Special Feature: Challenges of Internal Combustion Engines for Achieving Low-carbon Society

Research Report

Development of Thermo-swing Insulation Coat "SiRPA" (Sirica Reinforced Porous Anodized Aluminum)

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ABSTRACT This work assessed the application of porous anodized aluminum films to thermo-swing wall insulation (TSWIN) technology. Films having low thermal conductivity and low volumetric specific heat capacity are preferable for such applications, meaning that a high level of porosity is desirable. It was found that increasing the concentration of crystalline Si in the substrate effectively increases the film porosity. The anodized film must also have sufficient strength to withstand use in a combustion chamber. Generally, increasing the porosity leads to embrittlement, but we overcame this trade-off by reinforcing the anodized films with silica, which also increases the number of closed pores that are beneficial during TSWIN applications. The resulting material is referred to as silica reinforced porous anodized aluminum (SiRPA).

KEYWORDS Anodized Film, Aluminum Alloy, Temperature Swing, Engine, Piston, Porosity

1. Introduction

Improving the thermal efficiency of engines is an effective means of reducing fuel consumption. Reduction of losses such as cooling and exhaust losses is an important aspect of thermal efficiency, with cooling losses accounting for the largest proportion of loss. Many studies were carried out in the 1980s regarding the feasibility of insulating the combustion chamber walls. The majority examined insulation methods using ceramics and other materials with low thermal conductivity and high heat resistance, although ceramics with air films were also assessed.[1-4]

These methods were found to reduce the heat flux from the combustion chamber wall to the cooling water, but a hotter combustion chamber wall reduces the intake efficiency. As a result, NOx emissions were increased and knocking was also promoted in gasoline engines.

Kosaka et al. proposed the so-called thermo-swing wall insulation (TSWIN) approach to maintaining a low temperature during the intake and exhaust strokes, while reducing the heat flux to the cooling water during the compression and expansion strokes.[1] It was believed that this method would mitigate the issues encountered in past studies.

Implementing TSWIN requires the application of a film having both low thermal conductivity and low heat capacity on the combustion chamber wall. The chamber wall temperature has high responsiveness to the combustion gas temperature. In addition, the TSWIN film must exhibit strong adhesion to the chamber wall and sufficient robustness for use in a combustion chamber.

Anodized aluminum films are considered to satisfy the above characteristics when used in conjunction with an aluminum alloy piston.[5] The present paper discusses control of the anodized aluminum film porosity so as to ensure suitable thermal properties as well as film reinforcement to allow the film to withstand the combustion chamber environment.

2. TSWIN Materials

2. 1 Thermo-swing Insulation Technology

This section explains the basic principles of the TSWIN method. **Figure 1** schematically shows the gas and combustion chamber wall temperatures as functions of the crank angle. It is evident that a conventional metal combustion chamber maintains a constant temperature during the compression and expansion strokes. This leads to a large difference between the gas and chamber wall temperatures at top dead center (TDC), such that the thermal flux increases at TDC along with the cooling losses. As discussed, various insulation methodologies have been developed to address this problem, typically using thermal barrier coatings composed of materials with low thermal conductivity (such as zirconia or other ceramics) with a thickness of several millimeters on the combustion chamber wall. In such cases, the chamber wall temperature (see the plot labeled “Traditional insulation” in Fig. 1) is elevated but constant throughout the stroke cycle. This increases the intake gas temperature, thus lowering the volumetric efficiency and increasing NOx emissions. In contrast, TSWIN reduces the heat loss without affecting the volumetric efficiency or NOx output, since the chamber wall temperature follows the combustion gas temperature (see the plot labeled “TSWIN”). As noted, for this to occur, the film must possess both low thermal conductivity and low volumetric specific heat capacity. In this technique, the swing width is defined as the difference between the minimum and maximum chamber wall temperatures, and increasing this value improves the fuel efficiency.

2. 2 Selecting Materials for TSWIN

Potential materials for chamber wall films are selected based on the criteria discussed in Sec. 2.1. In addition, the film must be highly reliable under the high-temperature and high-pressure conditions found in the combustion chamber. These criteria suggest that the preferred candidate would be a closed pore ceramic composite with controllable porosity[4] and sufficient strength at high temperatures and pressures. For these reasons, we selected an anodized aluminum film for examination as a component of the TSWIN process.

