Component Change Due to Plasma Thermal Spray Coating and the Effect of Heat Treatment on Film Composition

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Concerning the plasma thermal spray of Sn alloys, we have confirmed through EPMA analysis that the material ratio of the thermal spray coating differs from the material ratio of the thermal spray raw material. We have verified that this phenomenon is due to the high temperature of the plasma exceeding the evaporating temperature of the component elements. Therefore, by conducting thermal spray using thermal spray raw materials which are adjusted beforehand with consideration to changes in the component ratio, a thermal spray coating of the target component ratio was achieved. Furthermore, by conducting heat treatment that causes composition changes on the thermal spray coating after thermal spray, an adhesion power that exceeds shear strength was attained. The resulting thermal spray coating does not separate from the surface of the base material, as external forces cause breakage to occur within the coating. Therefore, a thermal spray coating with high reliability was achieved.

Key Words: thermal spraying, plasma spraying, adhesion, coating, white metal, heat treatment, EPMA

1. Introduction

The thermal spray method is known as a surface treatment method which enables thick coating treatment[1], with a wide variety of compatible materials and high versatility. Wire arc method is a simple and convenient thermal spray method, although the coating is more likely to contain non-melted components and porosity using this method[2], and the quality of the thermal spray coating may be poor. The plasma thermal spray method, which renders materials into a high-temperature melted state, is used as a processing method to reduce non-melted components. This method produces a higher quality state of melted coating compared with the wireless arc method[3,4]. However, most of the research up until now concerning the effects of the high temperature of the plasma on the coating examines the oxidation of thermal spray materials[5], leaving room for the examination of aspects such as changes in the element component ratio of the coating.

There are many types of materials compatible with the thermal spray method. Whilst there are many examples of using hard thermal spray materials[6,7] from among these types for the purpose of improving wear resistance, few examples exist that examine the use of soft materials. However, the compatible characteristics and seizure resistance of a soft coating are often demanded in the application of material to sliding components in addition to the wear resistance of a hard coating. Soft coatings are particularly susceptible to wear, and there is great demand for thick coating treatment which takes advantage of the characteristics of the high quality plasma thermal spray method. Tin (Sn) alloys are the leading example of suitable soft materials, as they are known for their high seizure resistance[8].

The improvement of adhesiveness is also an important issue insofar as the practical application of thermal spraying is concerned. There are cases[9,10] which observed improvement in the adhesiveness of the thermal spray coating by preheating the base material. However, as tin alloys have a low melting point, preheating the base material may cause melting flow of the coating and lead to difficulties in achieving a uniform coating thickness. Therefore, it is difficult to adopt preheating of the base material as a means of improving the adhesiveness of thermal spray coating with materials of low melting points.

Improving adhesiveness of the thermal spray coating can, for example, be achieved through laser heating the coating after thermal spraying[11,12]. Laser heating, however, can only be applied to limited types of heating surfaces due to the difficulty of applying this method to cylindrical internal surfaces, and requires the introduction of elaborate equipment. If possible, we aim to curb the cost of accessory equipment and raise versatility within heat treatment of thermal spray coating by utilizing simple methods such as using a heat treatment furnace. In particular, it will be more effective to reduce non-melted particles and porosity[4] within the thermal spray coating through simple heat treatment. Not only can adhesive strength be improved, but other effects such as changes in

coating composition may also be obtained through heat treatment of the coating. Further changes in the physical properties of the coating can also be expected from these structural changes.

This report first examines component change during plasma thermal spraying. Next, it investigates improvements to the adhesiveness of the thermal spray coating by a simple heat treatment furnace in order to increase adhesiveness. It also focuses on structural changes of the thermal spray coating caused by heat treatment, and examines the possibility of imparting added value through heat treatment.

