Development of a Cu-Al-Mn Shape-Memory Alloy and its Application to an Ingrown Toenail Correcting Clip

1. INTRODUCTION

Furukawa Techno Material Co. Ltd. has commercialized a Cu-Al-Mn shape-memory alloy which has been developed by Tohoku University as an ingrown toenail correcting clip and it has been launched by Reckitt Benckiser Japan Ltd.

The shape-memory effect has been found in a number of alloy systems and it had been actively researched on a copper-alloy system, such as a Cu-Al-Ni alloy. However, because of its poor workability and its insufficient shape-memory property, the reality is that a Ti-Ni alloy is the only major shape-memory alloy which has been put to practical use. Although the Ti-Ni alloy has a wide field of application, it has not been put to practical use except for a shape of wire and tube because of its poor workability.

In consultation with Tohoku University, we have improved the shape-memory property of the Cu-Al-Mn alloy and have succeeded in putting it to practical use as an ingrown toenail correcting clip. That is the world's first application of this alloy.

An ingrown nail is a symptom where a nail curves in a transverse direction. It commonly appears in a first toe. The nail bites into a toe and it often accompanies pain. Although there are various treatments such as a correcting method using a Ti-Ni alloy superelastic wire, the burden on the patients, the complicated medical procedures and the high cost were the problems.

The newly developed Cu-Al-Mn alloy has a good workability and can easily be processed into a plate and a three-dimensional shape. Also, as it requires no forming block during a shape-memory treatment, it can cut costs significantly. For these reasons, it has been commercialized after a number of experiments and monitor tests.

2. ALLOY DESINGNING AND TEXTURE CONTROL

Tohoku University's research shows that a high-workability Cu-Al-Mn shape-memory alloy can be achieved by the following alloy designing and the texture control.

By adding Mn to a ternary alloy of Cu-Al-Mn, β phase, which shows martensitic transformation, comes to exist widely. The β phase shows order transformation and the order-transformation temperature is highly dependent upon Al content. When the Al content decreases, its cold workability significantly increases. The reason of it is explained by the fact that the decrease of the Al content brings the decrease of the order-transformation temperature.

On the other hand, the shape-memory effect shows a property decrease at less or equal to 16 at%Al, which generates an A2 disordered structure. As explained above, the optimum composition which has a good shape-memory property and a high workability at the same time is confirmed to be a Cu-17 at%Al-Mn (Mn is 10 – 13 at% for the sake of adjusting martensitic initiation temperature (Ms)).

Next, this alloy requires texture control to achieve a good shape-memory property. Figure 1 shows the relation between the grain sizes (d), which are standardized by the wire diameters (D), and the superelasticity after tensile tests. Figure 1 (a), in which crystal grains penetrate the diameters, shows a superior superelasticity property. Also, this alloy is confirmed to be effective for the increase of a superelasticity property because the {112} <110> recrystallization texture is generated by a thermomechanical treatment.

Table 1 shows the properties of the Cu-Al-Mn alloy and other shape-memory alloys. The prime property is that the Cu-Al-Mn alloy shows greater or equal to twice as much cold working rate in comparison to other alloys. That brings not only the improvement of manufacturability but the achievement of a good superelasticity strain rate which is comparable to that of the Ti-Ni alloy by enabling texture control.

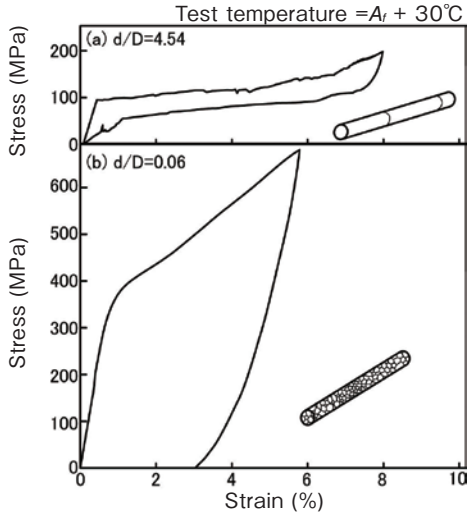

Figure 1 Superelastic behavior of Cu-Al-Mn alloys in different grain sizes.

Table 1 Comparison of Cu-Al-Mn and Other Shape-Memory Alloys.

	Maximum cold working rate (%)	Superelasticity strain (%)	Temperature dependency of superelasticity stress ($MPa℃^{-1}$)	Simplicity of shape-memory treatment
Cu-Al-Mn	>60	7.5	2.4	○No forming block
Ti-Ni	30	8	5.7	× Forming block required
Cu-Al-Mn	10	2	–	–
Cu-Zn-Al	30	2	–	–

Another practical advantage is that the Cu-Al-Mn alloy can show more stable superelasticity to temperature changes because its superelasticity stress is less dependent on temperatures than in the Ti-Ni-alloy.

3. PROPERTIES OF THE CLIP

As explained above, the Cu-Al-Mn shape-memory alloy has superior workability. Therefore, it is applicable to complex-shape products which are difficult to be manufactured using existing the Ti-Ni alloy. As shown in Figure 2 (a), we have commercialized a new ingrown toenail correcting device. This product is attached to a nail with four double-folded hooks as shown in Figure 2 (b). It corrects an ingrown nail with the recovery force caused by the superelasticit

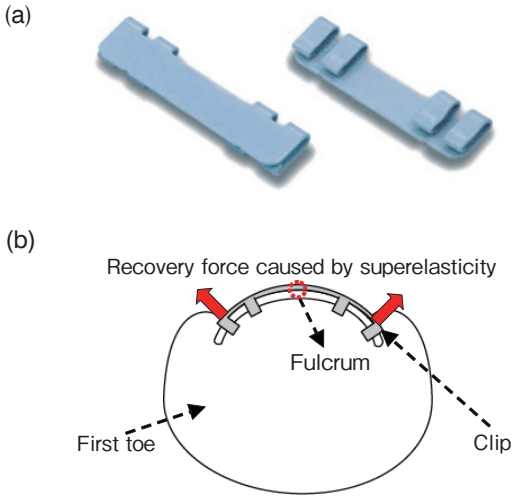

Figure 2 (a) Ingrown toenail correcting clip. (b) Correcting method.

