News From Japan

Yoshimichi Ohki

Development of a Clay Coating on Metal as a New Electrical Insulating Substrate

For various industrial purposes, metal with an inorganic substance coated on it is widely used. Typical objectives of such coatings would be functional, decorative, or both. Although the adjustment, addition, or improvement of strengths of adhesion, wettability, anticorrosion, water resistance, wear resistance, and antimicrobial activity are the main purposes of functional coatings, ceramic or oxide coatings on metals are also adequate for use as a substrate of a power electronic module [1]. Ceramic coatings on metals for this application must have superior thermal durability, high thermal conductivity, and good electrical insulating ability.

Ichinen Chemicals Co. Ltd., Fujisawa, Japan, has recently developed a method to coat clay on the surface of metal such as stainless steel. Stainless steel is one of the most popular and useful metals for industries and in our daily lives. Because of its high corrosion resistance and good processability, stainless steel has been widely used for making a vast variety of products ranging from daily commodities such as tableware to industrial goods such as structural frames and piping. In order to enhance the corrosion resistance or surface electrical insulation performance further, proper ceramic coating must be done on the surface of stainless steel.

A variety of methods to coat stainless steel are known. First, organic polymers or paints are usable for simple and light coating. However, organic coats have relatively poor heat resistance and weak wear resistance. Second, sol-gel methods are suitable to make thin inorganic compound coatings. However, they are not adequate to make a dense and thick ceramic coating, because a crack would occur during the calcination of the gel precursor. Sputtering and laser deposition are also good methods to fabricate inorganic thin films, but their feasible sizes and growth rates are not adequate for most industrial purposes. With these backgrounds, the development of a simple, low-cost, and easy-handling process that can coat a ceramic or inorganic layer on the surface of metal is desirable.

Ichinen Chemicals uses clays to fabricate various kinds of ceramics through a calcination process. Clays are easily dispersed in water to make pastes for use in wet coating. One typical starting aqueous solution is a mixture of 10 wt% synthetic hectorite $Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$, with an average particle size of approximately 60 nm, 0.4 wt% polyoxyethylene lauryl ether, 1.5 wt% ethanol, 4 wt% ethylene glycol monobutyl ether, and 84.1 wt% ion-exchanged water.

After the hectorite clay was immersed in the ion-exchanged water for 20 minutes, all organic additives were added to the solution and mixed for 20 minutes. Then, the solution became an aqueous paste of clay as shown in Figure 1. Here, the organic additives help the dispersion of the clay in water, by which we can control the viscosity of the resulting paste. Next, the clay paste was spin coated onto an ultrasonically cleaned stainless steel plate. All these processes were conducted at room temperature. Then, the plate samples were dried for 1 hour at 105°C and subsequently calcinated for 2 h at 600°C in an oven. In some cases, half of the plate surface was covered with transparent tape to prevent coating on that portion.

In Figure 2, the lower half shows the portion coated with the clay, and the upper half shows the portion not coated but covered by the tape. An interference pattern is visible only on the lower portion, which shows clearly that a transparent thin coating of clay, or ceramic derived from clay, was formed on the surface. It is also clear that the coat can protect the surface of stainless steel from oxidation at the high temperature of 600°C during the calcination, because the coated portion maintained the metallic appearance or silver color of the original stainless steel in contrast to the uncoated portion that became dark brown in color.

The pencil hardness test was conducted on the coating using a conventional tool to estimate the adhesion of the clay or ceramic coating to the stainless steel substrate. In the test, a weight of 750 g was loaded on pencils with various values of hardness from 6B to 6H. Then, the pencil was put on the clay-coated stainless steel plate at an angle of 45°. The presence of a scratch on the clay surfaces was checked to determine the pencil hardness. As a result, the pencil hardness of the coated surface was found to be 6H, which is sufficiently hard enough to be peel-proof, confirming that the developed clay or ceramic coating has excellent adhesion to the stainless steel.

Figure 1. Aqueous paste of clay.

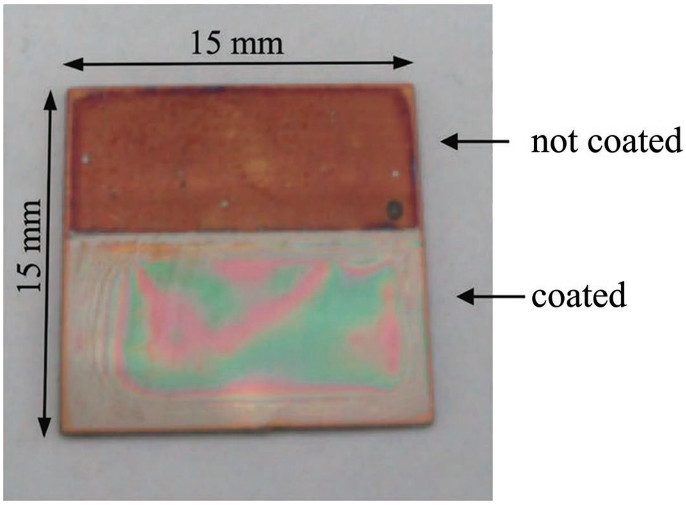

Figure 2. Stainless steel plate after the heat treatment at 600°C in air; the lower half was coated with the developed clay coating.

