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R&D OF COPPER ELECTROPLATING PROCESS FOR POWER COUPLERS: EFFECT OF MICROSTRUCTURES ON RRR

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Abstract

In order to develop optimum copper plating process for power couplers, we investigated the influences of plating parameters on Residual Resistivity Ratio (RRR) and microstructure of copper layers. This investigation revealed that the microstructure of copper layer is closely related to RRR.

INTRODUCTION

Power couplers for superconducting cavities are required to have both low-thermal conductivity and high-electrical conductivity, because high-thermal conductivity and low-electrical conductivity could generate unexpected increase of heat load in high power RF operation. In order to combine these contrary properties, power couplers are made of stainless steel plated with copper plating of 10 to 30 μm in thickness [1, 2]. As electrical conductivity of copper layer affects dynamic heat load, it is crucial to optimize plating parameters (e.g. plating bath composition, heat-treatment condition, copper layer thickness, and so on).

In this study, we measured RRR and observed microstructures of multiple samples with different plating parameters.

RRR MEASUREMENT

Experiment

RRR measurements were carried out with a small cryostat and a digital multi-meter in KEK/COI. This system can measure the temperature dependence of the electrical resistance from room temperature to 4 K. In this study, we mainly measured the electrical resistance of 150x5x0.5mm of copper plated stainless steel plate (SUS316L). Figure 1 shows the measurement system with the small cryostat and the sample holder with four samples.

Figure 2 is an example of temperature dependence of electrical resistance. Electrical resistance of metals decrease with temperature decreasing generally.

RRR of copper plating was calculated by the following equation.

$$\mathrm{RRR} = \frac{R_{\mathrm{Cu}}(300\ \mathrm{K})}{R_{\mathrm{Cu}}(5\ \mathrm{K})}; \quad \frac{1}{R_{\mathrm{Cu}}} = \frac{1}{R_{\mathrm{Cu/SUS}}} - \frac{1}{R_{\mathrm{SUS}}}$$

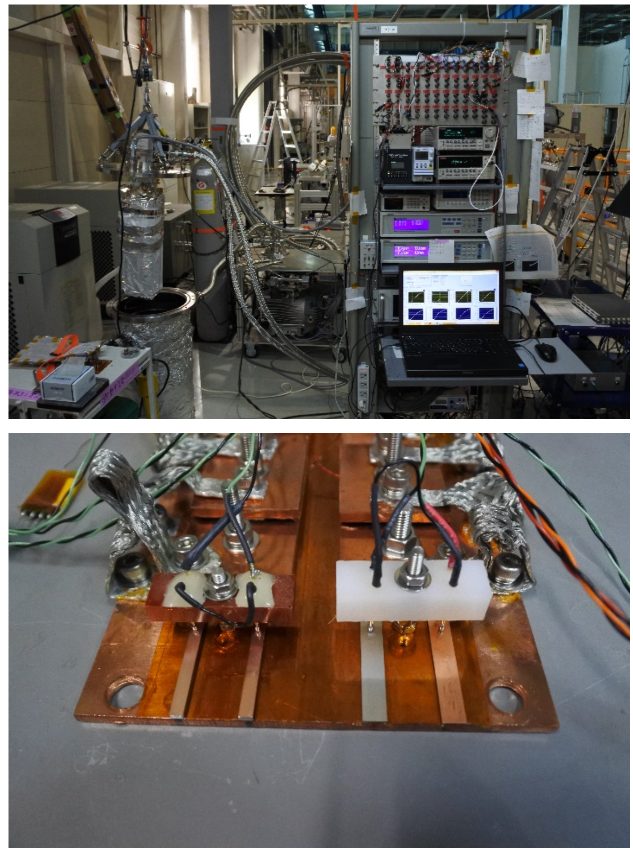

Figure 1: Residual Resistivity Ratio (RRR) measurement system (upper) and four samples on the holder (bottom) in KEK/COI.

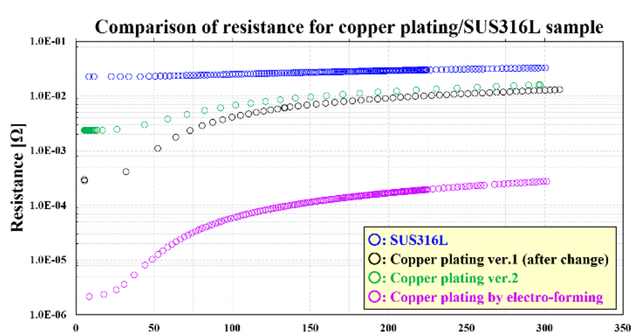

Figure 2: An example of temperature dependence of the resistance.

