Humidity-Aging Resistant Steel Cord

Tetsuya NAKAJIMA*, Akifumi MATSUOKA, Kenichi YAMASHITA, and Hiroyuki FUJIOKA

Steel cords are widely used as reinforcing material for automobile tires. The adhesion of steel cord to rubber and long-term durability are increasingly critical factors not only in terms of fuel efficiency improvement but also the technological advancement of automobiles such as electric vehicles and automated driving. Focusing on the humidity heat resistance as an indicator of long-term durability, we have developed a ternary alloy plating with cobalt (Co) added as the third element in the brass plating of ordinary steel cord, and established its mass production technology ahead of the world. In this development, we also clarified the plating-rubber adhesion and its deterioration mechanism, enabling quantitative and quick evaluation of the effect of adhesion performance improvement. This innovative plating technology has substantially increased the durability of tires compared to conventional ones, being keenly anticipated by customers.

Keywords: low fuel consumption, EV, durability, plating, analysis technique

1. Introduction

Modern automobile tires (“tires”) consist of rubber manufactured by elaborately blending various additives and reinforcement wires. Reinforcement wires are made from chemical fibers (such as polyester, nylon, and aramid fiber), natural fibers (such as cotton), and steel (such as bead wires and steel cords). Steel cords are essential tire components due to their advantages such as low cost, high compression stiffness, and good balance between strength and flexibility.

Recently, vehicle performance has been improved remarkably, and low fuel consumption is taken for granted. In addition, automated driving and electric vehicles (EVs) are about to come into widespread use. These vehicles also use tires to transmit the motion of moving forward, turning, and stopping. Ever higher performance is required of tires. Tire manufacturers have been competing intensely to develop products that achieve high performance, low fuel consumption, high durability, and low cost.

Adhesiveness between rubber and plating, which is one of the important properties required of steel cords, is attained by the adhesion reaction attributed to copper sulfide (Cu_xS) generated by combination of sulfur (S) in the rubber with copper (Cu) in the plating. Low adhesiveness leads to a significant decrease in the durability of tires, and may result in a burst*[1] while driving at high speeds. Thus, it is the most important requirement to ensure adhesiveness over the long term.

Meanwhile, the usage conditions of tires vary, including the vehicle type, usage frequency, temperature, humidity, speed, and weight of carried cargo. It is extremely difficult to evaluate adhesiveness under the respective conditions.

However, the actual phenomena of adhesion and aging reaction had not been fully understood. To improve adhesiveness, it was required to elucidate the mechanism.

To cope with these issues, we took two highly innovative approaches. First, we became the first company in the world to utilize the cutting-edge technology of adding cobalt to conventional brass plating in mass production to dramatically improve the adhesion durability. Second, we developed an advanced analysis technique to quantitatively simulate adhesion and aging reaction.

These efforts have contributed greatly to improving the performance of tires, which have been highly evaluated by our customers. The details are reported below.

2. Tires and Steel Cords

2-1 Structure of a tire

Figure 1 shows the structure of a standard tire. Steel cords are used as belts (breakers) to reinforce the circumference of the tire just like a hoop and as carcass (plies) to reinforce the tire sides and tread surface in the radial direction.

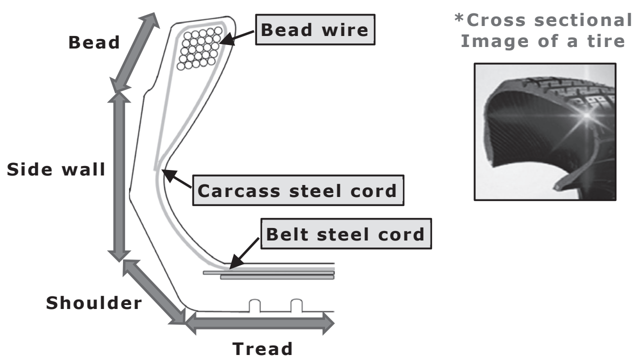


Fig. 1. Structure of a tire

Stranded wires made from nylon, cotton, steel, and other materials are used as belts and carcass. They are used mainly because they can achieve strength, flexibility, and fatigue resistance at the same time. Recently, fiber materials such as aramid fiber and carbon fiber have been developed and used for various products. In tires, steel is used for most tires because it helps achieve required characteristics such as high-speed performance, control stability, and riding comfort at high levels and at low cost.

