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Investigation of Aluminum Coating with Dispersed Nanoscale Quasicrystalline Particles Produced by Cold Spray

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Quasicrystalline phase has the mechanical properties which are excellent in high hardness, high temperature strength, and so on. Recently, heat resistant aluminum alloys with dispersed nanoscale quasicrystalline particles have been developed. Since the material is exposed under elevated temperature when the conventional thermal spray is used for production of the aluminum coating, it is apprehensive about quasicrystalline phase decomposing to intermetallic compound phase. In this study, aluminum coating with dispersed quasicrystalline particles have been produced by using the cold spray which can comparatively be operated at lower temperature. Rapidly solidified aluminum alloy powders were produced by high pressure gas and water atomization process. The cold spray was carried out on helium gas; 3 MPa and 400°C conditions. The obtained coating had a comparatively precise microstructure which seldom contains macroscopic voids. As a result of X-ray analysis and DSC measurement, the quasicrystalline dispersed structure is maintained even after the cold spray coating process. Also from TEM observation, quasicrystalline dispersed structure was retained in the internal coating. Furthermore, the metallic bond occurred at particle-particle interface and particle-substrate interface. As mentioned above, producing the aluminum alloy coating with dispersed nanoscale quasicrystalline particles have been succeeded.

Keywords: aluminum-based alloy, quasicrystalline phase, cold spray coating, high elevated-temperature strength

1. Introduction

In the viewpoint of protecting global environment, the needs of the weight saving to automotive parts are growing year by year[1)]. Especially for engine parts, improvement of the heat resistant material is required. In order to fulfill to such requirements, new aluminum-based extruded bulk alloys with very high ultimate tensile strength at elevated temperature was developed[2)]. Figure 1 shows the ultimate tensile strength of the developed alloy, compared with conventional high strength aluminum alloy. The developed alloy has high strength even at elevated temperature of 300°C or more. This is considered to be caused by the structure with fine and uniform dispersion of the quasicrystalline particles which show excellent hardness, and are very stable at elevated temperatures, as seen in Fig.2[3-4)]. However, production of the extruded bulk alloy takes a lot of processes and costs.

In this research, aluminum coatings with dispersed nanoscale quasicrystalline particles have been produced by using the cold spray, which can be operated at comparatively low temperatures[5-6)]. If this is realizable, it is thought that efficient strengthening of the components is attained with this technology.

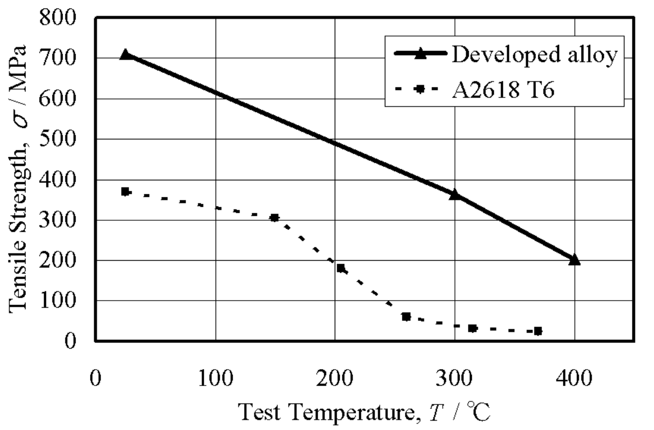


Fig. 1. Temperature dependence of ultimate strength as a function of testing temperature for the developed alloy ($Al_{93}Fe_{2.45}Cr_{2.45}Mo_{0.5}Ti_{0.8}Co_{0.8}$) produced by extrusion of the atomized powder.

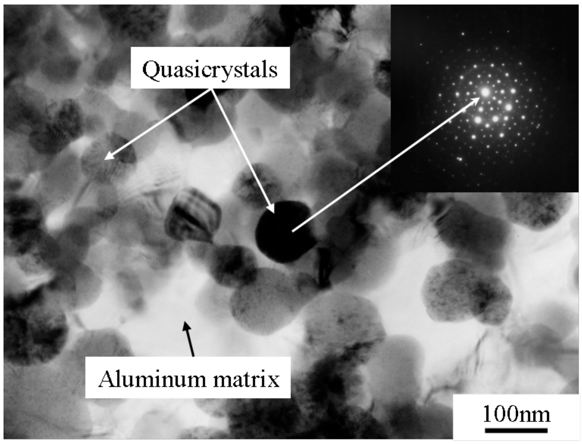


Fig. 2. Bright field electron micrograph and selected area electron diffraction pattern for the developed alloy ($Al_{93}Fe_{2.45}Cr_{2.45}Mo_{0.5}Ti_{0.8}Co_{0.8}$) produced by extrusion of the atomized powder.