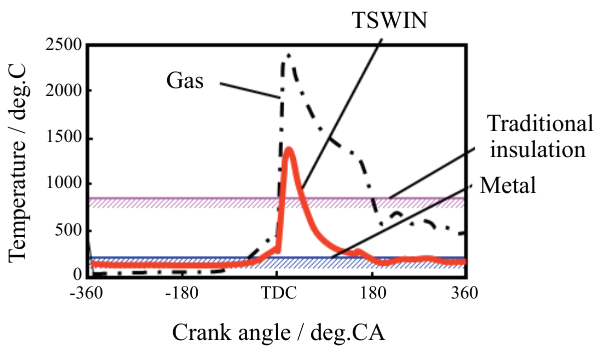

Fig. 1 Gas and combustion chamber wall temperatures as functions of crank angle.

Anodized aluminum films based on porous aluminum oxide are already widely used in piston ring grooves.

Anodization of an aluminum alloy in a diprotic acid (such as sulfuric acid) generates a porous surface film, and **Fig. 2** presents a diagram of the nano-structure of a porous anodized aluminum film[8] composed of hollow oxide columns. These hollow sections typically have widths of several tens of nanometers and hence are defined as nano-pores. The most widely used anodized films are 10-20 micrometers in thickness, whereas a TSWIN film is approximately 70 μm thick. The structure of an anodized film intended for TSWIN is shown in **Fig. 3**. A highly porous film is preferable

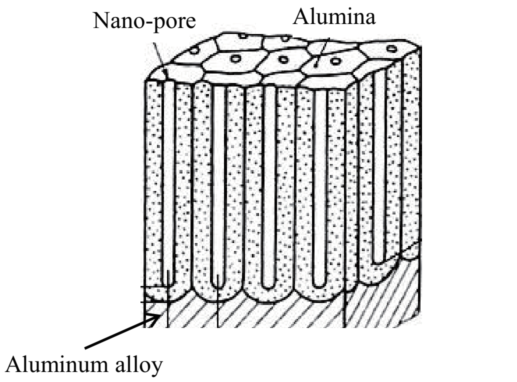

Fig. 2 Structure of porous anodized aluminum.[6]

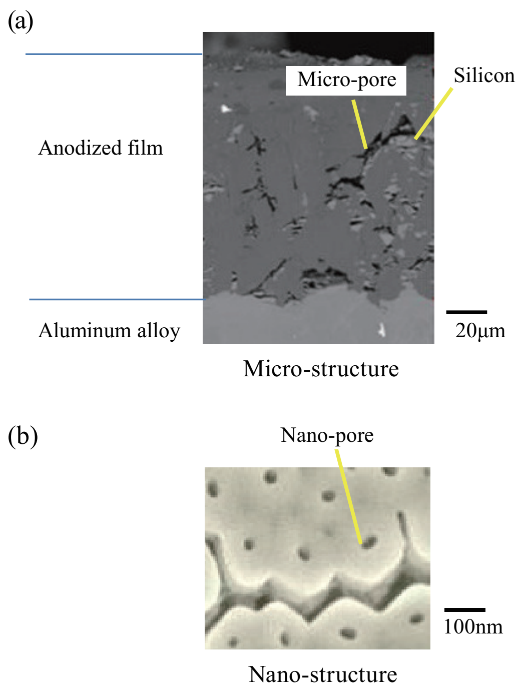

Fig. 3 Structure of porous anodized aluminum employed in TSWIN technique.

in the TSWIN technique.

The process used to cast aluminum alloys for engine pistons tends to create numerous crystallites due to the presence of Si and other compounds, which are typically detrimental when applying an anodized coating because such compounds are not anodized during electrolysis. In addition, the presence of crystallites during electrolysis tends to generate pores with widths of about 10 μm, depending on the size of the crystallites, which are defined as micro-pores. Micro-pores decrease both the thermal conductivity and volumetric specific heat of the coating and so we can use this feature for TSWIN. Thus, films intended for TSWIN are more porous than standard anodized aluminum films.