2-2 Steel cords and usage

As shown in Photo 1, a steel cord consists of several to dozens of steel wires, whose diameter is about 0.15 to 0.40 mm (mainly 0.70 to 0.90% high carbon steel), that are stranded together. The surface of the element wires is plated with brass by alloying copper (Cu) and zinc (Zn) to ensure workability in the wire drawing process and adhesiveness with rubber.

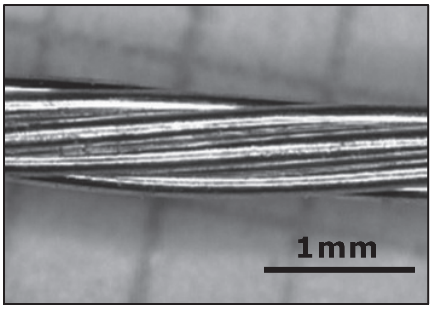


Photo 1. Magnified image of a steel cord

Multiple steel cords are embedded in rubber and processed into a sheet (see Photo 2), which is used as a tire reinforcement component.

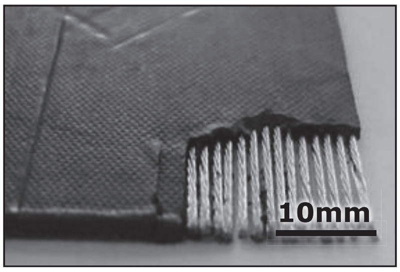


Photo 2. Rubber sheet with steel cords embedded

3. Use environment and requirements for tires

Tires are manufactured and used around the world. The use of tires is expected to increase further due to the expansion of automotive society.

Today, tires are often used in severe environments. For example, tires are generally subject to high loads in daily use in developing countries such as high internal pressure (which is almost equivalent to high air pressure), overload, continuous long-haul driving, and driving on bad roads. Under these circumstances, the durability of tires that is directly related to safety has been drawing increasing attention. Durability consists mainly of three factors: (1) wear resistance of the tread (grooves), (2) resistance to rubber aging (cracks), and (3) long-term adhesiveness between steel cords and rubber in tires.

It has been found that continuous high loads applied to a tire cause moisture ingress from the thin part of the rubber, resulting in corrosion of the plating of the steel cord surface and decreased adhesiveness between the cords and rubber, leading to lower durability. Thus, there is a growing need to improve the long-term adhesiveness between steel cords and rubber (i.e., (3) of the three durability factors above).

To improve the long-term adhesiveness between steel cords and rubber, we considered it effective to increase resistance against humidity aging. We worked on the development of steel cords with excellent humidity aging resistance achieved by corrosion-resistant plating.

4. Adhesion between Steel Cords and Rubber

As discussed above, the adhesiveness between steel cords and rubber is a very important characteristic. This section explains the method of evaluating adhesiveness.

For steel cord products, the adhesion score of finished products is evaluated. Specifically, steel cords are embedded in rubber, which is vulcanized*2 at about 150 to 180°C. Subsequently, rubber is removed to visually evaluate the amount of rubber remaining on the plated surface (full marks: 5 points, in 0.5-point increments) (see Photo 3). This evaluation is conducted to check the initial phase adhesiveness immediately after vulcanization (i.e., adhesion condition of a new tire).