2. Experimental procedures

Rapidly solidified powders were produced by the atomization method, which consists of a combined high-pressure gas and water atomization process[7]. The chemical composition of the powder is shown in Table1, and the mean particle diameter was 14.14μm. Table 2 shows testing conditions of the cold spray. Nitrogen gas or helium gas was used as process gas. The nozzle intake temperature and pressure were 400 °C and 3 MPa, respectively. The substrate surface was degreased and was not blasted before spraying.

The microstructure of the coating was examined by optical microscope from a mirror-finished cross-section. The structure of the coating was characterized by X-ray diffraction analysis (XRD). The microstructural observations were conducted by transmission electron microscopy (TEM) for the coating at the internal region and interface region between substrate and coating.

For the evaluation of the mechanical properties of the coating, Vickers hardness measurements were carried out. Also the coating tensile tests were performed at room temperature (RT), 300 °C and 400 °C. Coated specimens of 6 mm gage width, 8 mm gage length and 1.5 mm thickness for the tensile test were cut off from coating by wire electric discharge machining. For the tensile test at elevated temperatures, soaking of 100 hours was performed at each temperature.

Table 1: Chemical compositions (atomic %) of the aluminum powder

Al	Cr	Fe	Ti	Co
94.96	2.24	1.68	0.56	0.56

Table 2: Conditions of the cold spray

Process gas	Nitrogen or Helium
Nozzle intake temperature	400 °C
Nozzle intake pressure	3 MPa
Spray distance	20 mm
Gun traverse speed	100 m/s
Substrate	AA5052 (AlMg2.5)

3. Results and Discussion

3.1 Microstructure

Figure 3 shows the microstructure of cold spray coating produced with nitrogen gas. In the macroscopic image (Fig.3 (a)), the coating which has thickness of 500 μm or more was formed. However, at the internal coating region of (A), some macroscopic voids were generated (Fig.3 (b)). On the other hand, Fig.4 shows dense microstructure of cold spray coating produced with helium gas. It also has about 500 μm thickness (Fig.4 (c)), and there are almost no voids at internal region of (A)

(Fig.4 (d)). It is thought that the different microstructures were caused by difference in gas velocity between nitrogen gas and helium gas. According to difference of gas constant, flow velocity of helium gas is much higher than that of nitrogen gas. Therefore, in the case of using helium gas, the spray particles deformed intensively, which resulted in a dense coating.

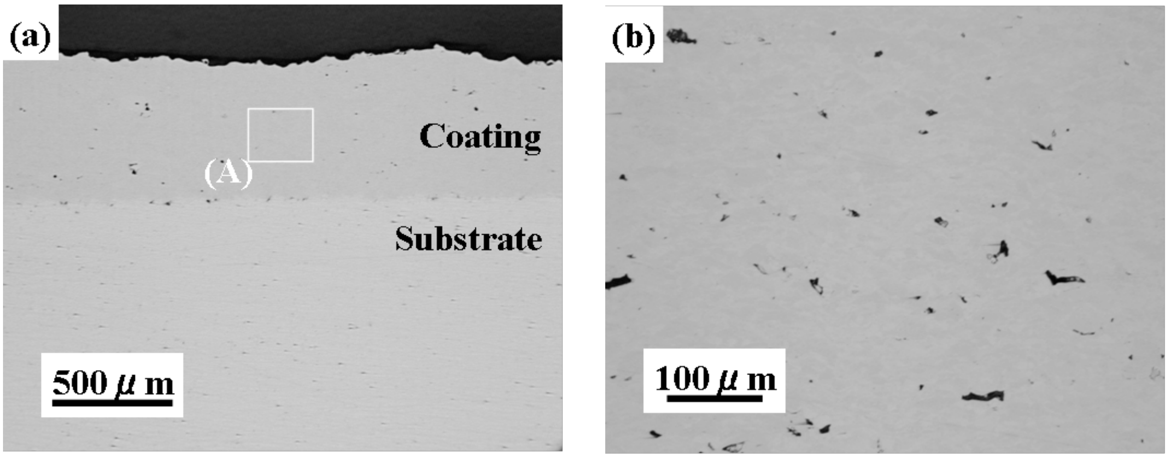


Fig. 3. Microstructure for cross-section of cold sprayed coating with nitrogen gas.
(a) Macroscopic image and (b) the magnified image.