3. Evaluation of Porosity

It is important to evaluate the heat capacity and thermal conductivity of a film in order to predict improvements in thermal efficiency, and these thermal properties depend on the porosity. In the present study, the porosity was estimated using two procedures. The first estimated the overall volume of both open and closed pores, termed V_1. This value was calculated using the equation

$$V_1 = 1 - \frac{\rho_1}{\rho_a} , \qquad (1)$$

where ρ_1 is the bulk density of the film and ρ_a is the density of alumina. Here, ρ_1 is calculated based on the film dimensions (as determined by measurements of the microstructure) and its mass.

The second procedure estimated the volume of only closed pores (V_2), which is related to the insulation performance. This required the apparent volume of the material, which was determined by Archimedes' method, and was calculated using the equation

$$V_2 = 1 - \frac{\rho_2}{\rho_a} , \qquad (2)$$

where ρ_2 is the apparent density.

In addition, the nano-pore volume was measured using the nitrogen adsorption method. This method is suitable for determining the pore distributions or quantity of nano-pores less than 100 nm in size. The micro-pore volume could then be obtained by subtracting the nano-pore volume from the total pore volume.

4. Results and Discussion

4. 1 Control of Porosity

In order to improve the swing width, it is necessary to increase the porosity of the film. Anodized films contain two types of pores: nano-pores (up to several tens of nanometers in width) generated by aluminum anodization, and micro-pores (several tens of micrometers in width) formed over Si crystallites. This occurs because the crystalline material cannot be anodized, but the aluminum around the Si is anodized and expands. It is believed that the relative fraction of nano-pores and micro-pores is affected by the anodization conditions. **Figures 4** and **5** respectively

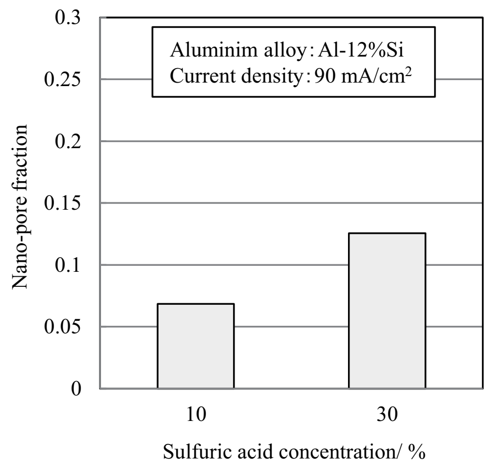

Fig. 4 Fraction of nano-pores in anodized aluminum films for different sulfuric acid concentrations.

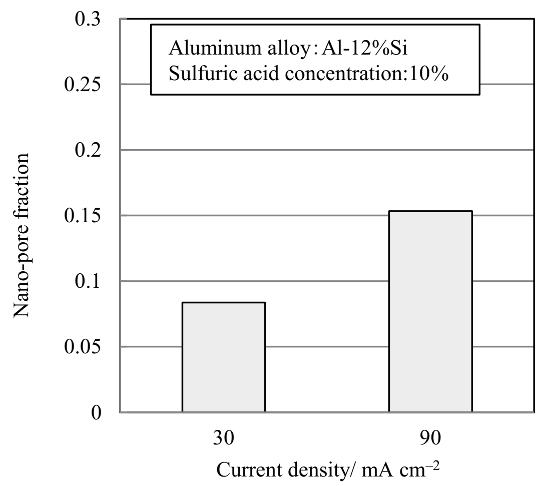

Fig. 5 Fraction of nano-pores in anodized aluminum films for different current densities.

show the nano-pore fraction for different sulfuric acid concentrations in the electrolyte and applied current densities. It can be seen that increasing the sulfuric acid concentration increases the nano-pore fraction. This occurs because the alumina dissolves in the electrolyte, leading to expansion of the pores.(7) Figure 5 demonstrates that a higher current density also increases the nano-pore fraction. This effect is attributed to an increase in the temperature of the electrolyte that in turn accelerates the dissolution of alumina.(8)

The formation of a micro-pore above a Si crystallite is schematically illustrated in **Fig. 6**, while **Fig. 7** plots the relationship between the amount of Si and the porosity. Although the amount of nano-pores is not correlated with the Si concentration in the aluminum alloy, the amount of micro-pores increases with increasing Si concentration. This indicates that the proposed mechanism for micro-pore generation over Si crystallites is reasonable. Figure 7 shows that the micro-pores account for approximately 80% of the total void volume in anodized Al-12%Si.

