Pre-coated Titanium Sheet with Excellent Press Formability

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Plate type Heat Exchangers (PHEs) are one of the main applications for commercially pure titanium. The plates, each consisting of a titanium sheet press-formed into a complex corrugated pattern, are directly linked to high performance such as that seen in the thermal conductivity of the PHE. Now Kobe Steel has newly developed a pre-coated titanium sheet with excellent press-formability, whose design includes a lubricant coating that is easily removed by alkaline cleansing.

Introduction

Plate type heat exchangers (hereinafter referred to as "PHEs"), which exploit large amounts of sea water as their cooling media, are used in industrial fields including chemical plants, power-generating facilities and large transport vessels. PHEs employ large amounts of titanium for their primary parts such as their plates and piping because titanium exhibits excellent resistance against seawater corrosion. Now PHEs have become one of the main applications of titanium[1)]. **Fig. 1** illustrates the operating principle of a PHE. A PHE is an apparatus for exchanging heat between hot water and seawater, each flowing in the opposite direction, wherein the flows are separated by titanium plates. Heat exchange occurs directly via these titanium plates. Each plate consists of a titanium sheet which is formed into a complicated corrugated shape and determines the heat transfer performance of the heat exchangers. The plate materials are also required to have increased strength, as the PHEs are increasingly being operated at higher pressures.

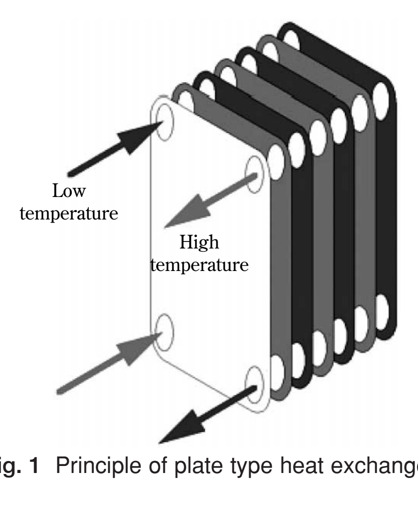

Fig. 1 Principle of plate type heat exchanger

Conventional PHEs use the softest grade of commercially pure (CP) titanium. If PHEs can employ harder CP titanium while preserving the favorable formability of the soft material, the application of titanium will expand to higher pressure applications with possible weight reduction achieved by wall thinning. Thus, a material for PHE plates is required to have both favorable press formability and high strength.

The strength and formability of a material, however, are in a trade-off relationship. Thus, Kobe Steel first focused on surface lubrication as a means for improving formability. Various methods have been known for such lubrication. One common approach is to attach a lubricating film to the surface to be formed[2)]; however, this method costs time and money for attaching and detaching the film in actual operation. Another approach is to oxidize, or to nitride, the surface[3)]; however, this method suffers from hardness and brittleness in the resulting surface layer, making the layer prone to crack in press patterns that are difficult to form. It also suffers from the fact that the surface layer may inhibit heat transfer. Taking these facts into account, Kobe Steel developed a method of pre-coating a lubricant, such that the pre-coated layer can be removed easily during the alkali cleaning that follows press forming. This method has enabled the use of JIS Class-2 CP titanium with a higher strength than that of conventional JIS Class-1 CP titanium, with the conventional press formability.

This paper introduces an adequate evaluation method uniquely developed for numerically evaluating the press formability of the titanium sheets used for PHE plates. Also introduced is a titanium sheet pre-coated with lubricant, which was developed using this evaluation method.

1. Kobe Steel's approach to evaluating press formability

During press forming, cracking occurs more frequently at sites called "flow passages" or "gaskets". The deformation mode at these sites is close to the mode of biaxial stretch forming[4), 5)]. Thus, the Eriksen value is used as a simple index of press formability. In reality, however, not only stretching, but also other deformation modes, such as deep drawing, come into play together. Thus, a method must be established for quantitatively evaluating press formability in real-life situations.