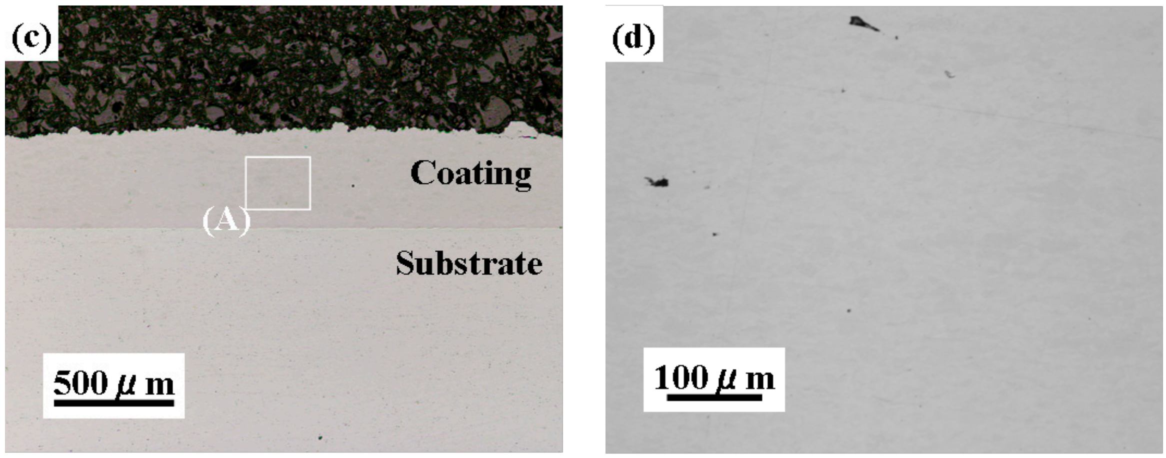


Fig. 4. Microstructure for cross-section of cold sprayed coating with helium gas.
(c) Macroscopic image and (d) the magnified image.

3.2 Structural analysis of the cold spray coating

When the sprayed material is exposed to much higher temperature in the conventional thermal spray coating, quasicrystalline phase has a possibility of decomposing into intermetallic compound phase[8]. To analyze the structure of the cold spray coating, XRD analysis was carried out. Figure 5 (a) shows XRD pattern of the rapidly solidified powder before cold spraying. The XRD peaks of the alloy correspond to those of fcc-aluminum phase and quasicrystalline phase. The XRD patterns of the cold spray coating produced with nitrogen gas and helium gas are shown in Fig. 5 (b) and (c), respectively. There is almost no difference in the patterns between rapidly solidified powder and cold sprayed samples. This suggests that the quasicrystalline phase is retained after cold spraying.

Figure 6 shows TEM microstructures of cold spray coating produced with helium gas. The observed field corresponds to the center of the coating. Grey or black particles are quasicrystalline particles, and white region is fcc-Al matrix. Nanoscale quasicrystalline particles are dispersed in the aluminum matrix phase. It means that microstructure of the original powder is retained after cold spraying. The dotted line in Fig. 6 (a) shows the interface between adjoining powders.

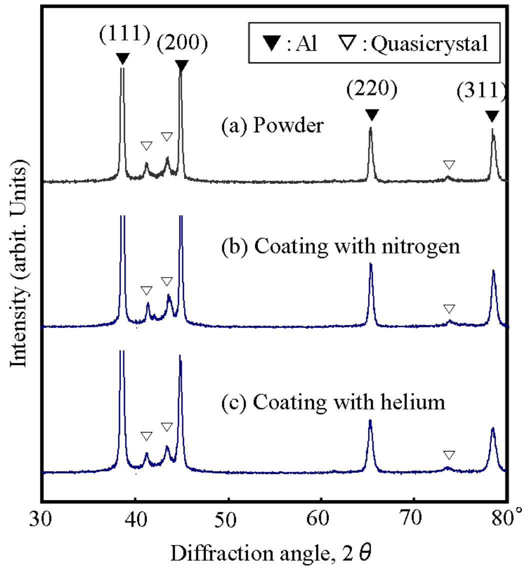


Fig. 5. X-ray diffraction patterns of (a) atomized aluminum powder dispersed with quasicrystalline particles, (b) cold spray coating with nitrogen gas and (c) cold spray coating with helium gas.

