Technical Report

Development of Unique Functional Products of Stainless Steel

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Abstract

We have been developing various functional products based on stainless steel manufacturing technology. In this paper, we focused on two products, shaped stainless steel and Al/SUS clad sheets, and introduce their manufacturing technology and product characteristics. For the lean-type duplex shaped stainless steel, experimental results revealed the scale formation behavior due to atmospheric heating during the manufacturing process, and the characteristics of the material and examples of structural products were presented. For Al/SUS clad sheet, the bonding mechanism and fracture mechanism were clarified in consideration of the effect of heat treatment on the bonding strength.

1. Introduction

The Naoetsu Area of Nippon Steel Corporation's East Nippon Works has operated as a production center specialized in high-functionality products based on the manufacturing technology of stainless steel accumulated through years of operation; besides stainless steel, it has also developed and manufactured a variety of titanium and nickel products.[1, 2] Of these, thin sheets of pure nickel have long been used as a material indispensable for use in an alkaline environment such as the production facilities of caustic soda. Pure nickel foils used for the lead tabs of cathodes of lithium-ion batteries and thin sheets of Fe-Ni alloys having excellent magnetic properties are important products that support the latest information technology society. Unique stainless-steel products of the Naoetsu Area include section steel necessary for strengthening social infrastructure and used mainly for water treatment facilities of lakes and rivers, and clad sheets laminated with sheets of different metals, the joining technology in mass production which has been made viable thanks to the development of the rolling technology of stainless-steel thin sheets. These products have been developed based on the expertise of vertically integrated technical management to control melting and casting of different steel grades, rolling, heat treating, and processing them into individual products of prescribed quality.

Of these products of stainless steel unique to Naoetsu, this paper focuses on stainless steel sections and thin sheets clad with aluminum (as the symbol for stainless steel in the Japanese Industrial Standards (JIS) is SUS, the clad sheets are hereinafter referred to as Al/SUS sheets), and describes their manufacturing technology and product characteristics referring to some examples.

2. Stainless-steel Sections

Stainless-steel sections are used, as mentioned earlier, for water treatment facilities of lakes and rivers, the structural parts of kitchen worktables, etc. Excellent corrosion resistance and consequent characteristics of being maintenance-free and clean in water environments are essential for these applications. For this reason, mostly SUS304 and SUS316 under JIS (hereinafter all the SUS designations indicate grades of stainless steel under JIS), typical austenitic stainless steels having excellent corrosion resistance and high strength, are used for those applications. As for the product shape, mainly angles and channels in long pieces are sold in the market.

The market demand for high-functionality products is strong in the field of stainless-steel sections, and especially after the Great East Japan Earthquake in March 2011, the scale of the infrastructure facilities built for reconstruction tended to be large, and reduced thickness and lighter weight are required for the construction materials to increase strength and extend the service life (corrosion resistance). Lean dual-phase stainless steel is attracting attention as a type of steel that meets this requirement.

2.1 Lean dual-phase stainless steel

Conventional dual-phase stainless steel has a two-phase structure consisting of an austenitic phase and a ferritic phase at room temperature, and has excellent strength (proof stress) and high corrosion resistance. However, it tends to be costly because of high contents of alloying elements, especially that of expensive Mo. Lean dual-phase stainless steel maintains the excellent strength characteristics of conventional dual-phase stainless steel, but its alloying costs are decreased by partially replacing Ni and Mo with Cr, Mn, and N, while the corrosion resistance is controlled to be equivalent

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to that of SUS304. Nippon Steel is supplied by Nippon Steel Stainless Steel Corporation with billets of NSSC 2120™,[3] a grade of lean dual-phase stainless steel developed by the latter, and rolls them into high-strength sections. Naoetsu's product range has been expanded recently by using the billets of another lean dual-phase stainless steel of higher corrosion resistance, UNS S32304 (23%Cr-4%Ni-1.5%Mn-Mo-N).