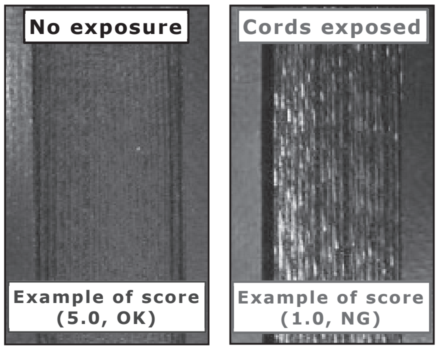


Photo 3. Adhesion score of steel cords and rubber

In addition to the initial phase adhesion evaluation above, the humidity aged adhesion score is also used to evaluate aging in high temperature and high humidity environments. For example, the same scoring is performed after exposure to an environment of a relative humidity (RH) of 80°C 95% for 150 hours. This condition is considered to be equivalent to usage for two years.

5. Development of a Steel Cord with Excellent Humidity Aging Resistance

5-1 Development efforts

To achieve a steel cord with excellent humidity aging resistance, it is essential to improve the long-term adhesiveness of rubber and plating. The concept of ternary alloy plating has long been advocated. It aims to suppress humidity aging of the adhesion layer by adding a third element to the existing brass plating (Cu-Zn alloys). Many manufacturers have been working on its development. We also worked on its development to become the first company in the world to use ternary alloy plating on a commercial basis for mass production. First, we compiled the required characteristics and criteria for selecting the third element. The details are shown in Table 1.

Table 1. Required characteristics and selection criteria in the development

	Required characteristics	Selection criteria
1	Ensure adhesiveness against humidity aging (improvement of humidity aging resistance)	improves corrosion resistance of Cu-Zn alloys
2	Minimize manufacturing costs (raw materials + processing)	- Inexpensive - Less likely to hinder workability - Less likely to be alloyed with Cu
3	No harmful effects on rubber	Contained in rubber
4	Simple plating technique	Plating technology has already been established to some extent

Figure 2 shows the results of reviewing the third elements to be added by taking into account the above-mentioned required characteristics.

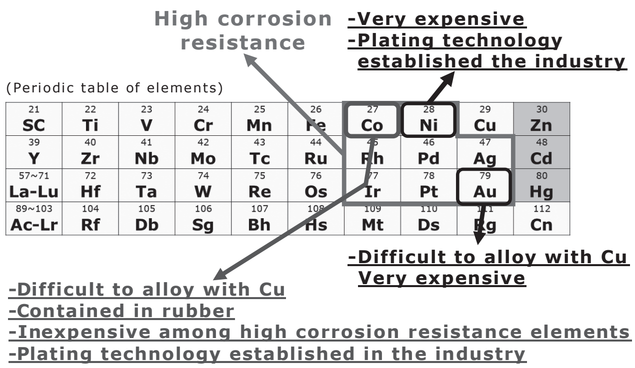


Fig. 2. Candidates of the third element to be added

We reviewed the candidate elements above based on the selection policy in Table 1, and concluded that cobalt (Co) was most appropriate. To achieve a steel cord with excellent humidity aging resistance, we selected ternary alloy plating with Co added to the brass plating.

5-2 Effect of a Co-added ternary alloy

Figure 3 shows the initial phase adhesiveness and humidity aged adhesiveness of conventional brass plating and Co-added ternary alloy plating.

Based on fabrication of various prototypes, we confirmed that the rate of Co added should be about 4.0 wt% to attain both humidity aging resistance and workability. We decided to evaluate the plating composition (wt%) of Cu:Zn:Co = 68:28:4.

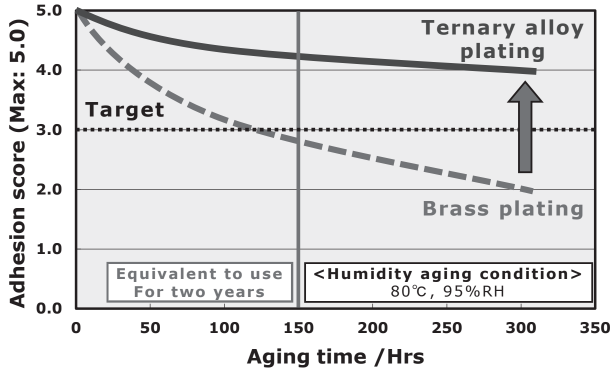


Fig. 3. Comparison of adhesiveness between brass and ternary alloy plating

As shown in Fig. 3, adhesiveness after humidity aging is improved dramatically. It is noteworthy that the adhesion score is 4.0 points or more in the extremely severe aging condition of 300 hours or more.