To achieve this, attempts have been made to quantify press formability by scoring the conditions of cracking and necking after pressing, according to the following methods. For simplified evaluation, pressing was conducted using a compact test die which simulates a fishbone pattern, also known as the herringbone pattern, which is commonly found in the heat transfer portion of PHE plates. Also used was a large die covering a size close to that of an actual PHE.

It is to be noted that there are still issues remaining, including the fact that the present press-formability evaluation does not correlate sufficiently well with actual production. Further study will be conducted to improve the evaluation accuracy.

1.1 Evaluation using compact die

The following describes the shape of the compact die.

- Size: 160mm square (forming portion: 100mm square)
- Pitch between ridges: 10.0mm
- Ridge height: 4.0mm
- Radii of ridges R : 0.4, 0.6, 0.8, 1.0, 1.4, 1.8 (mm)
- Number of ridges: 6

The test samples were sized to 160mm square and were pressed by an 80tonne hydraulic press. The ridges were formed with a height of 3.4mm, the height having been determined to exhibit clear differences in cracking conditions between JIS Class-1 and Class-2 titaniums.

After test pressing, the samples were quantitatively ranked by the existence or non-existence of cracks and/or neckings at predetermined sites, as follows. In a press-formed sample (**Fig. 2**), a total of 24 sites were selected for evaluation, i.e., the 18 convex portions represented by the crossing between the 6 ridge-lines, the sites of potential cracks, and the three broken lines (A-A', B-B', C-C'), and the 6 concave portions on the broken line A-A', the concave portions where cracks can also originate. The following scoring was applied for each site:

- No cracking (soundness) : score 4
- Slight necking : score 3
- Significant necking : score 2
- Small cracking : score 1
- Large cracking : score 0

Based on these scores, the overall score was calculated as follows:

$$\text{Score (\%)} = (\Sigma (E/R))/(\Sigma (4/R)) \times 100 \quad \cdots\cdots\cdots(1)$$

wherein E is the score at each measuring point and R is the ridge radius (mm) at each measuring point. No cracking at any of the sites yields 100%, while the cracking at all the sites yields 0%. The reason for dividing by R is to account for the effect of bending deformation at each ridge with radius R.

1.2 Evaluation using large die

The shape of the large die is as follows:

- Size : 500mm square; (forming portion : 300mm square)
- Pitch between ridges : 14.9mm
- Ridge height : 8.1mm
- Radius of the ridges R = 3.4 (mm)

The test samples were sized to 500mm square and were pressed by a 1,000tonne servo-press. The criterion used for the compact die was adapted, making the forming height of the ridge portions

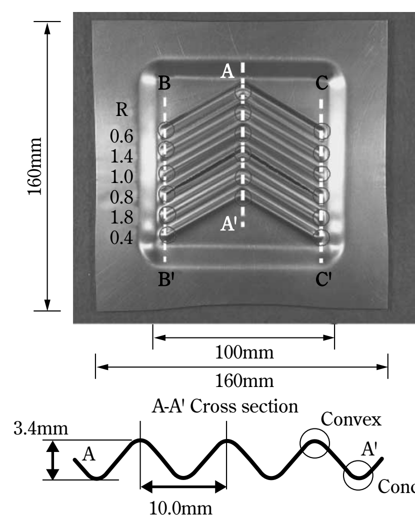

Fig. 2 Pressed test shape and positions for scoring in order to evaluate the pressformability using compact size test die

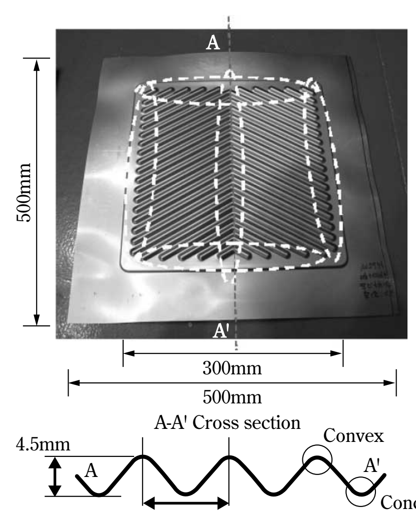

Fig. 3 Pressed test shape and positions for scoring in order to evaluate the pressformability using large size test die