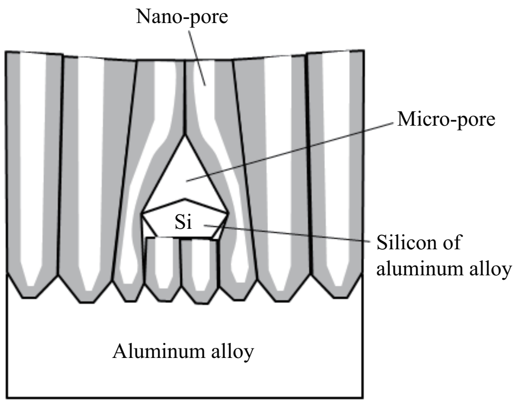

Fig. 6 Schematic diagram of anodized film on aluminum alloy.

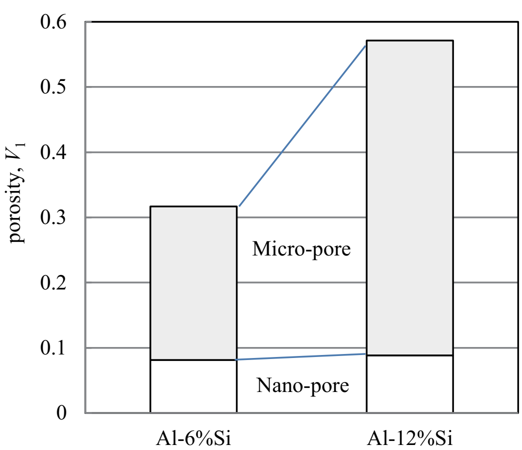

Fig. 7 Porosity of aluminum alloy films for different Si concentrations.

4. 2 Strengthening of the Anodized Film

The anodized 70-100 μm thick film formed on the top surface of an aluminum piston was subjected to an engine test, and a cross-section of the upper surface of the piston after the test is shown in **Fig. 8**. This image indicates that the anodized film collapsed as a result of the test, with the collapse occurring in the film. In order to determine the strength of the anodized film, micro-Vickers hardness measurements were performed. **Figure 9** compares the results for a conventional hard anodized aluminum film (hard alumite), the film for engine test and a silica reinforced porous anodized aluminum (SiRPA) film that we developed to have sufficient strength to withstand use in a combustion chamber. The test film hardness value was only about 25% of that of the hard alumite that is typically employed in engines. **Figure 10** shows scanning electron microscopy (SEM) images of

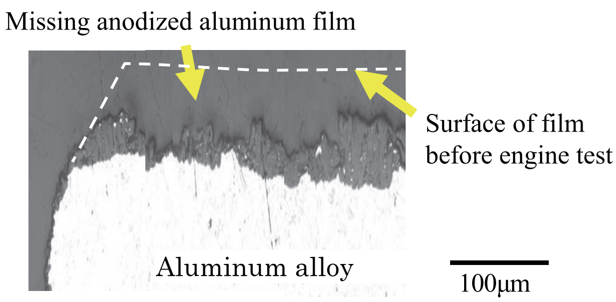

Fig. 8 Cross-sectional micrograph of anodized aluminum film following engine test.