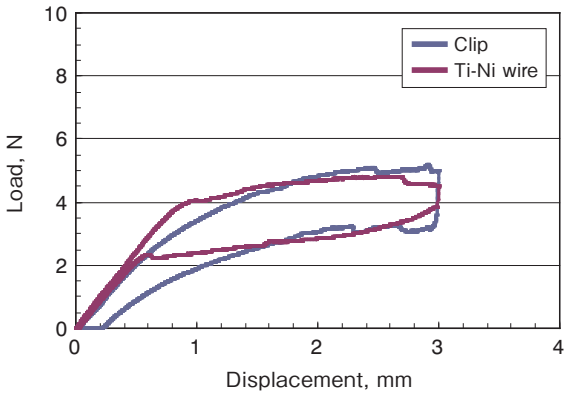

Figure 3 Superelastic properties of the Cu-Al-Mn clip and the Ti-Ni wire.

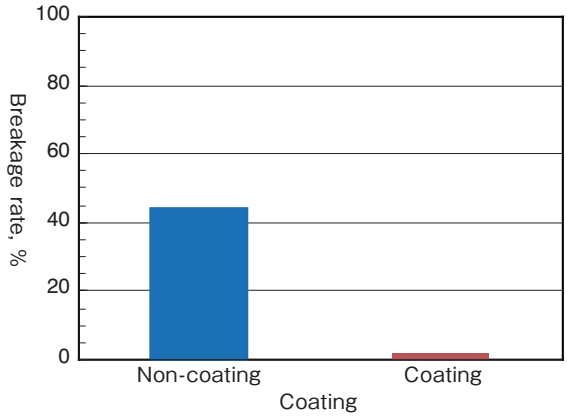

Figure 4 Result of coating in the stress corrosion test.

Different from usual spring materials, because the deforming stress of the superelasticity is not highly dependent on the strain, it can give nearly-constant correcting force to the nail regardless of the degree of curvedness. That causes less cracks and discomfort to the nail. Therefore, it is suitable for correcting ingrown toenails. The clip-on style enables the easiness of putting on and taking off, and does not necessarily require a treatment by the specialist. Therefore, it can cut treatment costs.

Different from the Ti-Ni alloy, this alloy's shape-memory treatment needs only a heat treatment, and doesn't need to be fixed by a die. Therefore, it can easily be shaped and memorized in a complex shape which has double folds as shown in Figure 2. For the shape-memory treatment, a heat treatment was conducted at 900℃ for about 10 minutes. When cooling it, rapid cooling was necessary to restrain α phase precipitate. Also, it is desirable to conduct an aging treatment at 100 - 200℃ for 15 minutes after the shape-memory treatment to stabilize the transformation temperature. At the time of commercialization, the reverse transformation end temperature (A_f) was controlled at about -20℃ to achieve good superelasticity in the usage environment.

To evaluate the elasticity of the clip, a three-point bending test was conducted. Figure 3 shows the chart resulted from the test. Although the Cu-Al-Mn alloy clip had some amount of residual strain, it had a sufficient displacement field with small amount of load variation after unloaded. Therefore it was confirmed to be sufficiently usable for correcting ingrown nails.

Because this clip is attached to a nail and used inside a sock and a shoe, it is exposed to a humid environment. Such an environment can generate a problem of corrosion. Because the load on the hook part which clips the nail becomes heavy during use, a rare phenomenon that the hook part is broken by stress corrosion was confirmed. Therefore, we concluded that surface coating is necessary at the time of commercialization. Coating was applied by electrodeposition to coat even inside the double-folded hook part. Then, it was submitted to a stress corrosion test. Figure 4 shows the percentage of the samples of the hooks that were broken by absence of coat-

ing. Coating reduced the breakage rate significantly and improved stress-corrosion cracking.

4 SITUATION OF PRACTICAL APPLICATION AND PATENT

In the clinical trial of the ingrown toenail correcting clip at the Department of Dermatology, Japan Red Cross Sendai Hospital, an early-stage of pain disappearance and an improvement in curvedness were confirmed. That means it is not only easy to put on and to take off, but has a superior correcting effect. It has been launched since March 2011 by Reckitt Benckiser Japan Ltd. as a brand “Dr. Scholl” for medical institutions. It has already been sold to about 1000 medical institutions and obtained a high reputation. Also, we are in the course of applying for patents of this technology both domestically and internationally.

5. CONCLUSION

We have commercialized an ingrown toenail correcting clip using a high-workability Cu-Al-Mn shape-memory alloy. We expect this clip to be widely adopted as a new and easy treatment for correcting ingrown nails. The Cu-Al-Mn shape-memory alloy will be an option for the materials of products which require formability and machinability.

This article is edited based on the paper, posting to Materia Japan vol.51, No.3, (2012), “Development of Cu-Al-Mn shape memory alloy and its application to ingrown toenail correcting clip” by Toyonobu Tanaka, Sumio Kise, Toshihiro Omori, Ryosuke Kainuma and Kiyohito Ishida.

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