2.2 Scale formation behavior of lean dual-phase stainless steel in heat[4]

Sections of lean dual-phase stainless steel are manufactured by hot-rolling material billets between grooved rolls and then annealing and pickling the rolled steel. The scale formation during these processes is different between conventional austenitic stainless steel such as SUS304 and lean dual-phase stainless steel, and consequently, the chemical composition and form of the scale differ even when the heating and heat treatment conditions are the same. In addition, there have been cases where the metallographic structure of the surface layer of lean dual-phase stainless steel changes partially as a result of scale formation. Such a change in the surface condition of the material may lead to rolling defects, and it is necessary to accurately understand the scale formation behavior in heat and the structural change of the metal surface layer. The metallographic structure of dual-phase stainless steel consists of roughly equal amounts of austenitic (γ) and ferritic (α) phases at room temperature, each of which is exposed at the metal surface. Because the oxidation behavior is different between the γ and the α phases,[5] the scale formation behavior of this type of steel is complicated, and the change in the surface condition from heating to high temperature to cooling is not fully understood yet. In consideration of this, using test pieces of UNS S32101 (21.5%Cr-1.5%Ni-5%Mn-Mo-N), a typical lean dual-phase stainless steel, we investigated the scale formation behavior during heating in normal atmosphere and the change in the metallographic structure of the material surface layer beneath the scale.

In the test, billet test pieces were heated to 1200°C, the normal heating temperature for hot rolling, in a reheating furnace of normal atmosphere, and the growth of scale was observed at different stages of heating. In addition, the phase distribution at the steel surface was measured by electron backscatter diffraction (EBSD) using test pieces heated for 1 and 10 h and then cooled.

Figure 1 shows the distribution of component elements at a section of the scale on the surface of a billet of UNS S32101 after heating in normal air at 1200°C for 1 h and then cooling; an energy dispersive X-ray spectroscope (SEM/EDX) was used for the analysis. There was (Mn, Cr)$_3$O$_4$ in the outer layer of the scale, Cr_2O_3 in the inner layer, and SiO_2 locally at the interface between the metal and the scale.

Figure 2 shows the phase distribution at a section of the surface layer of test pieces after heating in normal air to 1200°C for 1 and 10 h and then cooled. A layer consisting only of an α phase was found on the metal surface, and its thickness increased with heating time. By a separate measurement, the concentrations of Mn and N were found to be low in the single α phase layer. The low Mn concentration was considered due to the outward diffusion of solid-solute Mn as a result of scale formation. From the analysis results of thermodynamic calculation, it was predicted that the solid solubility of N in metal would lower with decreasing Mn concentration. From the above, it was presumed that the single α phase layer was formed at the metal surface as a result of the decrease of Mn and N due to oxidation to form the scale.

The stable quality of Naoetsu's section products has been secured by adequately controlling the process conditions based on the understanding of the phenomena peculiar to dual-phase stainless steel as clarified above.

2.3 Examples of products of lean dual-phase stainless steel and their applications

Table 1 shows the chemical composition of NAR-2120, a typical material of Naoetsu's product of lean dual-phase stainless steel, **Table 2** its mechanical properties, and **Fig. 3** is an example of its microstructure. (NAR-2120 is Nippon Steel's brand name of the sections produced by rolling billets of NSSC 2120.) NAR-2120 has a particularly high proof stress compared to SUS304, and is suitable for reducing the thickness of sections to decrease the weight of the final structures made of them. At present, Naoetsu's product lineup of sections of lean dual-phase stainless steel covers from small angles 5 to 9 mm in thickness and 40 mm in leg length to large channels 150 mm in height and 75 mm in leg length.

An example of final structural products for which NAR-2120 sections of Naoetsu are used is a high-strength inspection passage for bridges, elevated roads, factories, etc. (NS smart inspection pas-