6. Elucidating the Mechanism of Adhesiveness Improvement

In the steel cord industry, the attempt to change plating is a major milestone from the 1970s. To market the tires, it was necessary to launch a plating process completely free from problems.

Regarding adhesion between steel cords and rubber and aging, simulation tests were conducted by using the combination of brass plates and rubber.[(1)-(4)] These tests mostly elucidated the adhesion reaction, aging, and behavior of components in the plating and rubber (see Fig. 4).

However, efforts had not been made to elucidate the mechanism using actual tires. There was no choice but to conduct aging tests on tires on a test bench (machine) for evaluation.

To analyze adhesion between steel cords and rubber and aging condition in an actual tire and to elucidate the mechanism of adhesiveness improvement, we developed a

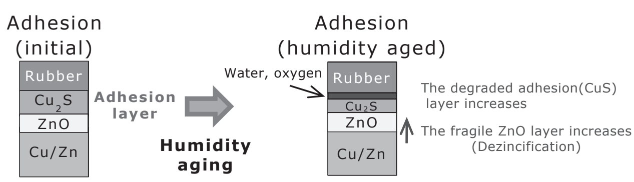


Fig. 4. Schematic diagram of the adhesion interface in the initial and after humidity aging

technique to directly observe the adhesion interface through the combination of two methods: (1) cutting samples from the relevant part (i.e., cutting adhesion interface samples from tires) and (2) fabricating samples for analysis (i.e., fabricating adhesion interface samples by using our focused ion beam [FIB] and scanning electron microscope-energy dispersive X-ray spectroscopy [SEM-EDX] technologies). This direct observation technique was innovative. A sample cut from a tire and processed for analysis is shown in Photo 4.

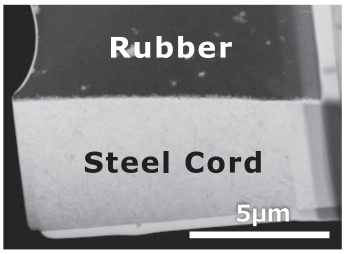


Photo 4. Sample cut from a tire

We worked to elucidate the mechanism of adhesion characteristics improvement in an actual tire by conducting an in-depth analysis of the adhesion interface of the sample by scanning transmission electron microscopy (STEM) and synchrotron radiation X-ray absorption fine structure (XAFS). The results are shown in Figs. 5 to 7.

Figures 5 and 6 show that, in brass plating (outlined plot), the volume of the adhesion layer (Cu_2S) decreases and the degraded adhesion layer (CuS) increases due to the progress of aging.

Meanwhile, in ternary alloy plating (filled plot), the decrease in the adhesion layer, increase in the degraded adhesion layer, and growth of the degraded ZnO layer were all suppressed.

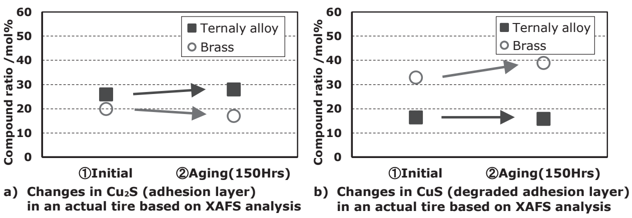


Fig. 5. Changes in the adhesion layer and degraded adhesion layer based on XAFS analysis

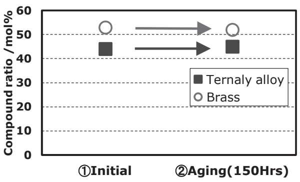


Fig. 6. Changes in the degraded layer ZnO based on synchrotron radiation XAFS analysis

Figure 7 shows that the surface oxide layer after aging (which mainly consists of ZnO) is thin in ternary alloy plating compared to brass plating.