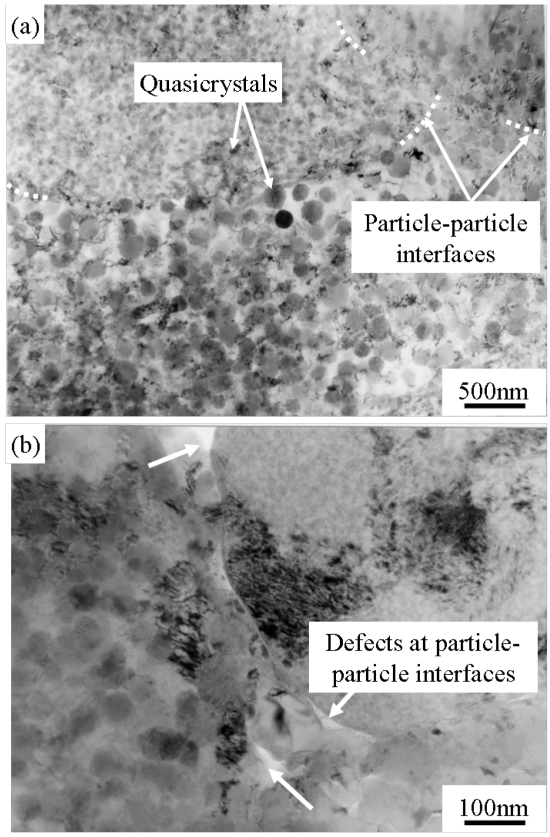


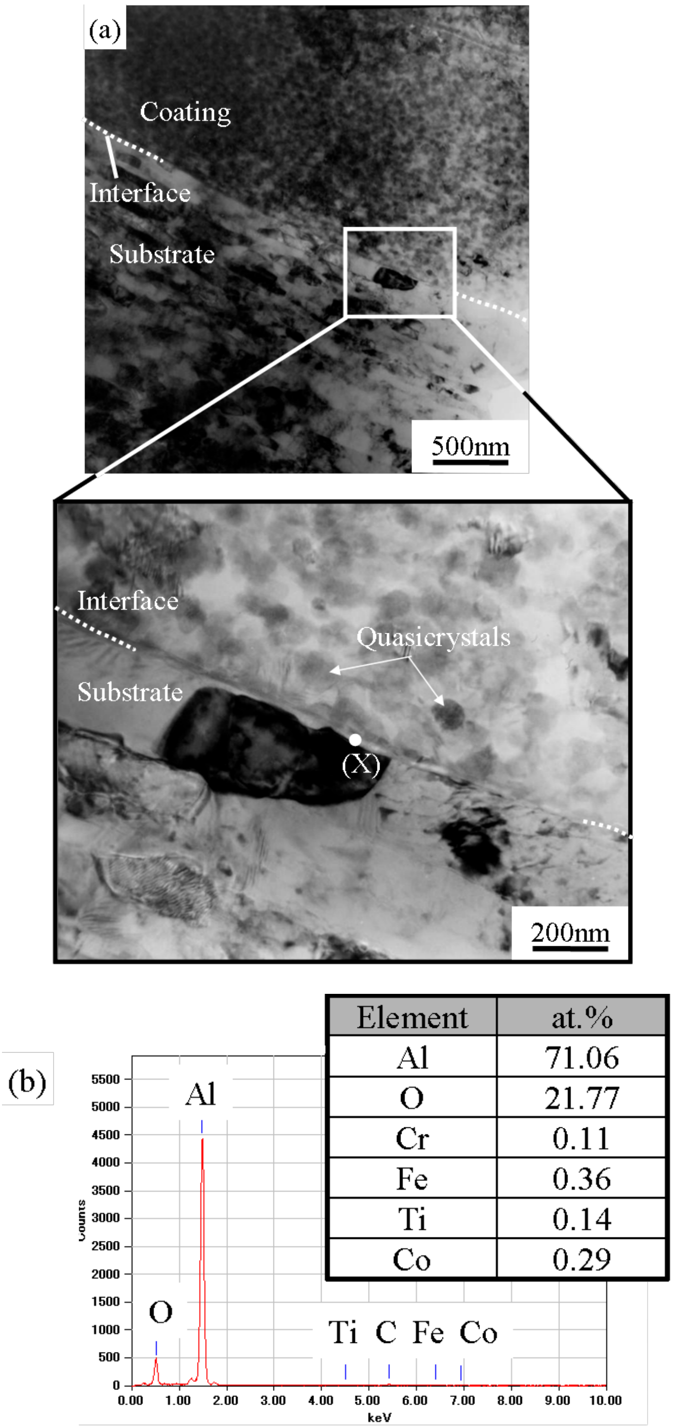
Fig. 6. TEM microstructures of the helium gas cold sprayed coating at the internal region. (a) Interfaces among particles with good bonding nature and (b) interfaces among particles with defects.