2. Experiment Method

2. 1 Test Materials

For the thermal spray method, the melted state of the raw material powder was favorable, and a plasma thermal spray gun (Sulzer Metco Japan Co., Ltd.) with low contamination from non-melted materials was used. For the thermal spray raw material, a tin-based antimony-copper-tin alloy with 7.5 wt% of antimony (Sb) and 3.5 wt% of copper (Cu), commonly known as "white metal" [8], was used. Carbon steel S45C (Carbon: 0.42-0.48%, Silicon: 0.15-0.35%, Manganese: 0.60-0.9%) and a 30x30x5mm plate were used as the base materials for thermal spray treatment. After grinding the base material surface to 1.6 µmRz (JIS), the specimen was blasted vertically for 10 seconds with ϕ200 µm steel balls at a distance of 300mm. Then the surface of the base material was plasma thermal spray coated with a 1mm thick layer of antimony-copper-tin alloy.

Heat treatment of the thermal spray coating was also examined as a way to further improve adhesiveness. A heating furnace (model PS-IIS, ESPEC Corp.) was used for the heat treatment of the thermal spray coating. The specimen for measuring coating adhesiveness and strength was wire cut from the base material after thermal spraying to a 6mm length x 5mm width x 1mm thick specimen as shown in **Fig. 1**.
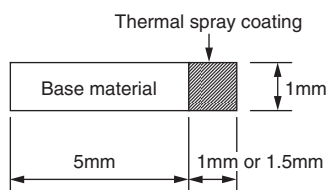

Fig. 1 Specimen

2. 2 Experiment Method

The hardness of the thermal spray coating was measured using a Micro Vickers Hardness Tester (Model MVK-E, Akashi Seisakusho Ltd.). The measuring load of the coating hardness was 50 N, and the load holding time was 30 seconds. A shear testing machine [13] was used to evaluate the measurements of adhesiveness and coating strength. Furthermore, the adhesive strength and coating strength were measured via a shearing blade after a load was added using an Amsler testing machine, so that shear strength will act on the surface of the coating and base material. The load where flaking of the coating occurs was measured and established as the adhesive strength. Moreover, by moving the position of the shearing blade to the center of the coating cross-section using the testing machine, the testing machine can induce shear failure within the coating. The yield load at which breakage of the coating occurs was valued as the coating strength.

The post-thermal spraying structure of the coating was observed using a metallurgical microscope, and the components were analyzed using an EPMA (EPMA: Electron Probe Microanalyzer, WDS: Wavelength Dispersive X-ray Spectrometer Model JXA-8800RL, JEOL Ltd.). The accelerating voltage of the EPMA is 15 kV, and the current of the probe is 1 µA. An XRD (XRD: X-ray diffractometer model RINT-1500V, Rigaku Corp.) was also used in the coating composition analysis.

3. Experiment Results

3. 1 Observation and Analysis of Thermal Spray Coating

With thermal spraying, a porous coating is obtainable, whereas coating properties with ductility characteristic of a tin alloy are difficult to obtain. In addition, the coating adhered mainly to the base material surface due to an anchor effect, which makes it difficult to obtain a high adhesive strength. Therefore, the states of deposition and adhesion of the coating were checked through cross-sectional observation of the coating.

Figure 2 shows the results from an observation of the thermal spray coating surface using a Scanning Electron Microscope (SEM). The white metal shows a low melting point and a favorable melted state of the thermal spray coating powder. Furthermore, through the use of the plasma thermal spray method, a dense coating with minimal porosity is achieved, with the exception of the surface layer. The coating is also relatively well adhered to the surface of the base material. A nickel-aluminum thermal spray coating layer was also used for the intermediate layer in the prototype shown in **Fig. 2**, however an intermediate layer is not deposited for trials discussed later in this report, in order to evaluate the characteristics of the tin alloy thermal spray coating layer without the influence of the intermediate layer.

