is presented in Figure 5**. The temperature difference between the single Cu plate and the sandwiches with clay layer in the middle after 50 s of heating was 75 °C, 86 °C, and 100 °C for kaolinite, bentonite, and montmorillonite, respectively. The thickness of all the coated clay layers in the sandwich was kept constant at ~500  $\mu$ m. The better thermal protection revealed for the monmorillonite in comparison with the other two clays stems from the fact that it has a lower thermal diffusivity (cf. **Table 1**).

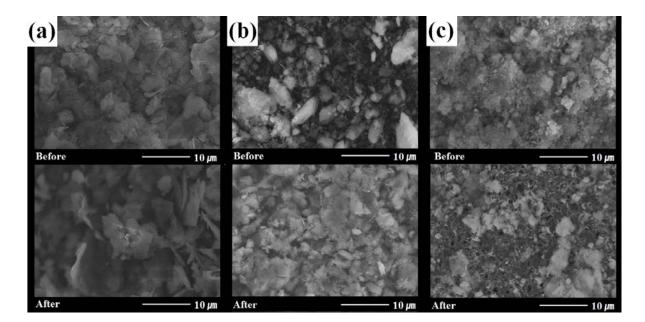


Figure 6. SEM image of supersonically sprayed deposited with (a) kaolinite, (b) bentonite, and (c) montmorillonite. Upper row is before heating and bottom row is after heating at 600°C.

The surface morphologies of all the clay films before and after using as a thermal barrier in a sandwich (at 600 °C), characterized by SEM, are shown in **Figure 6**. The first noticeable thing is that after deposition due to high velocity impact of particles on substrate the particle size in all cases reduced as compared to its original powder (**Figure 3**). On the other hand, heating did not result in any visible change in the deposited clay layers, as follows from the comparison of the upper and bottom row images in **Figure 6**.

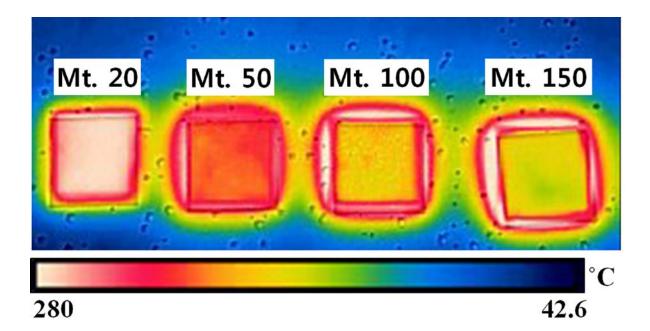


Figure 7. Effect of montmorillonite film thickness on the temperature distribution revealed using an infrared camera. The thicknesses of the films were from 20 to 150  $\mu$ m, which is denoted by the labels on top of the panel.

Temperature field over the top surface of montmorillonite films of different thicknesses located on top of a copper layer on a hotplate kept at a fixed temperature of  $300 \,^{\circ}$ C was revealed using an infrared camera (**Figure 7**). The thickness of the films increased from 20 to 150  $\mu$ m (left to right). Thicker films had lower temperature at the top, as illustrated by the color bar in **Figure 7**. In this figure on the left, the color of the film is white-red, which is around 280 °C, on the other hand, on the right, the color changes to yellow and the temperature is lower. As expected thicker film provide better thermal insulation.

The thermal insulation property of a montmorillonite film was demonstrated by a finger test (**Figure 8**). The figure on the left is a white-light image, whereas the figure on the right is an infrared image. A 700  $^{\circ}$ C lamp was underneath a Cu plate C coated with montmorillonite layer of thickness of 1 mm. Due to the presence of the layer, the temperature at the top was so low that a fingertip can be easily touched.



Figure 8. Thermal insulation performance of the fabricated films at 700 °C.

#### 4. Conclusions

Kaolinite, bentonite and montmorillonite powders were entrained by supersonic gas jet and deposited onto flexible substrates. As a result of significant impact energy, microscopic particles of these materials (clays) were further pulverized and strongly adhered to the substrates, thus forming coatings capable of withstanding multiple bending. The electrical conductivity of the layers of these materials were found to be low, while the heat transfer experiments revealed their perfect thermal insulation properties. Montmorillonite was found to be the best thermally insulating material.

