New Developments for Radiation Enhancements from Metal Surfaces by Using Nanoscale Materials in the Membrane

Koji Yamada¹² and Masami Matsuda¹

¹Future Product Co., Kita-Asaka, Saitama 351-0031, Japan
²Saitama University, Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

msmqx323@yahoo.co.jp, Koji Yamada

Abstract. The enhancements of thermal radiations from the surfaces of devices are very important for electric machines to prevent from heating up and/or efficiency degradations. In this investigation, new applications of micro-scale membrane of Si, SiO₂ etc. on the metal surfaces have been studied to cool down the temperature without breaking insulations of the devices by selecting materials. The modified black-body radiations were sensitively detected by thermisters with sub-second responses. The optimum membrane thicknesses were successfully determined by subtractions of radiation intensities between those at membranes with and without membrane, respectively. We obtained the best cooling condition in SiO₂ membrane with 20 µm for an Al-plate of 10cmx10cmx1mm. Further, we observed the detaching/attaching processes of massive molecule clusters from the metal surface as a sudden change in temperature changes just like the noises in the detectors. A characteristic pattern of temperature change was observed in diatomite membranes during the cooling process in a temperature range between 200-50°C. These radiation phenomena as a function of temperature might be available as a molecular analysis on the metal surface.

1. Introduction

The easy cooling methods of materials and devices are of great interest without any additional energy during cooling. In this study, we investigated on the enhancements of thermal radiations from metal surface by using attached membranes of nano-scale materials of Si, SiO₂ etc [1]. Here we made a mixture of membrane material and small amount of water as the solvent and also for the adhesive, and the baking temperatures were as low as 150-200°C. The observations of sample temperatures as a function of time elapsed have been technically performed by using CCD cameras. However, the real time temperatures with “high precision” with an error less than 0.1% might be very difficult, mainly due to refresh time of CCD elements or frame rates are slow as 10ms in general. Therefore, in this study we have been investigated on the improvements of temporal change in the thermister by solving an equation of temporally retarded propagation of the thermister resistances. As will be mentioned after, the sub-second resolutions of phenomena were attained.

On the material side of preparations of this investigation, the nano-scale powders for the membranes were obtained and from markets [2] which were usually made of the following manners so called as hydrolysis method of nano-scale SiO₂: The hydrophobic fumed silica was obtained by a hydrophobization treatment of fumed silica with an organosilane compound. After, the drying processes, the humed particle are obtained from the diffusion of original material in a furnace with a high temperature range more than1000-1500°C and collect powders from the dropping stream of the material. We used the these starting materials of Si (20-400nm), SiO₂ (Dia.<200nm) and Ag+SiO₂ (particle diameters<400nm) etc. The raw materials of nano-scale-powders were mixed with small amount of high purity water with 20MOhm or larger. The outside appearances of the mixed powder were just paste-like and these could be diluted with small amount of organic liquid, e.g. ethanol. The most important feature of the paste was the full mixing of the original material with the smallest amount of water to avoid residual H₂O molecules after baking process. The residual H₂O molecule might cause the breaking of bonding between the nano-particles. In the conventional method, the formed material might include the full of imperfections at the surface. To avoid this situation, the membrane might be better quality by limiting the thicknesses less than 20-40µm. All these processes were performed in a clean box with immersed clean air. The prepared mixture of pasts were coated on a metal by using a precision rolling bar with 20cm long, 1.5cm² and with a constant dips with 5cm along the bar direction to determine the coating thickness on the substrate of glass or metal.
The prepared substrates were baked at the low temperature of 150°C–200°C, 1hr in the ordinary atmospheric pressure. Here, the baking temperature must be performed at a temperature as low as possible, not to injure the device. The prepared samples in this experiment showed transparent in samples with thicknesses of 2-30 µm and showed a little bit opaque in those thicker samples [1]. The strengths of the membranes were strong enough and attached tightly on the substrate of glasses and metals, which were tested by scratching by using sound-papers [3].

2. The sample preparations and experimental procedures
We first performed the experiment on the transparencies of Si membrane and of SiO₂ in the visible light wavelength range. It was shown that the reflection become better at the metal surface with SiO₂ membrane than those without. Here we used conventional spectrometer with a tungsten lamp as the light source which was driven in a low voltage to obtain longer wavelength lights, and detected by a photomultiplier with S1 curve.