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Where R_{Cu} means the calculated electrical resistance of pure copper layer, $R_{Cu/SUS}$ is the resistance of copper plated SUS sample and R_{SUS} is resistance of non-plated pure SUS plate. This equation can be derived from parallel circuit model between pure copper layer and pure SUS plate. The procedure of measurement is as follow. After measuring the resistance of copper plated SUS sample ($R_{Cu/SUS}$), the copper plating is removed with nitric acid in order to obtain pure SUS plate, and resistance measurement is performed again (R_{SUS}). Then, the RRR can be calculated by $R_{Cu/SUS}$ and R_{Cu}. However, measurement of R_{SUS} is not always necessary, because the same lot of SUS plates always gives almost the same R_{SUS}. Each RRR measurement was conducted at least twice or more. Furthermore, as crosscheck of measurement system, RRR for several samples were confirmed in CEA and DESY.

Results

The Result of RRR measurements is shown in Table 1 and Fig. 3.

Group 1 is composed of samples with standard plating parameters. The plating thickness is 20 µm and plated with pyrophosphate copper plating bath. The RRR of sample (1-1) was about 15. Our target value is RRR > 30, however, obtained value was smaller than the target. On the other hand, RRR of sample (1-2) was over 70, which is high enough, although sample (1-2) and (1-1) were plated with same parameters. The only difference was that sample (1-2) was measured over 3 months after plated. We will discuss the matter in a separate paragraph.

Group 2 is composed of samples plated with copper sulfate plating bath. The RRR was over 40. It was suggested that there were any differences between copper pyrophosphate and sulfate.

Group 3 is composed of samples heat-treated at low temperature of 100°C or 200°C in atmospheric furnace. The heat treatment even at low temperature improved the RRR.

Group 4 is composed of samples with different thicknesses. Figure 4 shows thickness dependence of RRR. It is shown that increase of thickness improved the RRR. The result implies that the copper plating layer might not have a uniform structure, because the difference in thickness of the copper layer is cancelled in RRR calculation, if it is uniform.

Group 5 is composed of not plated SUS plate but a metallurgical oxygen free copper plate. The RRR was around 100. It is suggested that the structural difference between the plated metal and the metallurgical copper plate affects the RRR.

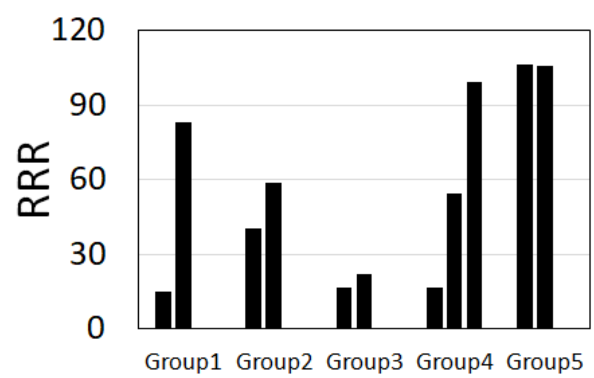

Figure 3: Result of RRR measurements.

Table 1: Result of RRR Measurements

Group	No.	RRR	bath-type	thickness	heat-treatment
1	1-1	15.1	pyrophosphate	20 µm	as plated
	1-2	83.2	pyrophosphate	20 µm	as plated (self-annealed?)
2	2-1	40.4	sulfate	20 µm	as plated
	2-2	58.9	sulfate	20 µm	as plated
3	3-1	16.8	pyrophosphate	20 µm	100 °C × 1h
	3-2	21.9	pyrophosphate	20 µm	200 °C × 1h
4	4-1	16.4	pyrophosphate	50 µm	as plated
	4-2	54.7	pyrophosphate	150 µm	as plated
	4-3	99.6	pyrophosphate	1.2 mm	as plated
5	5-1	106.3	metallurgical	1.0 mm	as received
	5-2	105.7	metallurgical	1.0 mm	as received

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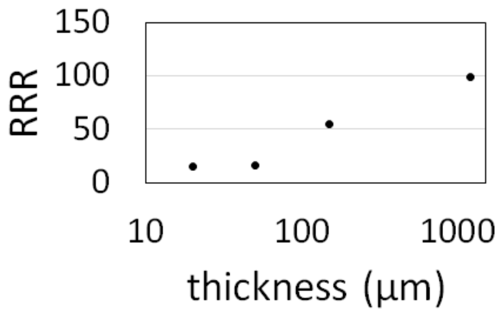

Figure 4: Thickness dependence of RRR.

