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Development of Hot-Rolled Titanium-Clad Steel Coils by Using Liquid Phase at Titanium-Steel Interface for Bonding

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Abstract:

Technology for bonding titanium and steel in air was developed for low-cost production of titanium-clad steel coils. A copper sheet is inserted between the titanium and steel to be bonded. A molten titanium-copper intermetallic compound is formed by the solid-phase reaction between the titanium and copper, and by rolling is squeezed out of the interface together with oxides and residual air. The fresh titanium and steel surfaces thus created are directly bonded. The optimum heating temperature and time for this process are 850 to 900°C and 300 to 1,800 s, respectively. The bond strength produced by the new process is about 180 MPa, which is lower than that of titanium-clad steel made by directly rolling together titanium and steel in vacuum, but is high enough for practical purposes.

1. Introduction

Titanium has superior corrosion resistance, but is very expensive compared with steel. Its high cost has prevented its popular use in roofing and automotive applications where corrosion resistance is an essential requirement. There have been studies made into the use of titanium-clad steel with a view to reducing cost while best utilizing the excellent corrosion resistance of titanium.

When titanium is heated to high temperatures at its bond interface with steel, it readily forms titanium-iron intermetallic compounds and titanium carbides, which drastically reduces the bond strength1). Therefore, titanium-clad steel cannot be made by the casting process or the hot rolling process as is the case with stainless steel-clad steel, but is made mainly by the explosive welding process at room temperature2-4). Recently, metallurgical factors that affect the bondability of titanium to steel have been studied, and technology has been established for making titanium-clad steel by the rolling process5-11). The rolling process, however, makes it indispensable to keep the titanium-steel interface under a vacuum12) and calls for a vacuum rolling mill13) that can keep the slab assembly operation and mill itself under a vacuum. These requirements prevented the cost of rolled titanium-clad steel production from being reduced to any significant extent.

Thus, rolled titanium-clad steel could be manufactured only with special equipment and by special methods, so that it could not take any form other than plates that can absorb the merit of cost savings, keeping the sheet form outside the feasible range of manufacture, technically and economically.

This report describes the history of technology development for joining titanium and steel in air, as well as the process design work conducted for cladding steel with titanium in air on the basis of the technology. The properties of titanium-clad steel produced by the new process are also presented.

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2. Basic Concept

Titanium and steel can be easily bonded by pressing their fresh surfaces against each other by rolling, for example. In hot air, however, oxides instantaneously form on the fresh titanium and steel surfaces to prevent them from being tightly bonded[14]. An idea was conceived to create a liquid phase once at the titanium-steel bond interface and then squeeze it out of the interface to bond the two metals together.

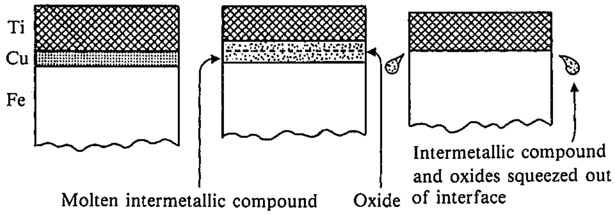
Removal of oxides and residual air from the interface is indispensable for metal bonding in the atmosphere, but residual air cannot be removed from an interface of solid-phase materials. It was decided to fill the interface with a liquid phase and use it as carrier medium in squeezing out the oxides and residual air from the interface.

A liquid phase, however, cannot be introduced at the interface of titanium and steel unless another substance is inserted between them. An idea was conceived of inserting a copper sheet between the titanium and steel (see **Fig. 1(a)**) and filling the interface with the titanium-copper intermetallic compound ($TiCu_3$ with a melting point of about 880°C[15]) formed by the solid-phase reaction between titanium and copper (see **Fig. 1(b)**).

When oxides and residual air are squeezed out of the interface together with the liquid phase, the fresh solid-phase surfaces come into direct contact for bonding (see **Fig. 1(c)**). The assembly is fast rolled at a high reduction rate in order to minimize the amount of residual liquid-phase material and enhance the direct contact of fresh metal surfaces. This heavy reduction process is none other than the normal continuous hot rolling process, and produces a hot-rolled titanium-clad steel in coil.