Next, the distributions of antimony and tin both demonstrated microstructural and even dispersion. This was indicated by the results of the EPMA analysis on the thermal spray coating cross-section, shown in **Fig. 3**. This dispersion microstructure is regarded as the rapid cooling structure [14] characteristic of the coating.
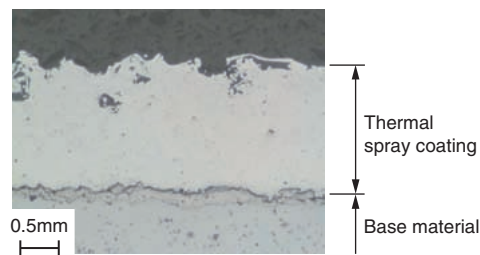
Fig. 2 SEM image of thermal spray coating cross-section
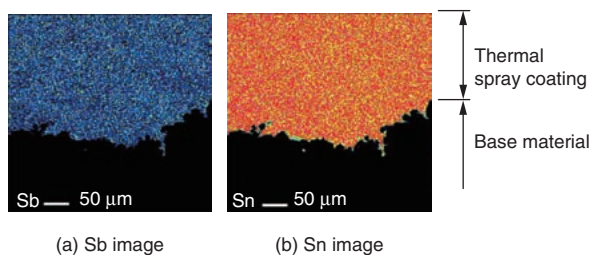

(a) Sb image   (b) Sn image

Fig. 3 EPMA analysis of thermal spray coating cross-section

3. 2 Adjustment of Component Change and Component Comparison of Thermal Spray Coating

Next, a quantitative analysis on the thermal spray coating was conducted using an EPMA. The component ratio is shown in **Table 1** as Material A. Changes in the component ratio of the thermal spray coating were seen in an analysis of the coating components. The component ratio within the coating after plasma thermal spray coating is 4 wt% of antimony, 11 wt% of copper, and 85 wt% of tin. The component ratio of raw materials before thermal spraying, shown in **Table 1**, demonstrates a decrease in the percentage of antimony and an increase in the percentage of copper within the coating.

Table 2 shows the boiling point, melting point and evaporation temperature of each element. For the evaporation temperature of each element, the temperature when the vapor pressure reaches 10^{-2} Torr was used as a reference value in order to compare the ease of vaporization for each element considering the pressure reduction during thermal spraying. The evaporation temperatures are copper > tin > antimony, the lowest being antimony at 678℃. Meanwhile, the particle temperature of plasma thermal spray is reported as being 1 500-2 300℃, even at a distance of 80mm from the mouth of the plasma thermal spray nozzle[15]. From this, it is estimated that the base material is exposed to temperatures high enough to vaporize at least antimony. As a related example[16], an attempted component separation was conducted with an iron-cobalt-nickel alloy using plasma reaction, and it is believed that changes in the components of the alloy, which is thermal spray raw material, also occurs in the process of plasma thermal spraying due to the high temperature of plasma reaction.

Table 1 Results of EPMA analysis on thermal spray raw material and coating

		Sb	Cu	Sn
Material A	Raw material (wt%)	7.5	3.5	bal.
	Thermal spray coating (wt%)	4	11	bal.
Material B	Raw material (wt%)	12	2	bal.
	Thermal spray coating (wt%)	8	4	bal.

Table 2 Characteristic temperature of each element

	Sb	Cu	Sn
Boiling point (℃)	1 587	2 562	2 602
Melting point (℃)	630.63	1 084.6	231.93
Evaporation temperature (℃)	678	1 273	1 189

Furthermore, considering the melting points, even the highest melting point temperature of copper is at 1 084.6℃, which is heated to a temperature where thermal spray particles are sufficiently melted. In other words, it is apparent that there is excellent melting of thermal spray raw materials within the high temperature plasma thermal spray method, however the elements with low evaporation temperatures vaporize and decrease.

This change in component ratio is assumed to affect the physical properties of the thermal spray coating. To obtain a thermal spray coating with the intended physical property values, it is desirable that the component ratio of the coating also be as intended. It is thought that adjusting the component ratio of the thermal spray raw materials with prior consideration of changes to the component ratio is effective in the adjustment of the coating component ratio for this purpose.

By adding antimony powder to a thermal spray raw material powder composed of 7.5 wt% antimony, 3.5 wt% copper, and 89 wt% tin, thermal spraying was conducted using Material B (thermal spray material comparison shown in **Table 1**, composed of 12 wt% antimony, 2 wt% copper, and 86 wt% tin. It was confirmed that a thermal spray coating with almost the exact intended component ratio of 8 wt% antimony, 4 wt% copper, and 88 wt% tin was obtained through the results of the EPMA analysis of the coating sprayed from Material B, in which the component ratio has been adjusted. These results where the ratio of antimony was increased within the raw material for thermal spraying also support the assumption that changes in the thermal spray coating component ratio occur from the selective loss of antimony which has a low evaporation temperature.