4.5mm. There are a total of 92 evaluation sites in the areas surrounded by the broken lines in **Fig. 3**, including ridge ends and ridge central regions (convex portions and concave portions). Scoring was conducted in the same manner as in the case of the compact die. It is to be noted that R is set to be constant to form a shape close to that of a real product.

$$\text{Score}(\%) = \Sigma E/(4 \times 92) \times 100 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

2. Features of lubricant pre-coated titanium sheets

To study the difference in deformation between film lubrication and press oil lubrication, samples were pressed by the compact die with a lubricant film and with a press oil (SUNPRESS S-304 manufactured by Sugimura Chemical Industrial Co., Ltd.). **Fig. 4** compares the cross-sections of the ridge lines (R = 0.8, 1.0, 1.8) of the pressed samples. In the area surrounded by dotted circles, the sheet thickness is decreased in relation to its periphery. The comparison indicates that film lubrication results in less cracking and necking compared with press oil lubrication. In the case of press oil lubrication, the die comes into contact locally with the titanium sheet as the forming proceeds, restraining and immobilizing the sheet. In the meantime, the forming continues as a whole, causing necking and eventual cracking. On the other hand, in the case of film lubrication, the die does not directly contact the titanium sheet as long as the film is not broken, which assures the fluidity of the sheet, allowing the supply of the material from the surrounding region. This is considered to be the reason for the resulting uniform deformation compared with the case of press oil lubrication. Thus, in order to obtain a high formability, it is important to reduce the friction force as much as possible.

To improve lubricity and, in particular, to reduce the kinetic coefficient of friction, a lubricant pre-coated sheet was prepared. **Table 1** shows the composition of the lubricant pre-coating. Acrylic resin was chosen as the base resin because it adheres well to the titanium sheet, sufficiently follows the deformation and can easily be removed by alkali. Colloidal silica hardens the coating. Polyolefin wax improves lubricity against dies and was added to reduce the kinetic coefficient of friction of the pre-coating.

To study press formability under different lubricity, three types of lubricated titanium sheets were prepared using JIS Class-2 CP titanium, which has properties as shown in **Table 2**. One type of sheet was coated with press oil (SUNPRESS S-304 manufactured by Sugimura Chemical Industrial Co., Ltd.), another was covered with a film having the composition of the pre-coated lubricant without polyolefin wax (i.e., acrylic resin + colloidal silica), and the remaining one was pre-coated with lubricant. The coatings were applied with a roll coater and were dried in a thermostatic oven into a thickness of 1.0 μm.

The coating thickness was adjusted by varying the solid content in the pre-coat solution. An X-ray fluorescence analyzer (MIF-2100, manufactured by Shimadzu Corporation) was used to quantify the amount of Si in the film. The coating thickness (μm) was determined from the coating quantity (g/m^2), obtained by Formula (3), which was converted by Formula (4).

$$\text{Coating quantity}(g/mm^2) = Si \times 60 \times 100/28 \times C \times 1000 \cdots (3)$$

wherein Si represents the amount of Si in the coating(mg/m^2), C represents the concentration of SiO_2 in the surface treatment composition(%), the numeral 28 is the atomic weight of Si, and the numeral 60 is the molecular weight of SiO_2.

$$\text{Coating thickness } (\mu m) = (\text{Coating quantity} \times 0.1/2.2) + (\text{Coating quantity} \times 0.9/1.0) \cdots (4)$$

Formula (4) is applicable to a coating, that is 10% SiO_2 (specific gravity 2.2) and 90% resin + wax (specific gravity 1.0).