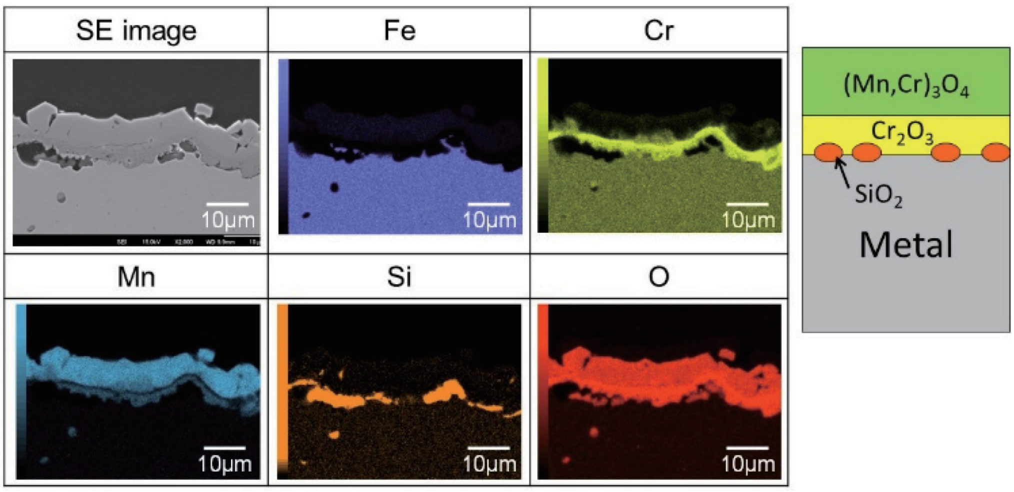

Fig. 1 Sectional distributions of component elements by SEM/EDX on the surface scale of UNS 32101 heated in normal atmosphere (1200°C, 1 h)[4]

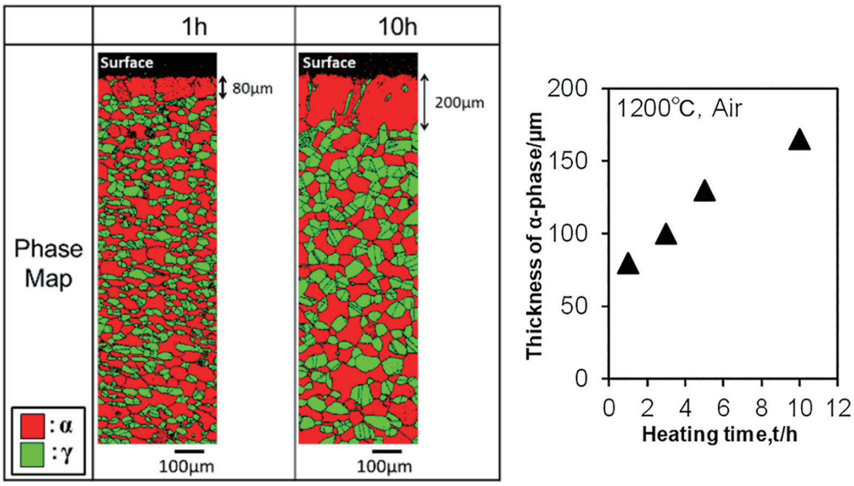

Fig. 2 Phase distribution of UNS 32101 heated in normal atmosphere at 1 200°C and thickness change of surface layer in *α* phase[4)]

Table 1 Typical chemical composition of NAR-2120 (mass%, Equivalent to NSSC 2120™)

	C	Si	Mn	Cr	Ni	Mo	Cu	N
NAR-2120	≤ 0.030	≤ 0.75	2.00–4.00	20.50–21.50	1.50–2.50	≤ 0.60	0.50–1.50	0.15–0.20
SUS304	≤ 0.08	≤ 1.00	≤ 2.00	18.00~20.00	8.00~10.50	–	–	–

Table 2 Mechanical properties of NAR-2120

	Proof stress / N·mm^{-2}	Tensile strength / N·mm^{-2}	Elongation (%)	Hardness HV
NAR-2120	≥ 400	≥ 600	≥ 25	≤ 310
SUS304	≥ 205	≥ 540	≥ 45	≤ 200

sage, NETIS registration number HK-200018-A,[*1] see **Fig. 4**).[6)] Taking advantage of the high strength and corrosion resistance of lean dual-phase stainless steel, the ease of installation and inspectors' workability at places with limited workspace are improved by the use of minimum thickness and lightweight materials. In addition, it is also expected to contribute to reducing environmental loads because of the long service life.

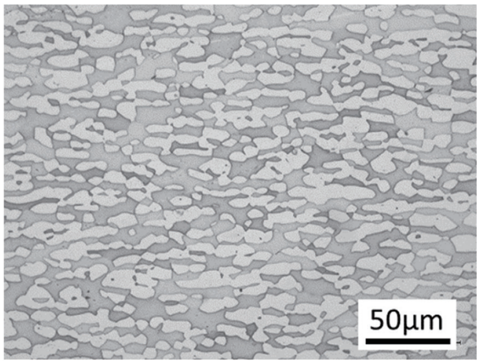

Fig. 3 Typical microstructure of NAR-2120 shaped steel (cross section perpendicular to R.D.)