As mentioned earlier, the coating was deposited using a material in which the component ratio has been adjusted, and the element distribution of the thermal spray coating cross-section was analyzed with an EPMA. EPMA analysis showed that the thermal spray coating was formed from a microstructure in which antimony was distributed evenly without visible segregation. The microstructure was a rapid cooling structure ordinarily seen in thermal spray coatings, and no notable changes due to alterations to the raw material component ratio were evident in a cross-sectional observation of the thermal spray coating.

3. 3 Heat Treatment of Thermal Spray Coating

A major issue of thermal spray coatings is the lack of adhesive strength of the coating to the base material. The base material is usually preheated at the time of thermal spraying[17] as a measure to improve adhesive strength. However, melting flow occurs with the tin alloy thermal spray coating due to preheating, making it difficult to control coating thickness. Therefore, preheating is not considered for the purposes of this report.

As a post-treatment to the thermal spray coating, we examined heat treatment for a brief period for the coating and base material surface that would create a melted or half-melted state. The thermal spray coating was the aforementioned rapid cooling microstructure, although heat treatment after thermal spray for the coating was thought to effect coating qualities other than adhesive strength or composition. Therefore, a study was conducted for the heat treatment of the coating after thermal spraying as a method to improve the adhesiveness and modify the structure of the coating.

The heat treatment pattern is shown in **Fig. 4**. After heating the antimony-copper-tin alloy past its melting point to re-melt it, the alloy was cooled naturally inside the furnace. The maximum heating temperature was set to 395℃, at which the temperature was held for 5 minutes. This allowed shortening of the holding time at high temperatures at which coating thickness can easily change due to melting of the coating. This heat treatment of the coating after thermal spraying exceeded the melting point of the thermal spray material, however no signs of melting were observed seemingly in the coating.
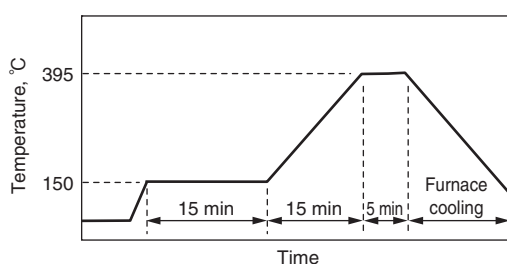

Fig. 4 Heat treatment pattern

3. 4 Structural Analysis of Thermal Spray Coating after Heat Treatment

Figure 5 shows the analysis after heat treatment of the thermal spray coating deposited from Material A (7.5% antimony-3.5% copper-tin) which has an unadjusted component ratio. The coating deposited from the raw material without component ratio adjustment maintains the microstructure characteristic of thermal spraying even after heat treatment, without any other visible structural characteristics.

Next, **Fig. 6** shows the analysis results after heat treatment of the thermal spray coating deposited from Material B (11% antimony-2% copper-tin) which has an adjusted component ratio. There are obvious changes within the structure of the heat treated coating deposited from the raw material with adjusted components. A cubic-shaped structure containing antimony and an acicular structure containing copper are visible in the EPMA analysis of the Material B coating after heat treatment. Furthermore, the presence of deposited materials from the heat treatment of the coating is demonstrated to differ depending on the component ratio of the thermal spray raw material. Based on the comparison of the coatings of both materials, it is thought that the cubic-shaped antimony structure and acicular copper structure occurring after heat treatment are formed by applying heat treatment under a specific element ratio.

