Development of the High Tensile Strength and the High Thermal Stability Copper Foil NC-TSH

1. INTRODUCTION

In recent years, LiB (lithium ion secondary battery) has rapidly risen in demands for automotive applications in addition to the conventional mobile applications. Copper foils are generally used for the LiB negative electrode current collectors. The copper foils are roughly classified into an electrodeposited copper foil and a rolled copper foil in accordance with the difference in their production methods, and the electrodeposited copper foil is frequently used for the LiB negative electrode current collector because it has an excellent elongation rate and a cost advantage compared to the rolled copper foil. Since the early stages of the LiB market in 1996, we have produced the electrodeposited copper foil NC-WS for the LiB negative electrode current collector, and it is widely used by customers as a global standard material for the LiB industry.

On the other hand, along with the market expansion, the LiB has been required to have higher energy density and an improved safety than ever. In response to such market demands, the use of next generation materials such as Si based, SiOx based and Sn based materials which can obtain higher energy density than the carbon active materials conventionally are used as the material for the negative electrode active material. The electrode material based on these active materials etc. is coated to the copper foil as the current collector, therefore the negative electrode is made.

However, these next generation active materials are much larger in the volume change at charging and discharging than the conventional carbon active materials, therefore larger stress due to the expansion and the shrinkage of the electrode material is exerted on the cop-

per foil and on the other members than ever before. It resulted in issues such as deterioration of the cycle characteristics of the LiB and deterioration of its safety, due to the occurrence of wrinkles and deformation in the copper foil during charging and discharging. Due to these conditions, a copper foil, that has a high tensile strength and maintains the high tensile strength while subjected thermal history in the LiB manufacturing process, is required. Also, in the next generation batteries called post LiB, for example, all-solid-state batteries, the stress exerted on the current collector tends to increase, then a copper foil having the high tensile strength and the high thermal stability characteristics, that is difficult to cause deformation in the manufacturing process and charging and discharging, is being required. We have developed a high tensile strength and a high thermal stability copper foil named NC-TSH to solve these issues.

2. FEATURES

The high tensile strength and the high thermal stability copper foil NC-TSH achieves a high tensile strength, a high heat resistance, a high elongation rate and a high electrical conductivity by adopting our own particular electrodeposited structure control technology. Table 1 shows various typical characteristics of the NC-TSH.

1) Satisfaction of both the tensile strength

and the elongation rate

Although the NC-TSH has the tensile strength increased by approximately 1.5 times compared to our conventional copper foil NC-WS, despite the decline in the elongation rate, which is a trade-off, that has been held to a minimum. Accordingly, the NC-TSH shows the characteristics where the wrinkles and deformation

Table 1	Mechanical properties and physica	I properties of the NC-TSH and other copper foils.
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Evaluation item	High tensile strength and high thermal stability copper foil NC-TSH	Our conventional copper foil NC-WS	Electrodeposited copper foil-A	Pure copper based rolled copper foil-B	Alloy based rolled copper foil-C
Tensile strength (MPa)	490	320	490	460	610
Elongation (%) ※ 6 μm thickness	5	7	4	2	2
Tensile strength after 200°C 1 hour heat treatment (MPa)	430	270	220	190	600
Electrical conductivity (%IACS)	95	99	99	99	75

of the copper foil during battery manufacturing are inhibited, and are hard to be broken.

2) High heat resistance

Figure 1 (a) shows an annealing curve with 1 hour heating. The NC-TSH maintains approximately 1.6 times of the tensile strength after heating at 200°C as compared to our conventional copper foil. Also, the tensile strength after heating at 200°C is kept at about 1.8 times larger than that of the electrodeposited copper foil-A used for the LiB application similar to our copper foil, even though the tensile strength before heating is about the same. As a result, the NC-TSH maintains a high tensile strength even when subjected to the thermal history in the LiB manufacturing process, and even when an active material having a large volume change such as Si based material is used, wrinkles and deformation of the copper foil at charging and discharging are effectively suppressed.

Figure 1 (b) shows the annealing curve of the NC-TSH compared to that of the rolled copper foils. The pure copper based rolled copper foil-B is rapidly annealed at around 150°C, and this is not suitable for applications requiring heat resistance. Although alloy based rolled copper foil-C is excellent in the heat resistance, it

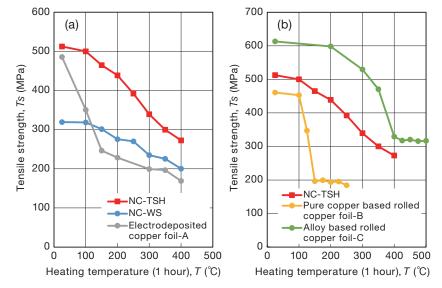


Figure 1 Thermal stability of the NC-TSH compared to of (a) other electrodeposited copper foils, (b) rolled copper foils.

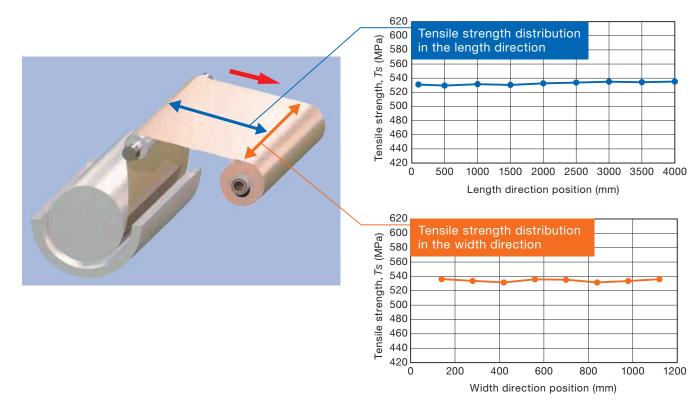


Figure 2 Tensile strength stability in the length or the width direction of the NC-TSH.

1200

is inferior in the electrical conductivity as described below.

3) Good electrical conductivity

The electrodeposited copper foil is generally characterized by its high purity copper foil and its high electrical conductivity. The NC-TSH has a sufficiently high electrical conductivity value of 95% IACS in addition to having a high heat resistance. The alloy based rolled copper foil-C showing the excellent heat resistance is inferior in the electrical conductivity to 75% IACS due to the presence of alloying additive elements. Decreasing the electrical conductivity of the copper foil causes an increase in the internal resistance of the LiB and an increase in the amount of heat generation due to the Joule effect.

4) Characteristic stability in the widthand the length directions

Figure 2 shows the tensile strength distributions of the NC-TSH in the width and the length directions. In manufacturing the high tensile strength electrodeposited copper foil, in-plane fluctuation in the tensile strength was recognized as an issue within the industry. In contrast to this, the NC-TSH shows the excellent characteristic stability when adopting our own particular process control technology.

3. CONCLUSION

The high tensile strength and high thermal stability copper foil NC-TSH developed by the Company has a higher tensile strength as compared to the conventional electrodeposited copper foil, it also has the characteristic that is hardly annealed by heating. By taking this advantage, the NC-TSH suppresses wrinkles and deformation of copper foil during the LiB manufacturing process, also during charging and discharging even when the next generation active material is used, thus the NC-TSH contributes to the improvement of the LiB energy density, the reliability and the safety. Moreover, by achieving above characteristics with the electrodeposited copper foil having a cost advantage compared to the conventional rolled copper foil, it contributes to cost reduction of the LiB.

Based on the electrodeposited copper foil manufacturing technology that has been developed over many years, we propose materials with the optimum configuration, such as a rust prevention treatment and a presence / absence of roughening treatment according to customer's request specifications.

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