3. Clad Thin Sheets

Clad metals made by laminating and integrating dissimilar metals of different mechanical properties are functional materials capable of offering higher or new functions that single-metal materials do not have; it is possible for one metal to compensate for the shortcomings of the other(s), and benefit from the features of all constituent metals at the same time. The application of Al/SUS clad thin sheets has expanded to cooking utensils with electromagnetic cookers such as induction-heating rice cookers becoming popular in Japan from the 1990s. In recent years, it has also been used for the brake rotors of competition mountain bikes because it is effective at preventing problems caused by excessive heating due to friction.[7)]

A technology has been established for producing Al/SUS clad

Fig. 4 NS smart inspection passage for bridges, factories, etc. (NETIS registration number HK-200018-A)[6)]

[*1] New Technology Information System (NETIS) is a database system of the Ministry of Land, Infrastructure, Transport and Tourism of Japan designed to provide and share information related to new technologies in the field of the construction industry.

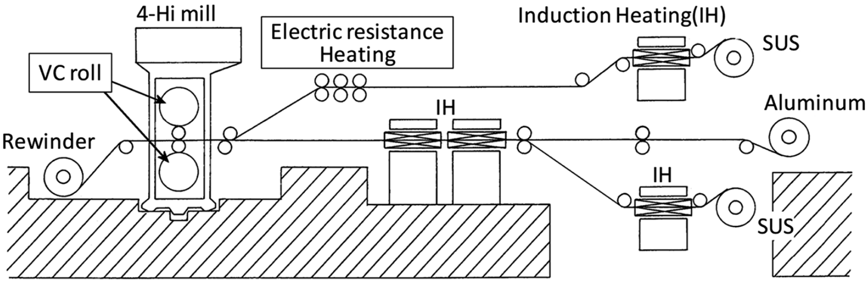

Fig. 5 Outline of clad coil production line[7)]

sheets in large-width coil in quantities by the warm rolling and laminating method. However, there was no unified understanding regarding the bonding mechanism and the effects of heat treatment after the bonding by rolling. In this situation, we studied the microstructural changes at the bonding interface during the heat treatment using specimens of two-layer clad sheets of 16Cr stainless steel and aluminum.

3.1 Bonding method of Al/SUS clad sheets[7, 8)]

In the joining method by warm rolling, sheets or coils of component metals are preheated, laid on each other, and then rolled together. By this method, aluminum is softened by the preheating, and it is possible to easily improve the adhesion of the metals at the interface. The upper limit of the preheating temperature is defined by the melting point of the material (660°C in the case of pure aluminum) and also from the viewpoint of suppressing the formation of intermetallic compounds at the interface after the bonding. As a result, the material temperature just before the rolling is in the range roughly of 200 to 400°C in usual practice. Stainless steel barely softens in this temperature range, and both the metals have sufficient resistance to oxidation. This method is, therefore, excellent for industrial production in that vacuum equipment or heating furnaces of special atmosphere are not required, and that the laminating rolling can be conducted in normal atmosphere.

Figure 5 shows an outline of a production line for clad sheets in coil. Here, the material sheets are preheated in-line, and immediately after that, rolled and joined together through a 4-high rolling mill and then wound into coils. **Table 3** shows the size of the clad thin sheets manufactured through the line. The maximum coil width for stable production is 914 mm, which enables manufacture of wide coils. To stably manufacture wide clad coils, it is necessary to ensure the uniformity of the material temperature and the reduction ratio of the mill in the width direction. Equipment measures are taken for this purpose: the material strips are preheated using direct resistance heating, and variable crown (VC) rolls are used as the backup rolls of the mill.

The clad thin metal sheets manufactured on this line are composed basically of two or three layers, aluminum being the base material, and it is possible to use a material other than stainless steel as the laminating metal. Appropriate material design according to the final use makes it possible to bring about new or enhanced functions that no single metal materials can offer.

3.2 Microstructure of joint interface of Al/SUS clad sheets[9)]

Two-layer clad sheets of 16Cr stainless steel and aluminum bonded together at a temperature of about 250°C were used as the specimens for the present test. The chemical compositions of the two metals are given in **Table 4**. Since it is difficult with thin clad sheets to measure the fracture load and the shear load of the bonding interface directly by applying vertical tension, the adhesion strength

Table 3 Size ranges of Al/SUS and Al/Ti clad sheets[7)]

Combination	Thickness (mm)		Width (mm)
	Total	SUS, Ti	
SUS-Aluminum (SUS/Al, SUS/Al/SUS)	0.6–3.3	0.3–0.8	≤ 914 (Max. 1000)
Titanium-Aluminum (Ti/Al, Ti/Al/Ti)	0.6–2.5	0.3–0.7	≤ 914 (Max. 1000)

Table 4 Typical chemical compositions of 16Cr-stainless steel and A1100 aluminum

16Cr-stainless steel (mass%)

C	N	Si	Mn	Cr	Fe
0.008	0.011	0.55	0.45	16.4	bal.