Figure 7 shows the results of the XRD analysis after heat treatment of the Material B coating. The formation of SbSn and Cu_6Sn_5 can be recognized from the high-strength peaks shown through XRD analysis of the coating after heat treatment. Based on a comparison of the XRD analysis in **Fig. 7** and the EPMA analyses in **Figs. 5** and **6**, we can regard the cubic-shaped structures and acicular structures formed after heat treatment as SbSn and Cu_6Sn_5, respectively.
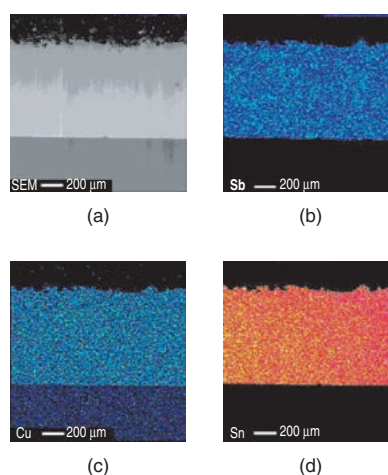

Fig. 5 EPMA analysis of Material A heat-treated after thermal spray
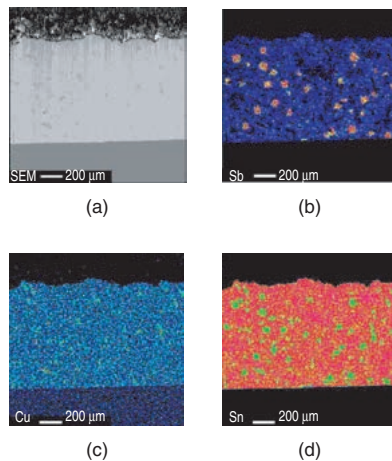
(a) (b)

(c) (d)

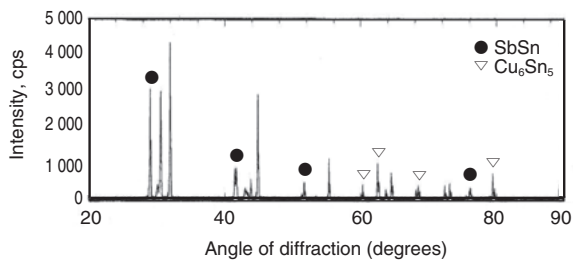**Fig. 6** EPMA analysis of Material B heat-treated after thermal spray

Fig. 7 XRD analysis of coating heat-treated after thermal spray

There is also a report on the high hardness of SbSn, Cu_6Sn_5 and the bulk material, tin[18]. The structure of the Material B coating after heat treatment is thought to be that of the soft bulk material reinforced with a deposit of slightly higher hardness. In the field of tribology, a coating such as this is identified as having low friction, wear resistance and seizure resistance. Through component ratio adjustment of the thermal spray raw material and heat treatment of the coating after thermal spraying, a desirable coating structure was obtained for a tin alloy coating used in sliding applications.

3. 5 Changes in Hardness and Shear Strength of Thermal Spray Coating due to Heat Treatment

A study was conducted on the physical property changes of the thermal spray coating accompanying the aforementioned structural changes due to heat treatment. First, after heat treatment of the coating, the coating hardness was evaluated using the Vickers Hardness Tester, and the adhesive strength and shear strength were evaluated using the shear testing machine. **Figure 8** shows the measurement results for the hardness, adhesive strength and shear strength of the coating.

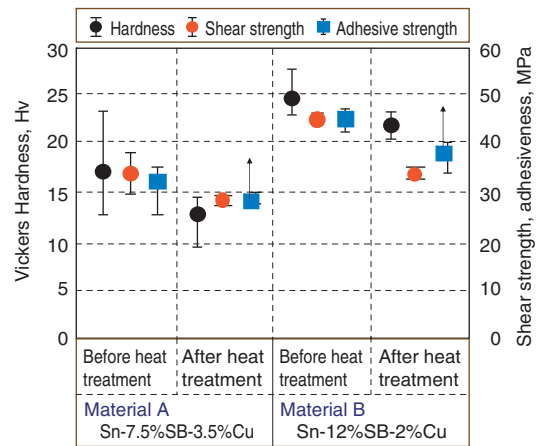First, a comparison of the coating properties according to differences in thermal spray material was made

Fig. 8 Hardness, shear force and adhesiveness of Material A and B before and after heat treatment

for the coatings before heat treatment. The coating hardness of Material B (adjusted component ratio) is approximately 1.4 times higher than Material A (non-adjusted component ratio). Material B also exhibits a high shear strength value, approximately 1.3 times that of Material A. The results of the component ratio adjustment show the same level of difference in the hardness and shear strength of the coatings, confirming that the coating properties changed according to the adjustment of the raw material component ratio.