## Acknowledgements

This work was primarily supported by the Special Research Grant by the College of Engineering at Korea University. This research was also supported by GFHIM of NRF (2013M3A6B1078879), NRF-2013R1A2A2A05005589, and KETEP-20133030010890. The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for its funding this Prolific Research group (PRG-1436-03).

## References

BLITZ, I.P., 2011. Thermal transport in self-assembled nanostructures, Ph.D. Thesis, p. 21.

- Brigaud, F., Vasseur, G., 1989. Mineralogy, porosity and fluid control on thermal conductivity of sedimentary rocks. Geophysical Journal International 98, 525-542.
- Cao, X., Vassen, R., Stoever, D., 2004. Ceramic materials for thermal barrier coatings. Journal of the European Ceramic Society 24, 1-10.
- Curry, N., Markocsan, N., Li, X.-H., Tricoire, A., Dorfman, M., 2011. Next generation thermal barrier coatings for the gas turbine industry. Journal of thermal spray technology 20, 108-115.
- Dogar Cetin, Gurses Ahmet , Karaca Semra, Koktepe Sevda, Mindivan Ferda, Kubra, G., 2014. Investigation of thermal properties of PUF/clay nanocomposites. Applied Surface Science 318, 59-64.
- Evans, A.G., Mumm, D., Hutchinson, J., Meier, G., Pettit, F., 2001. Mechanisms controlling the durability of thermal barrier coatings. Progress in materials science 46, 505-553.
- Kim, D.-Y., Lee, J.-G., Joshi, B.N., Latthe, S.S., Al-Deyab, S.S., Yoon, S.S., 2015. Self-cleaning superhydrophobic films by supersonic-spraying polytetrafluoroethylene–titania nanoparticles. J. Mater. Chem. A 3, 3975-3983.
- Kim, D.Y., Sinha-Ray, S., Park, J.J., Lee, J.G., Cha, Y.H., Bae, S.H., Ahn, J.H., Jung, Y.C., Kim, S.M., Yarin, A.L., Yoon, S.S., 2014. Self-healing reduced graphene oxide films by supersonic kinetic spraying. Adv. Funct. Mater. 24, 4986-4995.
- Lee, H.Y., Jung, S.H., Lee, S.Y., You, Y.H., Ko, K.H., 2005. Correlation between Al2O3 particles and interface of Al–Al2O3 coatings by cold spray. Applied Surface Science 252, 1891-1898.
- Li, Y., Li, C.-J., Zhang, Q., Yang, G.-J., Li, C.-X., 2010. Influence of TGO Composition on the Thermal Shock Lifetime of Thermal Barrier Coatings with Cold-sprayed MCrAlY Bond Coat. Journal of thermal spray technology 19, 168-177.
- Lin, Z., Renneckar, S., Hindman, D.P., 2008. Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers. Cellu 15, 333-346.
- M. Plotze, U. Scharli, A. Koch, Weber, H., 2007. Thermophysical properties of bentonite, International Meeting-Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, France, pp. 579-580.
- Meera, K.M.S., Sankar, R.M., Murali, A., Jaisankar, S.N., Mandal, A.B., 2012. Sol–gel network silica/modified montmorillonite clay hybrid nanocomposites for hydrophobic surface coatings. Colloids Surf. B. Biointerfaces 90, 204-210.
- Pelot, D.D., Jun, S., Yarin, A.L., 2015. Bentonite dispersions: Transition from liquid-like to solid-like behavior and cracking. Journal of Non-Newtonian Fluid Mechanics 219, 50-64.

Ray S. Elliott, Baltimore, M., 1970. Thermal barriers for cables. US patent 3509269.

Schulz, U., Leyens, C., Fritscher, K., Peters, M., Saruhan-Brings, B., Lavigne, O., Dorvaux, J.-M., Poulain, M., Mévrel, R., Caliez, M., 2003. Some recent trends in research and technology of advanced thermal barrier coatings. Aerospace Science and Technology 7, 73-80. Woodland, P.C., Clock G. E, R.C., M., 1967. Thermal barriers for electric cables. US Patents 3344228.