Figure 3 shows the X-ray diffraction patterns obtained with CuK*α* radiation of the coated samples before and after the calcination at 600°C. Both patterns exhibit the (00L) lines of clay, which means that clay fragments were present in the coating. The interlayer space of the clay fragments was calculated from the (001) lines and was found to change from 1.4 to 1.0 nm. This indicates that the thermal dehydration occurred between the layers of the clay. Other (00L) lines appear more clearly after the heat treatment, indicating more packing and densification of the clay fragments, which brought about a hard coat.

To examine the interface between the coating and the stainless steel substrate, a cross-section of the coated surface was exposed using focused ion beam bombardment. The exposed surface was then characterized by transmission electron microscopy together with energy dispersive X-ray spectrometry (EDX). Figure 4 shows a cross-sectional bright field transmission electron microscopy image of the coating on a stainless steel plate calcined at 600°C. A smooth coating with a thickness of 0.6 µm, with no cracking, is clearly seen on the stainless steel substrate. Inside the coating, it appears that clay fragments were stacked. The presence of voids is also evident. As mentioned above, the present clay-derived ceramic coating was prepared using a wet coating process of the clay paste, which formed bubbles due to the release of solvent or surfactants during the drying and calcination processes. These processes might have caused the irregular stacking of the clay fragments, which resulted in the voids. The interface between the coating and the stainless steel surface has excellent adhesion without peeling or voids. Based on the EDX analysis of the interface region, iron (Fe) was confirmed to be present. Since the original clay contains no iron, iron was clearly diffused from the stainless steel into the coating at the high temperature, which seemingly adhered the coating tightly to the stainless steel.

To summarize, Ichinen Chemicals has succeeded in the fabrication of a clay-derived ceramic coating on a stainless steel substrate with a submicron thickness using a simple wet coating process using an aqueous clay paste followed by calcination at 600°C.

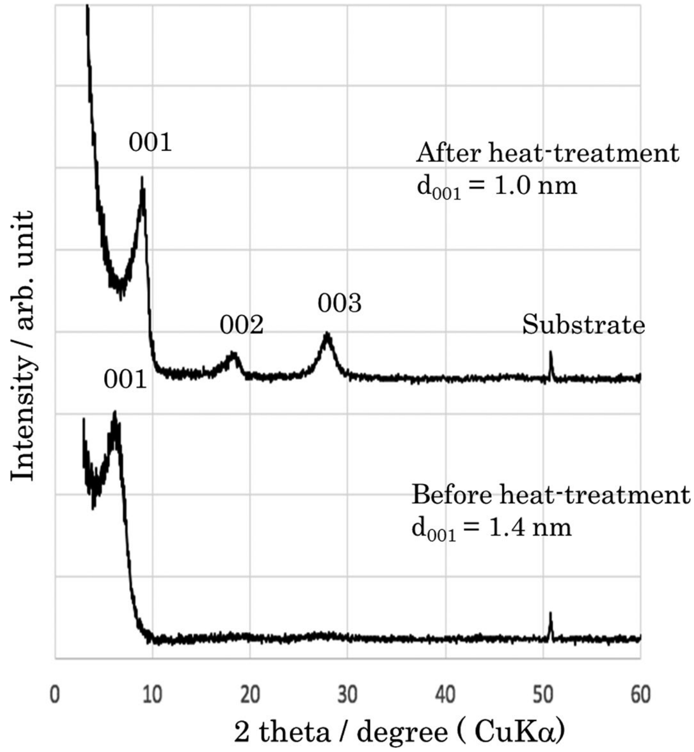

Figure 3. X-ray diffraction patterns of stainless steel plates coated with the developed aqueous clay paste, before and after heat treatment at 600°C.

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References

[1] Y. Ohki, "News from Japan—Development of an insulated metal substrate with high thermal conductivity," *IEEE Electr. Insul. Mag.*, vol. 33, no. 4, pp. 67–69, 2017.

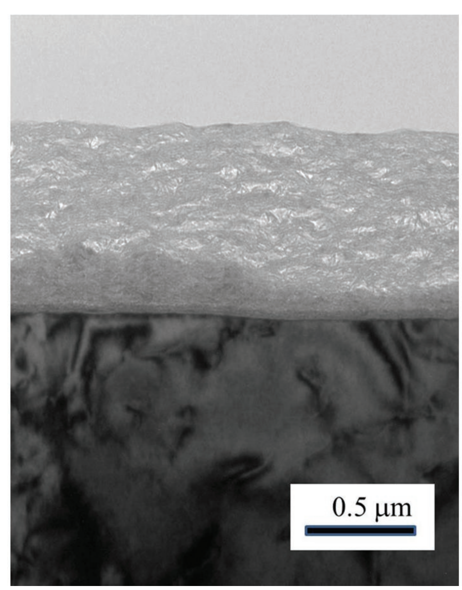

Figure 4. Bright field transmission electron microscopy image of the cross-section of the interface between the clay coat and the stainless steel.