The press formability was quantified based on the method using the compact die as described in Section 1.1. The kinetic coefficient of friction was

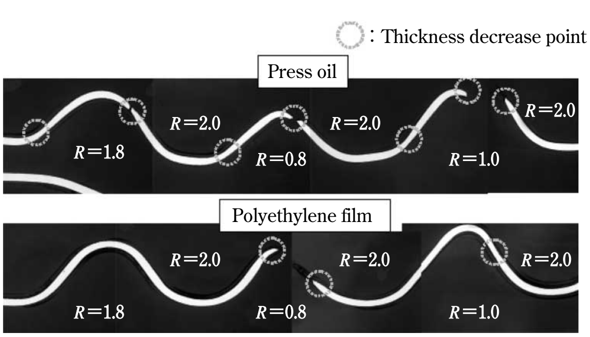

Fig. 4 Comparison between cross sections of pressed samples using press oil and polyethylene film as lubricant

Table 1 Composition of pre-coated layer

	mass%	Contents
Resin	80	· Acrylic resin consisted of alkylacrylate-methacrylate copolymer
Colloidal silica	10	· Amorphous SiO_2 · Alkali Na_2O
Wax	10	· Polyolefin wax

Table 2 Tensile properties of JIS Class-2 titanium sheet

Tensile direction	0.2%Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
L direction	243	396	31
T direction	288	389	29

measured by a tester (HEIDON by Shinto-Science) in the longitudinal direction with a test load of 500g, a sliding speed of 100mm/min and a sliding distance of 40mm. The partner material was a stainless steel ball of ϕ10.0mm.

Fig. 5 shows the relationship between the kinetic friction coefficient and press formability of the pre-coated sheet that was prepared. It can be concluded, despite the limited data, that the kinetic friction coefficient of the material is decreased by the application of the coating comprising resin and colloidal silica and is further decreased by the addition of polyolefin wax. This is accompanied by an improvement in formability.

To determine the optimum pre-coating thickness for press forming, the effect of pre-coat thickness on press formability was studied using JIS Class-2 CP titanium sheets having the properties shown in Table 2. **Fig. 6** shows the results. Formability improves with increasing coating thickness up to 0.5μm, but beyond this thickness, the improvement saturates. This result indicates that, within the range of deformation examined in this study, a coating as thin as 0.5μm serves the purpose.