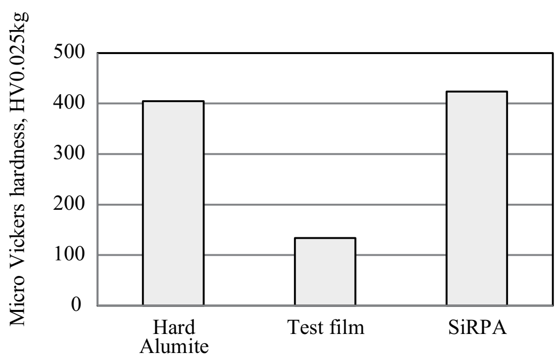

Fig. 9 Comparison of hardness of different films.

the nano-structure of hard alumite and the test film, from which it is evident that the test film contains larger nano-pores and separated columns. The structure and hardness of the test film are different from those of the alumite because the test film is thicker (70 µm versus about 10 µm for the anodized film) and was anodized for a longer time, leading to a larger amount of dissolution and a softer film.[7] For this reason, it is necessary to reinforce the anodized film. The reinforcement material should ideally resist deterioration, have sufficient heat resistance during the engine stroke cycle, and have sufficient fluidity to permeate into the nano-pores and column boundary regions. In the present work, perhydropolysilazane was selected as the reinforcing agent because it converts to silica upon heating. Silica has sufficient hardness and heat resistance while the perhydropolysilazane possesses a suitable degree of fluidity.

Figure 11 shows the Si distribution in a sample of the SiRPA and before reinforcement as determined by scanning transmission electron microscopy (STEM)

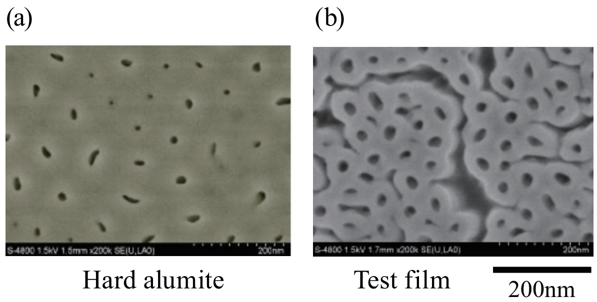

Fig. 10 SEM images of nano-structure of anodized films.

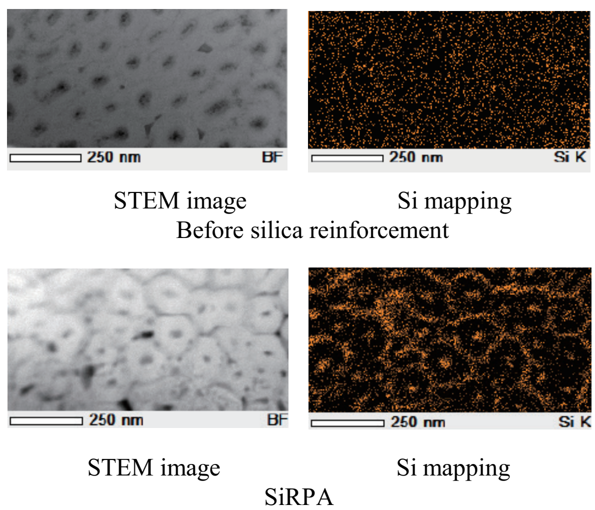

Fig. 11 Si distribution in anodized film.

and energy dispersive X-ray spectroscope (EDX). It can be seen that the Si is present within the nano-pores and intercolumnar spaces in the SiRPA, demonstrating that the anodized film is reinforced with silica. This reinforcement is reflected in the increased hardness of the SiRPA seen in Fig. 9.

4. 3 Effect of Reinforcement on the Quantity of Closed Pores

As noted, both low thermal conductivity and low heat capacity are preferred for TSWIN, meaning that a high proportion of closed pores is desirable, because heat transfer due to convection is suppressed and the intrusion of unburnt gases into the pores is eliminated. As described in Sec. 4. 2, SiRPA is reinforced by silica in the nano-pores and intercolumnar spaces. It is also possible that the amount of closed pores was also modified as the silica filled the pores or covered the film surface.

As shown in Fig. 7, the majority of the porosity is associated with micro-pores. Thus, if the silica does not fill the micro-pores, both reinforcement and a high concentration of closed pores may be realized. Therefore, the state of the micro-pores in the SiRPA and the closed void volume (V_2) had to be confirmed.