Next, the heat treated thermal spray coatings were examined. The hardness of the Material A coating decreases by approximately 25%. Meanwhile, the decrease in hardness of the Material B coating stops at around 10%. Furthermore, through heat treatment, shear strength decreases by 15% in the Material A coating, and decreases by 25% in the Material B coating. Concerning the physical property changes of the coating due to heat treatment, hardness largely decreased in the Material A coating, and shear strength largely decreased in the Material B coating. In other words, the tendencies of hardness and shear strength are reversed between the materials.

The decrease in coating hardness can be regarded as the annealing effect of the heat treatment. In this case, it is estimated that the decrease in hardness of the Material B coating was eased by the deposition of hard structures such as SbSn and Cu_6Sn_5. In contrast, the shear strength tendencies of the Material A coating and Material B coating are reversed, with greater decrease in the shear strength of the Material B coating. It is estimated that the densities of the antimony and copper within the tin decreased due to the formation of deposits within the Material B coating, leading to a decrease in the shear strength of the coating.

3. 6 Changes in Adhesive Strength of Thermal Spray Coating due to Heat Treatment

Next, a study was conducted on the expected changes to the adhesive strength of the coatings due to heat treatment. A comparison of the raw materials revealed that the adhesive strength before heat treatment of the Material B coating was 1.4 times that of the Material A coating. In regards to changes in adhesive strength after heat treatment, the adhesive strength of the Material A coating decreased by approximately 10%, while the adhesive strength of the Material B coating decreased by approximately 15%. Although this appears to be a decrease in adhesive strength, this value cannot directly be established as adhesive strength. This is because with measurement of adhesive strength through the shearing method, if shear failure within the coating precedes interfacial peeling of the coating/base material, it is difficult to obtain a measured adhesive strength value that surpasses the shear strength of the coating. Within this experiment as well, shear evaluation of adhesive strength of heat treated materials shows no peeling of the coating on the base material surface. Taking this into account, arrows were appended to the data plot of **Fig. 8** in order to express the absence of visible peeling.

As shown in the measured results in **Fig. 8**, before heat treatment the adhesive strengths of the coatings are less than the shear strengths, however, after heat treatment, the adhesive strengths surpass the shear strengths. As this characteristic in which the adhesive strength of the coating surpasses shear strength is not appear before heat treatment, it is attributed to improved adhesive strength due to the melting of the coating near to the surface of the base material, and the result of changes in the coating structure. Concerning the coating, we confirmed the differences due to the existence of reheat treatment of breakage after shear testing. **Figure 9** shows the results of a light microscope observation of the coating after shear testing. The non-heat treated coating (a) in **Fig. 9** shows breakage at the coating and base material interface, which is the weakest area. On the other hand, the heat treated coating (b) shows breakage within the coating, the weakest area, but shows no breakage at the coating and base material interface. That is, it was confirmed that peeling at the coating and base material interface does not easily occur after heat treatment of the coating, which supports the estimation that the adhesive strength after heat treatment is higher than the value in **Fig. 8**. The improvement in adhesiveness due to heat treatment is estimated to be the result of the coating melting and increasing contact area with the plate, which improves anchor effect.

It is predicted that the base material surface coating will not easily peel when a coating with greater adhesive strength than shear strength is machined by shear failure

within the coating, even when, for example, shear force is used on the thermal spray coating during machining. As the coating surface is rough after thermal spraying, preventing breakage enabling post-processing of the coating is a favorable characteristic for the thermal spray coating, which often requires post-finish processing. A thermal spray coating with greater adhesive strength than shear strength due to post-thermal spray heat treatment was confirmed to have sufficient characteristics for practical application.
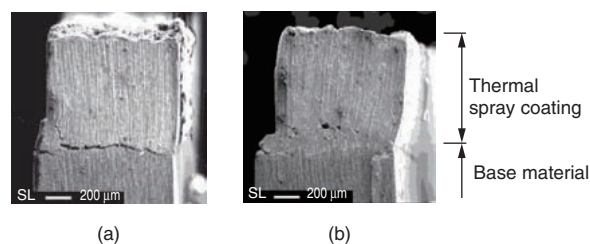