A1100 aluminum (mass%)

Si	Fe	Cu	Mn	Al
0.10	0.58	0.13	0.01	bal.

of the cladding joint was evaluated in terms of the peel strength similar to what is specified in Part 3 "Adhesives – 180° peel test for flexible-to-flexible bonded assemblies (T-peel test)" of JIS K6854 "Adhesives – Determination of peel strength of bonded assemblies." **Figure 6** shows the outlines of a test piece.

Figure 7 shows the change in the peel strength of as-rolled clad sheets and those heat treated at 200 to 600°C after the rolling. There was no difference in the peel strength between the as-rolled specimens and those heat-treated at 200°C; this is because the material sheets have already undergone a thermal history of 200°C or higher during the process of rolling and joining. The peel strength began to increase clearly when the heat treatment temperature was raised to 300°C, and it increased further as the temperature rose, hitting a maximum at 450 to 500°C. When the specimens were heat treated at 500°C for a long time, a brittle intermetallic compound of Fe and Al formed near the interface, and the peel strength decreased sharply.

Figure 8 shows bright-field images of the bonding interface taken through a transmission electron microscope (TEM). In either of the as-rolled specimen shown in part a) or another heat-treated at 400°C for 300 s shown in part b), an intermediate layer having multiple internal structures was confirmed there at the interface. The intermediate layer was found to exist in the entire interface area, and no interruption or significant change in its thickness was observed. That of the as-rolled clad sheet shown in Fig. 8 a) had a thickness of about 20 nm in the entire field of view and an internal structure consisting of a plurality of irregularly undulating sub-layers. On the other hand, that of the heat-treated sheet shown in Fig. 8 b) had, similarly to the above, a uniform thickness of about 20 nm, but its internal structure was more uniform, consisting of flat sub-layers of less undulation, and islands of another phase, presumably a foreign phase, were found scattered therein.

As a result of structural analysis of these bonding interfaces using a high-resolution TEM, the thickness of the intermediate layer of both an as-rolled sheet and another heat-treated at 400°C was roughly 20 nm, and no atomic diffusion beyond that range was confirmed to have taken place. In the intermediate layer of the as-rolled sheet, there were various types of oxides in different shapes in which mainly Fe and Al were mixed with small amounts of Cr and O. It is presumed that, because of the mixed existence of the oxides, the intermediate layer had the multiple structure of a complicated and undulating shape. When clad sheets are heat treated at 400°C for 300 s after the bonding by rolling, the composition of the mixture of oxides before the heat treatment is changed, that is, Al is bonded strongly to oxygen to form amorphous Al oxide, and this Al oxide becomes dominant. As a result, the intermediate layer is reconfigured into one composed of a plurality of uniform sublayers. It is presumed that oxides containing Fe were partially reduced by Al, and remained in the intermediate layer as islands of α-Fe. It is presumed also that the intermediate layer plays the role of a binder between the two metals, and at the same time, as a barrier to suppress the mutual diffusion of the two metal elements during heat treatment at 500°C or lower, and thus prevents the formation of the Fe-Al intermetallic compounds.

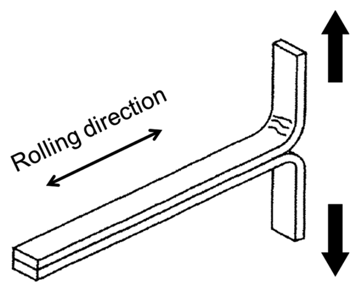

Fig. 6 Shape of test piece for peel test

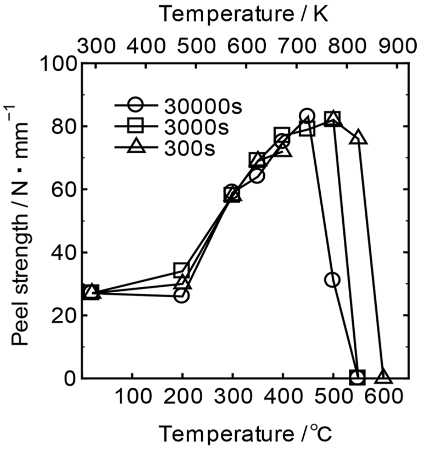

Fig. 7 Effect of heat treatment conditions on peel strength[9)]