3. Test Methods and Specimens

The possibility of bonding titanium and steel through the intermediary of copper was explored according to the idea described above. Titanium and steel bars, each measuring 10 mm in diameter, were butted through a 0.4 mm thick copper sheet, and heated and pressure welded under specified temperature conditions in vacuum and air, respectively, using a compression test machine. The pressure welding test specimen was cooled, machined into a tensile test specimen (with a parallel section diameter of 8 mm), and evaluated for bondability by tensile strength. The test temperature was 600 to 1,000°C for 300 to 7,200 s, and the butt compression load was set at 9.8 MPa (1 kgf/mm^2) when the specified temperature was reached. The load was then gradually reduced, until it became almost zero after 300 s at 1,000°C, in particular. The load was not increased in the middle of the test nor was it controlled at a constant level. For the purpose of comparison, titanium and steel were directly pressure welded without the copper insert.



(a) Materials (b) Heating (c) Rolling

Fig. 1 Conceptual diagram of bonding process by squeezing liquid phase out of interface
(a) Materials: Cu was inserted at interface and heated.
(b) Heating: Molten Ti-Cu intermetallic compound was formed at interface.
(c) Rolling: Oxide and other substances were squeezed out of interface together with molten Ti-Cu intermetallic compound.

To investigate the bond interface, the specimen was cooled with liquid nitrogen as required and was broken in air by impact force. The titanium bar used in the pressure welding test was JIS Class 2 commercially pure titanium, the steel bar was JIS SS400 steel, and the copper sheet was commercially available pure copper. The chemical compositions of the steel and titanium used are given in **Table 1**.

Laboratory rolling test was then conducted under the pressure welding test conditions that produced good bondability values. The laboratory test used JIS SS400 steel (20 mm thick) as base metal, JIS Class 2 commercially pure titanium (3 mm thick) as cladding metal, and commercially available pure copper (0.5 or 1 mm thick) as insert. These metals were cleaned in acetone, overlapped in air, and covered with 0.5-mm thick SS400 steel through a separating alumina-based paste to prevent warpage, separation and displacement before and during rolling. The SS400 steel cover was welded to the base metal in the test specimen. Some portions were left unwelded to allow the escape of residual air during heating.

The specimen was rolled with the cover into a thickness of 2 or 3 mm. The bondability of the clad steel was evaluated qualitatively by edge machinability and 180° bending test or by the shear peel strength test described in JIS G 0601. JIS G 0601 covers clad steel 8 mm or more in thickness, but was applied with necessary modifications to the 3-mm or less thick clad steel described in this report. Successfully hot roll-bonded titanium-clad steel was examined for the thickness of the intermetallic compound layer and the presence or absence of oxides at the interface by the electron probe microanalyzer (EPMA) or computer-aided X-ray microanalyzer (CMA)[16] that has a wide scope of analysis.

4. Test Results and Discussion

4.1 Possibility of bonding titanium and steel by utilizing liquid phase

The butt welding test of bar specimens verified the possibility of bonding titanium and copper in air as well as in vacuum to such a strength level that the clad metal could be machined. A molten substance was seen dripping in a small amount from the bond interface of the specimen pressure welded with the copper insert at 900°C or higher. Elemental analysis by the EPMA identified the leaking substance as a titanium-copper intermetallic compound. The liquid-phase intermetallic compound was found neither in specimens pressure bonded at 850°C or lower nor in those pressure bonded without the copper sheet insert. When the

Table 1 Chemical compositions of bonding test materials (wt%)

Material	C	Si	Mn	P	S	sol Al	N	O	H	Fe	Remarks
Steel	0.118	0.007	0.366	0.014	0.003	0.022	0.0026	0.0013	—	—	
Ti	0.008	—	—	—	—	—	0.010	0.131	0.0054	0.004	JIS-TP35H

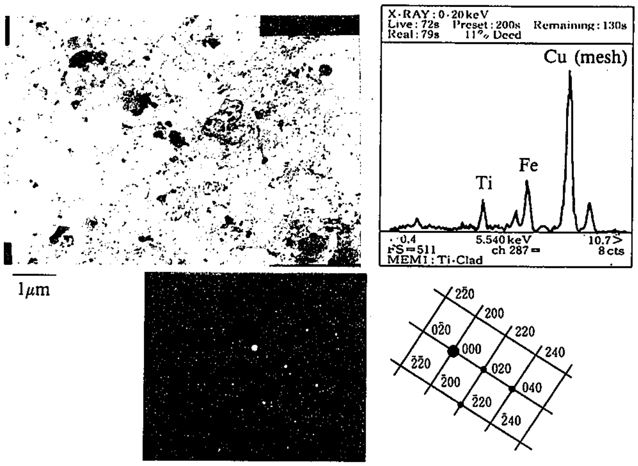


Photo 1 Electron diffraction and EDS elemental analysis of residual precipitate at bond interface between titanium and steel

cross section of the bond of specimens roll bonded in air was analyzed by the EPMA, no oxygen was detected. The effect of squeezing out the liquid phase from the interface is considered much smaller in the test than in the actual rolling mill operation because the butt stress decreases with time. Nevertheless, oxides were extinct in the bond interface tested. This is probably because any oxides that eluded the squeezing force were reduced by the strong reducing power of metallic titanium with all the remaining oxygen atoms being dissolved in the titanium.