The difference in the size of the quasicrystalline particles in each powder is based on the difference in the cooling rate at the time of powder production. At the interface between particle and particle, there is no evidence of melting, but each powder joined in the state of the solid phase. However, there are some defects at another region of particle-particle interface as shown in Fig.6 (b).

Figure 7 (a) shows TEM microstructures of the cold spray coating with helium gas at the interface region between coating and substrate. There is also no evidence of melting at the interface. As shown in the magnified image, quasicrystalline particles are dispersed in aluminum matrix phase. It means that the microstructure of the original powder is retained even at interface between coating and substrate. The dotted line shows the interface between coating and substrate. The substrate and powder are joined in the state of the solid phase. However, at point X, it became clear that the thin oxide film remains as a result of TEM/EDS analysis (Fig.7 (b)). On the other hand, aluminum grains of the substrate are refined to submicron size. It is considered to be attributed to large strain to have been introduced into the substrate by the powder collision in the cold spray process.

3.3 Mechanical Properties of the cold spray coating

Figure 8 shows results of Vickers hardness tests of the cold spray coatings. For reference, the dotted line shows the hardness of the extruded bulk alloy produced with the equivalent powder. Cold spray coating produced with helium gas or nitrogen gas has hardness higher than that of the extruded bulk alloy. In the extruded bulk alloy, dynamic recrystallization occurred in the aluminum matrix under hot extrusion. On the other hand, since the cold spray was processing at comparatively low temperatures, work hardening occurred in the aluminum matrix. It is thought that the process difference caused the difference in their hardness. There is also hardness difference between the coating deposited using helium gas and the coating using nitrogen gas. Since particles deformed more intensively in the case of helium gas, it is thought that much work hardening was produced.



Element	at.%
Al	71.06
O	21.77
Cr	0.11
Fe	0.36
Ti	0.14
Co	0.29

Fig. 7. (a) TEM microstructures of the helium gas cold sprayed coating at the interface between particle and substrate. (b) TEM/EDS analysis result at the interface between particle and substrate (at the point of (X)).

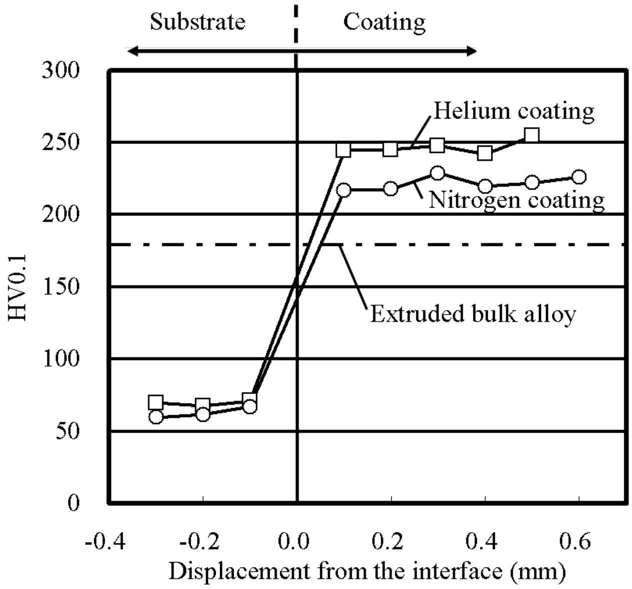


Fig. 8. Vickers hardness of the cold sprayed coating compared with extruded bulk alloy with the same powder.