3.3 Fracture mechanism of Al/SUS clad sheets at forced peeling[10)]

A peel test was conducted using test pieces of as-rolled clad sheets and those heat treated at 300 and 400°C for 300 s after the bonding by rolling, the peeled surfaces were observed through a scanning electron microscope (SEM), and the fracture mechanism was studied based on the observation results. The possible sites of fracture were the Al base metal, the 16Cr stainless-steel base metal, and the intermediate layer. **Figure 9** shows the area fractions of the fracture sites inferred from the SEM observation results of the fracture surfaces.

The failure of the as-rolled clad sheets was judged to have occurred in the intermediate layer on 59% of the fracture surface. In the case of those heat treated at 300°C, on the other hand, the area ratio of the fracture of the Al base metal was dominant at 55%, and the ratios of the 16Cr stainless-steel base metal and the intermediate layer were smaller than those in the case of the as-rolled specimens. A raise in the heat treatment temperature from 300 to 400°C did not cause any significant difference in the area fractions of the fracture sites, but that of the aluminum base metal increased to 62%, and that of the intermediate layer decreased accordingly. As seen in Fig. 7 above, peel strength was increased as a result of heat treatment at 300°C or higher. This is presumably because the fracture of the aluminum base metal became dominant, and at the same time, the ductility of aluminum was restored by heat treatment, the aluminum

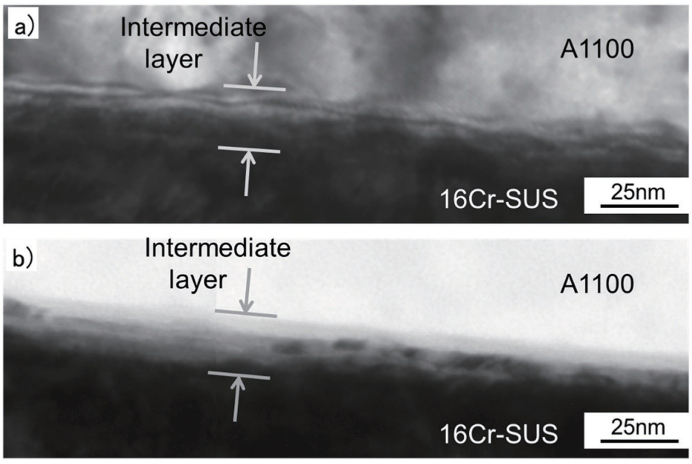

Fig. 8 TEM micrographs of bonding interface: a) as rolled, b) heat treated at 400°C for 300 s[9)]

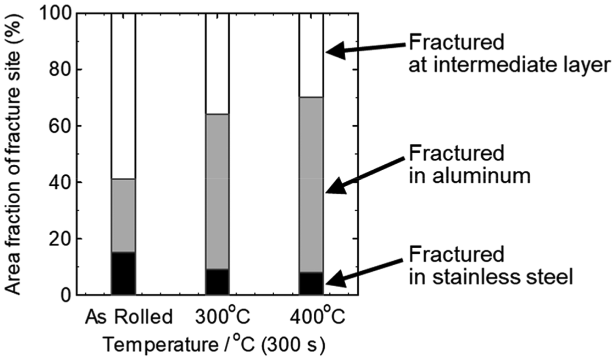

Fig. 9 Relationship between area fraction of fracture site at peel test and heat treatment temperature[10)]

base metal was elongated and deformed by the peeling force until it failed, and consequently, the area in which Al was plastically deformed was increased. As a result, the peel strength per unit width was increased.

4. Conclusion

The present paper focused on stainless-steel sections and Al/SUS clad sheets as examples of the original products of the Naoetsu Area developed on the basis of stainless-steel production technology, and explained their manufacturing methods and product characteristics. Stable production of sections of lean dual-phase stainless steel has been achieved by adequately controlling the process conditions based on the understanding of material-specific phenomena such as scale formation and growth during heating in normal atmosphere. High strength and good corrosion resistance, characteristic of lean dual-phase stainless steel, are effectively used for weight reduction and long service life of final structural products made of the sections. Focusing attention on the effects of heat treatment on the strength of the bond between aluminum and stainless steel of Al/SUS clad thin sheets, we clarified the mechanisms of the interface bond and its fracture. The findings of the study are utilized for improving the use of the product.

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