The enhancements of infrared light emission were observed by constructing the experimental apparatus as shown in Figure 1. The sample was set at the central position in between the thermistors (S1 and S2 in Figure1) with the activation energy of \( E_A = 0.290 eV \) (=3380K) to observe the blackbody radiation which is modified by the coated membrane. One more thermistor (S) with \( E_A = 0.343 eV \) (=3995K) [2] was attached tightly at the sample surface with a very small size as 1mm Φ to minimise the heat capacity in comparison with those of S1 and S2. It will be shown later that the improvement of the temporal responses as short as 0.2s was achieved by solving the an equation of the retarded propagations in thermistors. The precise observations of the resistances and temperatures in the thermister were realied by using a 16-bits ADC and recorded up to 100kwords up to 200s (2ms/w). Note here that the sample was supported all by the edges of glass substrates to minimise the contacting cross section between the sample and glass supporters. Here, it must be also noted that the incidental electric power to detect the resistances in thermisters, must be less than 10µW which was inevitably limited by the observing incidental small radiation power.

Figure 2 shows examples of samples of Al-plate with SiO₂ coatings and conventional fittings of soft iron with and without coating of SiO₂.

3. Experimental Results
The observable temperature range was in between 0 and 200°C, which was limited by the thermisters. The time lag of the response was corrected by a method of retarded propagation of temperature which
will be explained later in discussions. As explained before, the membranes are made of nano-scale powder of SiO$_2$ etc. with the solvent of smallest amount of water. The strength of attached membrane was very tight and attached directly with the metal surface within nano-meter distance between membrane and metal without any adhesive material as shown in Figure 2. The experiments on the cooling effects of membranes as shown in Figure 2 were performed by using a device in Figure 1. All the samples showed the monotonic temporal decreases with time elapses as expected before. The sample temperature ($T$) and the first derivative with time $t$ ($-dT/dt$) followed exactly by exponential functions of ($T-T_0$). However, precise curves of ($-dT/dt$) with high temporal resolution include turbulent noises around at the function of $T-T_0$, as shown in Figure 4.

![Figure 3](image1.png)  
**Figure 3.** Experimental results of the cooling effects in soft iron fittings with and without cover by SiO$_2$ membrane with 100µm in a temporal range up to 220s in the l.h.s. figure. The r.h.s. figure shows the first derivative of sample temperature with respect to time $t$.

![Figure 4](image2.png)  
**Figure 4.** The cooling effects of membranes at Cu surface with membrane with Ag nano-powder in SiO$_2$ with thicknesses of (a) 22µm and (b) 8µm, one side coated respectively

It is apparent to observe the enhancements of cooling effects by larger radiations. The time delay caused by the heat capacity of the thermistor is corrected in this investigation which will be also discussed later. It must be noted here that the coating of SiO$_2$ was performed both sides of the surfaces, or only one side for simplicity. The temperature decreasing rate became 2 times than that without coating in this experimental condition.

Figure 4 shows two different samples of Cu-plates with Ag powder+SiO$_2$ coating with the different coating thicknesses. Here, the experiment of radiation efficiency was performed as a function of the coating thickness. It will be also shown together with the experimental results in the discussion. In Figure 4(a) and (b), the inserted lines with red and blue, stand for the approximated two lines of responses in a low temperature range between 40-80°C (red line) and that in a higher temperature than 80°C (blue line), respectively. It must be noticed here that the turbulences of the curves were not reproducible and the physical origins of the phenomena will be discussed later. Further, the temporal behavior of $-dT/dt$ shows a proportional function of ($T-T_0$) decay in this temperature range with some turbulences around at the function of $T-T_0$, as shown in Figure 4. For the improvement of responses, the retarded propagations of sequential equations at each point were developed.