Fig. 9 Specimen after adhesiveness evaluation

4. Conclusion

A tin alloy plasma thermal spray coating with a dense and even composition was obtained through plasma thermal spraying. On the other hand, components changes were observed due to the influence of high temperatures during plasma thermal spraying, which were regarded as a problem with the plasma thermal spray method. By adjusting the raw material after first considering changes to the component ratio of the coating due to plasma thermal spraying, the intended component ratio for the coating was achieved. More specifically, it was discovered that plasma thermal spraying requires consideration of the raw material composition in regard to the target coating composition.

Through heat treatment to raise the adhesive strength of the coating, a coating that does not peel on the coating/base material interface was achieved. To prevent interfacial peeling of the coating, it was important that the adhesive strength of the coating surpasses its shear strength. Heat treatment causes a decline in shear strength due to softening of the coating, which further prevents interfacial peeling. The heat treatment method is particularly effective for raising the adhesive strength of tin alloys with low melting points. It can be expected that the simple method of heat treatment in a furnace is also applicable to thermal spray coatings on internal surfaces, for which methods such as laser heating are difficult.

Furthermore, with heat treatment of tin alloy coatings, hard cubic-shaped and acicular structures are deposited, confirming that coating quality adjustment is also possible. Within tin alloys in particular, this structural change was shown to inhibit the decrease of coating

hardness and increase adhesive strength of the coating to greater than the shear strength. Heat treatment after thermal spraying is effective in coating composition and coating quality adjustment and shows promise as a useful discovery which has found new possibilities within thermal spray technology.

Acknowledgements

References

1) N. Sakoda, M. Hida, Y. Takemoto, K. Sakakibara, T. Tajiri: Journal of the Japan Institute of Metals, vol.66, No.12 (2002) 1304-1310.

2) T. Watanabe, M. Usui: Journal of the Japan Institute of Metals, vol.63, No.1 (1999) 98-102.

3) S. Kuroda, H. Murakami: Materials Science and Technology, vol.75, No.8 (2005) 741-745.

4) K. Sonoya, C.Li, F.Li: Quarterly Journal of the Japan Welding Society, vol.19, No.1 (2001) 27-36.

5) Y. Hisada: Engineering Materials, vol.41, No.11 (1993) 59-63.

6) K. Toyokura: Engineering Materials, vol.41, No.11 (1993) 48-53.

7) S. Moroboshi, Y. Ozawa, S. Takahashi: Journal of Japanese Society of Tribologists, vol.42, No.12 (1997) 925-957.

8) K. Honda, I. Chida, M. Saito, Y. Ito, S. Sugiyama, K. Kobayashi: Quarterly Journal of the Japan Welding Society, vol.12, No.3 (1994) 379-385.

9) S.Tobe: Engineering Materials, vol.41, No.11 (1993) 36-41.

10) K. Honda, I. Chida, T. Fuse, T. Murakami, K. Kobayashi: Quarterly Journal of the Japan Welding Society, vol.14, No.3 (1996) 510-515.

11) Y. Inoue, T. Ono, T. Noutomi, A. Dewa, M. Toyota, M. Tsukamoto: Quarterly Journal of the Japan Welding Society, vol.19, No.1 (1991) 167-173.

12) K. Nakanishi, H. Tachikawa: Proceeding of the 64th Japan Thermal Spray Conference, (1996-10) 55-56.

13) J. Kitamura: Journal of Japan Thermal Spray Society, vol.47, No.1 (2010) 23-25.

14) Y. Horie: Engineering Materials, vol.41, No.11 (1993) 24-29.

15) Y. Shoman, M. Kouso, T. Narikiyo: Collected Abstract of the Japan Thermal Spray Conference, vol.45, ('89-9) 224-225.

16) A. Takeuchi, T. Watanabe: Journal of the Japan Institute of Metals, vol.63, No.1 (1999) 28-33.

17) M. Fukumoto, I. Ohgitani, M. Shiiba, T. Yasui: Quarterly Journal of the Japan Welding Society, vol.22, No.3 (2004) 398-402.

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