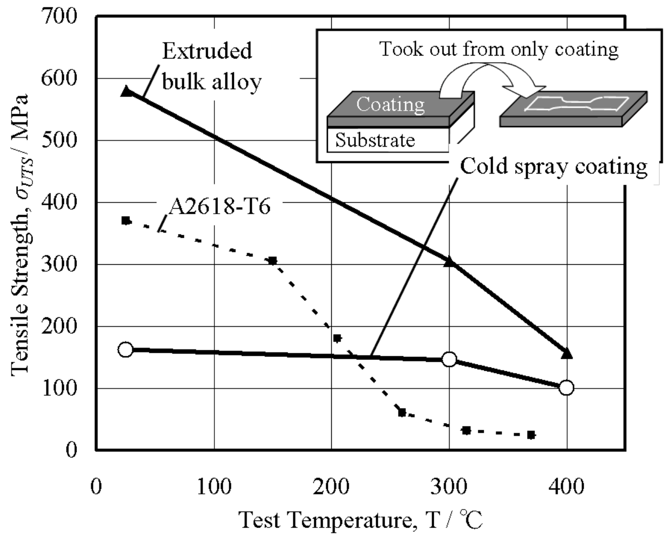


Fig. 9. Temperature dependence of ultimate strength as a function of testing temperature for the cold sprayed coating took out from only coating compared with the extruded bulk alloy.

In order to evaluate the mechanical property of the coating in detail, the coating tensile tests were carried out. The tensile test specimen was cut out from the coating produced with helium gas. Figure 9 shows relationship between tensile strength and testing temperature. The tensile strength of the coating is remarkably lower as compared with the extruded bulk alloy of the equivalent powder. Although the coating has high tensile strength at elevated temperature, it exhibited a strength lower than that of conventional aluminum alloy (AA2618) at room temperature. This result disagrees with the result of the hardness testing of the cold spray coating.

In order to clarify the factor of the disagreement, etched microstructural observation was carried out for extruded bulk alloy and cold spray coating. Figure 10 shows comparison of microstructure between extruded bulk alloy and cold spray coating. In the extruded bulk alloy, particles deformed severely and particle-particle interfaces are not clear. It means that good bonding formed among particles in the extruded bulk alloy. On the other hand, many defects were present at particle-particle interfaces in the cold spray coating. Based on the above, it is thought that lower tensile strength of the cold spray coating is resulted from the poor bonding nature at particle-particle interfaces.

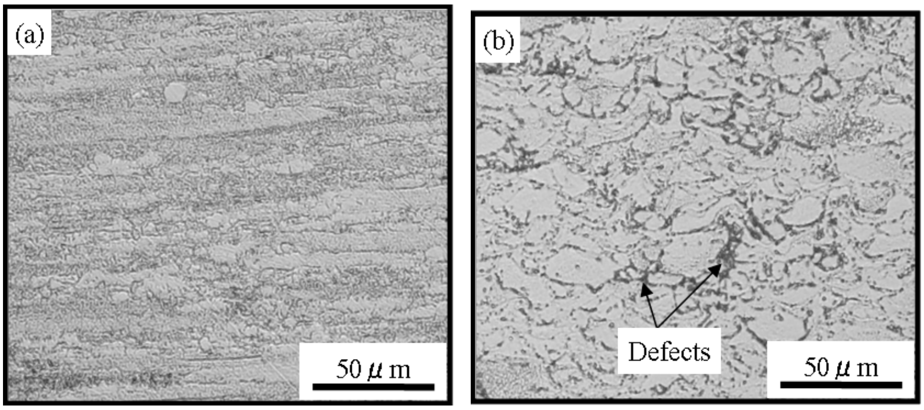


Fig. 10. Etched cross-section microstructure of (a) extruded bulk alloy and (b) cold spray coating produced with helium gas.

4. Conclusion

1) It was possible to produce the aluminum coating with dispersed nanoscale quasicrystalline particles by cold spray process.
2) The obtained coating exhibited a comparatively precise microstructure which seldom contains macroscopic voids.
3) From the TEM observation results, there is metallic bonding region at particle-particle interfaces and particle-substrate interfaces. However, the regions where the defects were generated, and an oxide film remained were also observed.
4) Although the hardness of the coating was higher than that of extruded bulk alloy, the tensile strength of the coating was much lower than that of extruded bulk alloy. It is thought that the results are attributed to the defects at particle-particle interfaces. Therefore, improvement of the bonding nature at the interfaces among particles is necessary in the further study.

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