Figure 12 presents a field emission-electron probe microanalysis (FE-EPMA) image showing the micro-pores in the SiRPA. This image shows that Si is not detected in the micro-pores. Hence, it is believed that the majority of the micro-pores were retained after reinforcement, presumably due to the small volume of perhydropolysilazane that could penetrate the pores compared to the micro-pore void volume. **Figure 13** summarizes the closed void volume (V_2) of the film before and after reinforcement by silica, and demonstrates that the closed void volume was actually increased by reinforcement. Thus, the reinforcement

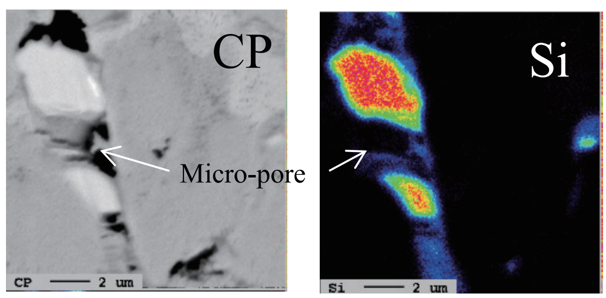

Fig. 12 Si distribution around micro-pores.

increased both the film strength and the amount of closed voids. It is probable that the closed void volume was increased as open surface nano-pores were obstructed by silica and micro-pore openings were covered by a silica film. This increase in the quantity of closed voids should also improve the heat shielding performance of the film,[4] and the thermal properties of the SiRPA are summarized in **Table 1**. Here, the thermal conductivity, λ, was calculated using the equation

$$\lambda = \rho \cdot C \cdot \kappa \,, \tag{3}$$

where ρ is the density, C is the specific heat (as determined by differential scanning calorimetry), and κ is the thermal diffusivity (as determined by laser flash analysis).

The κ value for the film was obtained from data for anodized aluminum using the double layer model. To evaluate the error induced by the density measurement method, the bulk density, ρ_1, and the apparent density, ρ_2, were used as ρ. The SiRPA was found to have a thermal conductivity 1% or less that of aluminum, while its volume specific heat was approximately half that of aluminum. The thermal properties of SiRPA are compared to those of other materials in **Fig. 14**.

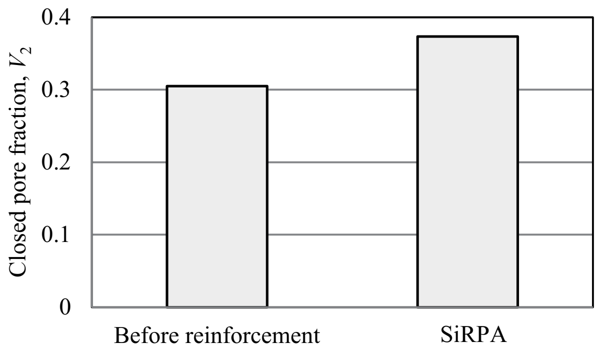

Fig. 13 Closed pore fraction before and after silica reinforcement.

Table 1 Thermophysical properties of SiRPA.

Used density in the calculation	ρ_1	ρ_2
Volumetric specific heat capacity kJ m^{-3} K	1300±140	2500±500
Thermal conductivity W m^{-1} K^{-1}	0.67±0.07	1.5±0.5

4. 4 Durability of SIRPA in a Combustion Chamber

To assess the durability of the SiRPA, a coating of this material was applied to the top surface of a piston (**Fig. 15**) and an engine breakdown test was performed (engine speed: 1400 rpm, common rail pressure: 58 MPa, exhaust gas recirculation rate: 40%, fuel injection quantity: 10 mm^3/stroke). The results confirmed that the thermal efficiency of the engine was improved by 1.8%.[9] The surface of the SiRPA before and after the engine breakdown test is shown in **Fig. 16**. The absence of peeling or cracking following

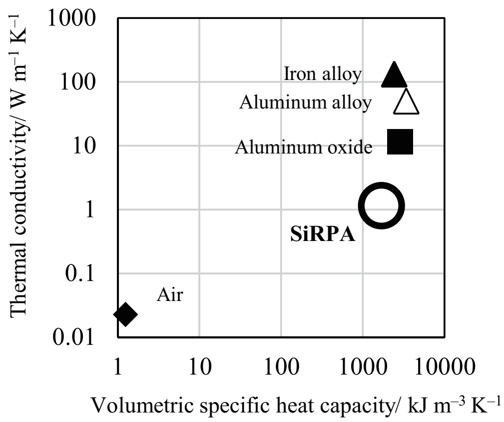

Fig. 14 Thermophysical properties of various materials.