MICROSTRUCTURE OBSERVATION

Experiment

The RRR measurement showed that change of plating bath type or increase of copper layer thickness drastically improved the RRR. In order to investigate the causes of the improvement, the cross-sectional microstructure observation with a confocal laser microscope was performed for (a) (pyrophosphate, 20 µm), (b) (sulfate, 20 µm), and (c) (pyrophosphate, 150 µm) after cutting, embedding in resin, polishing, and etching with 10 wt.% ammonium persulfate solution. Furthermore, Electron Back Scattered Diffraction Pattern (EBSD) analysis near surface of copper layer was conducted to obtain Inverse Pole Figure (IPF) map and grain diameter distribution. The color code of IPF map corresponds to the crystal plane orientation.

Results

The cross-sectional microscopic pictures, IPF maps, and distributions of grain diameter are shown in Figs. 5, 6, and 7, respectively.

The microstructure of Sample (a) (pyrophosphate, 20 µm), which is simulating Sample (1-1), was isotropic and fine. The mode value of grain diameter near the surface was
0.17 µm.

In contrast, the microscopic structure of (b) (sulfate, 20 µm), which is simulating sample (2-1, 2), was columnar and coarse. The mode value of grain diameter was 5.2 µm.

The microscopic structure of (c) (pyrophosphate, 150 µm), which is simulating sample (4-2), was anisotropic compared to 20 µm. The mode value of grain diameter was 0.27 µm. This indicates that increase of copper layer thickness is accompanied with coarsing of microstructure.

DISCUSSION

Microstructure observation revealed that the microscopic structure has a strong influence on RRR. Especially, coarser structure gives high RRR. The high RRR of the metallurgical copper plate is also should be due to the coarser microscopic structure, because metallurgical metals is generally coarser than that of plated metals.

From the above, we concluded that the higher RRR given by coarse structure may be due to small grain boundary resistance, because low temperature electrical resistance is dominated by scattering from crystallographic defects including grain boundaries (Mathiessen's rule [3]).

The high-RRR of samples (1-2) and low temperature heat-treated sample (3-2) also is considered to be due to less crystallographic defects. For sample (1-2), reduction of defects might occur due to self-annealing, which is phenomenon that the recrystallization of copper plating occurs even at room temperature with time [4]. Sample (3-2) can be explained similarly.

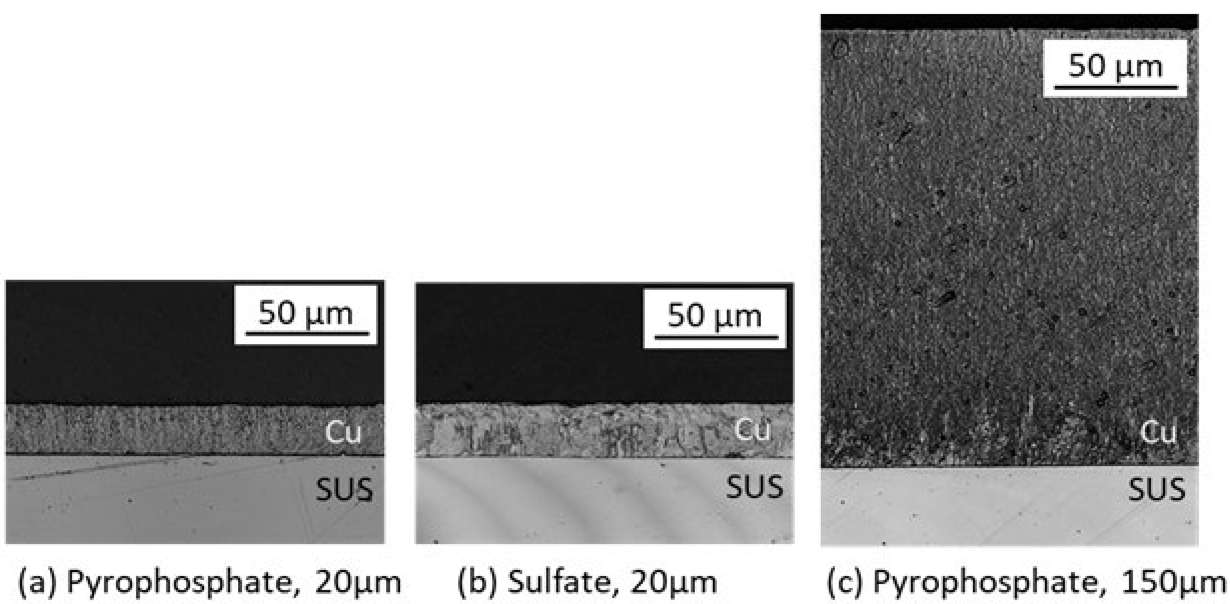

Figure 5: Cross-sectional microscopic pictures.