4. Discussions
The cooling effects by radiation enhancements at the metal surface were theoretically analysed, where phonons played an important role [4] and the nonlinear effects on temperature might be important. Here, the effects might be expressed by classical equation of thermal conduction as
\begin{equation}
\frac{dT(t)}{dt} = c(T - T_0) + ho
\end{equation}

Here, \( T \) and \( t \) stand for the sample temperature and time \( t \) after heating the sample, respectively. This coefficient \( c \) stands for all cooling mechanism as convections, radiations and etc. \( T_0 \) stands for the ambient temperature to be equal after the thermal equilibrium. The most simple case, the coefficient \( c \) might be a constant or it expresses some function of \( T \) or/and \( t \). Eq.(1) is precisely solved by the method of “variable separable” with the initial condition of \( T=T_i \) as

\begin{equation}
T(t) = (T_i - T_0) \exp\{-c(t)dt\} + T_0.
\end{equation}

Here, \( c(t) \) stands for a nonlinear dependence of thermal conductions in the wider temperature range. For this analysis, the temperature dependence of \( dT/dt \) as a function of \( T \) were well measured experimentally as shown in Figure 4, except the large fluctuations which might be caused by some molecular attaching/detaching processes at the surfaces. Here, we discuss on the cooling effects of the membrane without the effects of convections. For this purpose, we calculated the difference of the output voltages as defined by \( V_{12} = V_{S1} - V_{S2} \). Now, we adopt the first order approximation to consider the effects of both side convections are almost same. Figure 5 shows the derived voltages of The output voltages \( V_{12} \) as a function of membrane thicknesses \( d \).

![Figure 5. The cooling effects of membrane of SiO2 on the metal as a function of different thickness](image)

![Figure 6. The coefficients c as a function of different membrane thicknesses with \( T_i=200^\circ C \)](image)

Now, we discuss on the time delay of the thermistor, which is caused by the heat capacity of the material inside of the thermistor with about 3 second of order. To solve this problem, we tried the corrected temperatures \( T'_j \) at \( t=t_j \) which derived by the old \( T_j \) (\( j=0,1,2,\ldots,N \)) as

\begin{equation}
T'_j = 5T_{j+4} - (T_{j+3} + T_{j+2} + T_{j+1} + T_j), \quad (j=0,1,2,\ldots,N)
\end{equation}

\begin{equation}
= T_j + c_1(T_{j+1} - T_{j+2}) + c_2(T_{j+2} - T_{j+3}) + c_3(T_{j+3} - T_{j+4})
\end{equation}

\[ \text{[ } t=t_j \ (j=0,1,2,\ldots,N), \ (c_1=c_2=c_3=1) \text{ ]} \]
where $j$'s stand for the time $j_t$ defined by $j\Delta t$ ($N\Delta t=t_0, N=10^5, \Delta t=2\text{ms}, t_0=200\text{s}$) in analogue digital converter with clock frequency of $1/\Delta t$. $T_j$, $T_j'$ stand for an apparent and superficial temperature in the thermistor S and the corrected temperature at $t=t_j$, respectively. Note here that, Eq.3 and Eq.4 express the Markovian process with $4^{\text{th}}$ folds with the coefficients of $c_0=1> c_1> c_2> c_3=0$, where the extension of the effective time span is determined by the causality extent. Here, we set $c_0=c_1=c_2=c_3=1$ for discussions. By using smoothing process, the data number was reduced to $N=10^4$ and $\Delta T=0.1\text{s}$. We obtained the results as shown in Figure 7. It shows the temperatures $T_j$' (red) after corrections and $T_j$ (blue) those before. The time response were best fitted with 2.4s delay in the algorithm as shown in Eq.3. After the corrections, the superficial delay was improved by the total delay of 0.2s, which must be probed by independent other devices. Figure 8 shows the characteristic “spectra” of diatomite membranes which appeared in different samples and showed in the similar pattern.

![Figure 7. The effects of corrections of temporal delays due to heat capacity of thermister](image)

![Figure 8. The characteristic features of “spectra” in different Al-plate samples with diatomite membrane with the thickness of 20µm of just an ingradient expression except “diatomyte”](image)

**5. Conclusions**

In this investigation, we first presented the direct attachment of nano-material on the metal surfaces which show the large enhancements of radiations or cooling effects. The physical origin of the effect of direct coupling of nanomaterial on the metal surface must be examined in the future [4]. However, the first candidate of this mechanism might be the coupling by inter-atomic force or inter-molecule force as Lenard-Jones potential. The cooling effects are the conventional phenomena as those in characole membrane. However, this material is electrically conductive and dangerous when the carbon membrane is exfoliated by the damage. The method and the technology might be available to use these in electrical machines to improve the efficiency by cooling down.

**References**

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