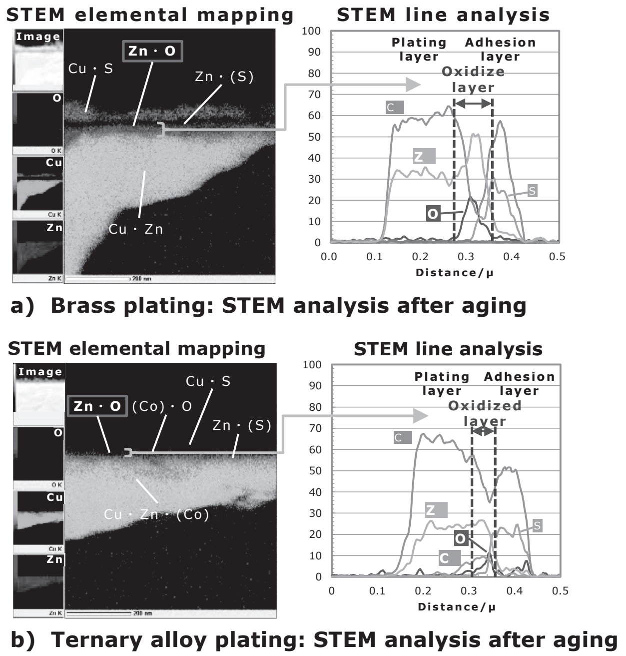


Fig. 7. STEM analysis of the adhesion interface

7. Results of Tire Durability Evaluation

We conducted a durability test on tires using ordinary brass plating and ternary alloy plating. The results are shown in Table 2. We evaluated steel cords for carcass (which makes up the tire frame) for comparison. We fabricated tires of the same specifications except for the steel cord plating.

Table 2. Tire durability test results

	Mileage until fracture *index
Brass plating	100
Ternary alloy	**147**

The durability of a tire with ternary alloy plating is about 1.5-fold that of one with brass plating. We verified that the ternary alloy plating significantly improves durability.

There have been growing expectations for tires that use this epoch-making plating technology.

8. Conclusion

We developed an epoch-making plating technology to meet the needs of improving the durability of tires for the future automotive society exemplified by electric vehicles and automated driving. Regarding the theme of elucidating the adhesion mechanism, our analysis and simulation technologies have made it possible to perform analysis of actual tires. These technologies offer a significant advantage in performance over competitors.

The automotive society is expected to change rapidly. Accordingly, demand for higher functionality will increase further. Obviously, it will be essential to further improve tire performance. We are convinced that our technologies will be actively utilized and will contribute greatly to developing the high-performance tires that meet future needs.

Technical Terms

∗1 Burst: A phenomenon in which a tire is damaged (ruptures). Burst makes a vehicle uncontrollable and poses significant hazards to the vehicle and the environment around the vehicle.

∗2 Vulcanization: The process of adding sulfur to rubber and heating the mixture. This process improves the strength, elastic limit, and wear resistance of rubber and is essential for rubber used for vehicle tires.

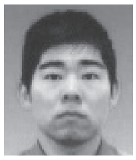
References

(1) Beecher, J. F.: Surface and Interface Analysis, 17, 245 (1991)
(2) Patil, P. Y.; Van Ooij W. J.: Rubber Chem. Technol., 79, 82 (2006)
(3) N. Amino: Nippon Gomu Kyokaishi, 90 (5) (2017)
(4) Y. Ishikawa: Nippon Gomu Kyokaishi, 90 (9) (2017)

Contributors

The lead author is indicated by an asterisk (∗).

T. NAKAJIMA*
• Assistant Manager, Advanced Materials Laboratory



A. MATSUOKA
• Assistant General Manager, Sumitomo Electric Tochigi Co., Ltd.

K. YAMASHITA
• Senior Assistant General Manager, Sumiden Steel Wire (Thailand) Co., Ltd.

H. FUJIOKA
• Group Manager, Analysis Technology Research Center