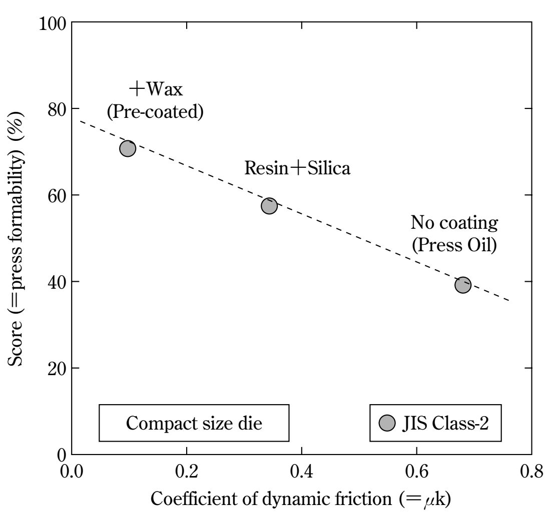

Fig. 5 Effect of coefficient of dynamic friction on press formability

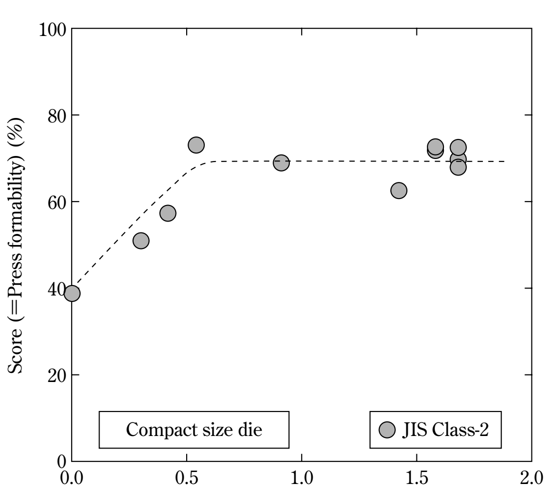

Fig. 6 Effect of thickness of pre-coated layer on press formability

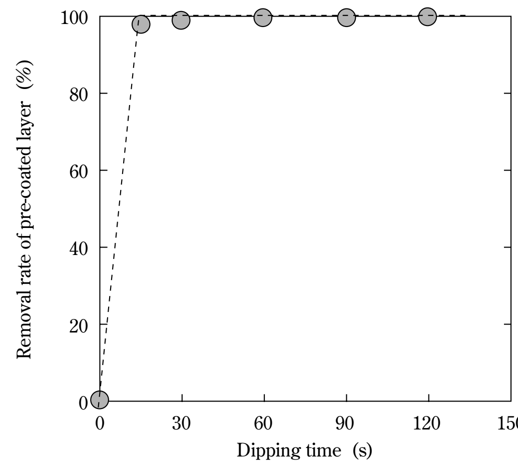

Fig. 7 Removability of pre-coated layer by dipping in alkaline cleaner bath

This lubricant pre-coating is applicable as-is to PHEs; however, heat transfer via the coating deteriorates the heat transfer performance. To resolve this issue, the coating was modified so that it can be removed by commonly-used alkali cleaning. The removability of the coating was evaluated by the test described below.

Each lubrication coating was measured for its coating quantity and subsequently immersed for a predetermined time in a cleaning solution which is generally recommended for titanium. After water cleansing and drying, the coating quantity was measured. The degreasing solution was a weak alkali, FINE CLEANER 4368 (manufactured by Nihon Parkerizing Co., Ltd.), which was diluted to a concentration of 20g/L. The bath temperature was set at 60℃. The removal rate of the coating was determined by Formula (6).

$$\text{Removal rate (\%)} = 100 \times (V_0 - V_1)/V_0 \quad \cdots\cdots\cdots (6)$$

wherein V_0 (g/m^2) and V_1 (g/m^2) are the coating quantities before and after the cleaning, respectively.

Fig. 7 shows the relationship between the coating removal rate and immersion time in the alkali solution. The results indicate that coating removal commences immediately after the coating is immersed. The coating is removed completely within 60 seconds. Since alkali cleaning is usually conducted for 1 to 3 minutes, the coating has been proven to be commercially applicable.

3. Press formability of lubricant-pre-coated titanium sheet for test production

Sheets of CP titanium, having different tensile properties and pre-coated with lubricant, were tested for their press formability. The result was compared with press oil lubrication and with film lubrication. **Fig. 8** compares the results. The large die was used for evaluating formability in a condition close to that of real press forming. The figure indicates that the pre-coated lubricant offers a favorable formability similar to that offered by lubricant film. It was also found that the JIS Class-2 material, having strength 15% higher than that of JIS Class-1, exhibits a formability similar to that of the JIS Class-1 material that is press oil lubricated.

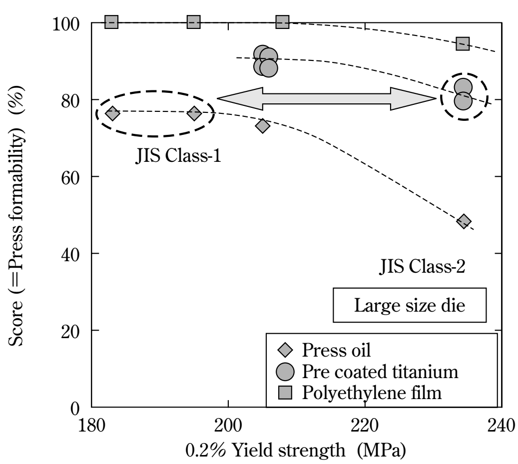

Fig. 8 Press formability of pre-coated JIS Class-1 and JIS Class-2, compared with using press oil and polyethylene film as lubricant

Conclusions

Kobe Steel developed a lubricant-pre-coated titanium sheet to be used for PHEs, a major application for commercially pure titanium. The pre-coating can be applied to JIS Class-2 material that has a strength higher than that of the conventional JIS Class-1, while retaining press formability close to that achieved by press-oil lubrication. The characteristics of the pre-coated titanium sheet have been introduced in this paper. This coating is also designed to be environmentally friendly. The coated layer, which is very thin, requires only light degreasing, leaves much less residue and can be used with much less concern than in the case of press oil. The newly-developed technology is widely applicable not only to PHEs, but also to various press-formed products.

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