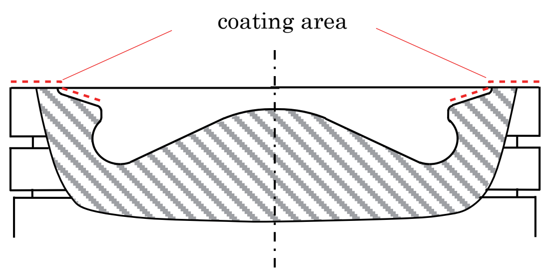

Fig. 15 Schematic of piston region coated with SiRPA.

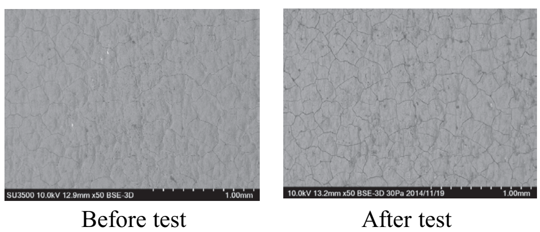

Fig. 16 SEM images of SiRPA surface before and after engine test.

the test demonstrates that the SiRPA had sufficient strength to withstand the combustion chamber conditions.

5. Conclusion

This work focused on the application of an anodized SiRPA film to an aluminum piston in order to test the TSWIN method. Both the film porosity and its viability in the combustion chamber were investigated. The conclusions are as follows:

1) The thermal conductivity of SiRPA is 1% or less than that of aluminum, while its volumetric specific heat is 50% or less.

2) The porosity of the anodized aluminum film results from a combination of micro-pores and nano-pores. The anodizing conditions have only a minimal effect on the porosity, while the effect of the alloy substrate composition (such as the Si content) is significant.

3) The SiRPA produced in this study does not collapse or peel off during the engine breakdown test. This material is an anodized aluminum film reinforced by the intrusion of insulating silica into the nano-pores and intercolumnar spaces using an inorganic glass agent (perhydropolysilazane).

4) The quantity of closed pores is also increased during reinforcement of the film and therefore the reinforcement improves the thermophysical properties of the material.

References

(1) Kosaka, H. et al., *Trans. Soc. Automot. Eng. Jpn.* (in Japanese), Vol. 44, No. 1 (2013), pp. 39-44.

(2) Assanis, D. N. and Mathur, T., *SAE Tech. Pap. Ser.*, No. 900903 (1990).

(3) Kawamura, H. and Akama, M., *SAE Tech. Pap. Ser.*, No. 2003-01-2265 (2003).

(4) Wakisaka, Y. et al., *Trans. Soc. Automot. Eng. Jpn.* (in Japanese), Vol. 47, No. 1 (2016), pp. 39-45.

(5) Nishikawa, N. et al., *Trans. Soc. Automot. Eng. Jpn.* (in Japanese), Vol. 47, No. 1 (2016), pp. 55-60.

(6) JIS H 0201: 1998, *Glossary of Terms Used in the Surface Treatment of Aluminum* (in Japanese).

(7) Nagayama, M. and Tamura, K., *Electrochim. Acta*, Vol. 12, No. 8 (1967), pp. 1097-1107.

(8) Sato, T. et al., *Theories of Anodized Aluminum 100 Q&A* (in Japanese) (1997), 262p., Kallos Publishing.

(9) Kawaguchi, A. et al., *Trans. Soc. Automot. Eng. Jpn.* (in Japanese), Vol. 47, No. 1 (2016), pp. 47-53.

Figs. 1, 3-16 and Table 1
Reprinted from Trans. Soc. Automot. Eng. Jpn. (in Japanese), Vol. 47, No. 1 (2016), pp. 55-60, Nishikawa, N. et al., Heat Insulation by "Temperature Swing" in Combustion Chamber Walls (Fourth Report) Film for Temperature Swing Heat Insulation,

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