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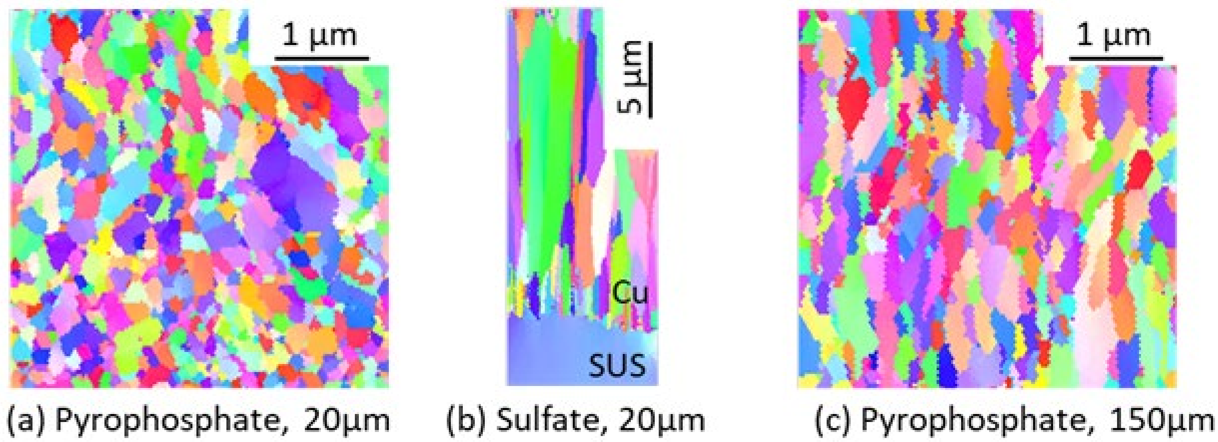

Figure 6: IPF maps of (a), (c)near the surface, (b)overall view. The color code corresponds to crystal plane orientation.

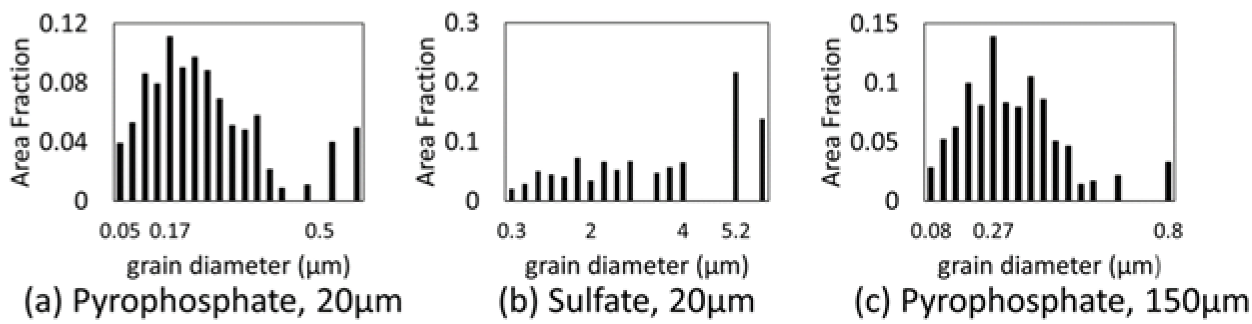

Figure 7: Grain diameter distributions in Fig. 6.

SUMMARY

We prepared multiple samples with different plating parameters, then conducted RRR measurements and microstructure observation. The investigation revealed below:

・Coarse structure, increase of thickness, self-annealing, and low temperature heat-treatment can improve RRR.

・Coarse structure improves RRR drastically improved due to less grain boundaries.

・Reduction of crystallographic defects increases RRR.

FUTURE PLAN

・Additional RRR measurement and EBSD analysis for high-temperature heat-treatment, because, in actual work, high temperature heat-treatment is performed for releasing gas or brazing.

・Investigating influence of other plating parameters such as bath-temperature, current density, pre-plating condition, etc.

・Fabrication of a cold part of STF type power coupler plated with better plating parameters.

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