Titanium and steel could not be directly bonded in air because of the formation of a thick oxide film at the interface, according to the conventional theory. The titanium-clad steel appeared to be tightly bonded in vacuum, but failed at the bond interface when machined to prepare a tensile test specimen. **Photo 1** shows the results of electron beam diffraction analysis and elemental analysis by energy-dispersive X-ray spectroscopy (EDS) of the residual precipitate extracted from the bond interface on the steel side of the failed specimen. The extracted residual precipitate was identified as TiC (hexagonal compound with a_0 = 0.43285 nm) because it had a hexagonal structure with a_0 = 0.4347 nm and because titanium was detected.

The above results showed that oxides and carbides are factors responsible for inhibiting the bonding of titanium and steel at the interface and can be removed from the interface if a melt is formed at the interface by using copper and is squeezed out of the interface. It was thus confirmed that titanium and steel can be bonded in air.

4.2 Titanium-steel bond strength

Specimens cooled after the bond test were found to be bonded to varying degrees, irrespective of whether the copper insert was used and whether the bond was made in air or vacuum. The specimens bonded at 700°C or above could not be bent or broken by hand, but the specimens heated to 650°C or lower broke at the butt interface when removed from the testing machine.

Fig. 2 shows the effect of heating temperature on the bond strength of specimens. The specimens that failed during machining are indicated by putting their bond strength at zero. All specimens failed at the bond interface, and there appeared to be no base metal elongation. The bond strength was the highest when the heating temperature was 850 to 950°C, about 70 MPa when the heating temperature was 900°C, and about 60 MPa when the heating temperature was 950°C. **Fig. 3** shows the effect of heating time on the bond strength of specimens when the heating temperature was 900°C. The bond strength was relatively high when the heating time was the shortest 300 s and steeply declined when the heating time exceeded 3,600 s.

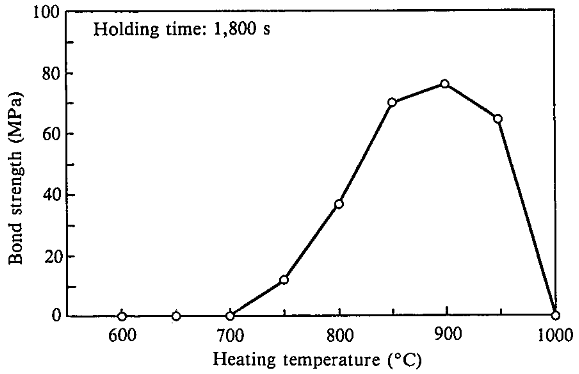


Fig. 2 Effect of heating temperature on bond strength (holding time: 1,800 s)

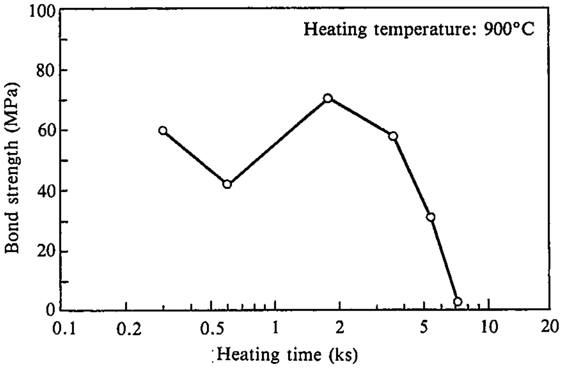


Fig. 3 Effect of heating time on bond strength (heating temperature: 900°C)

The bond strength of steel clad with titanium without the copper insert was about 100 MPa at the heating temperature of 900°C when tested by the same tensile test method and was higher than when the copper insert was used. Specimens pressure welded in air without the copper insert were bonded just after the pressure welding test, but were broken at the interface when machined to prepare tensile test specimens. A blue or light brown oxide visible to the naked eyes was observed at the interface of those specimens.

4.3 Optical microstructures of cross sections of titanium-steel bond interface

Photo 2 shows the optical microstructures of the bond cross sections of four specimens after heating and pressure welding test. Specimen A had titanium and steel bonded through a copper insert at 850°C. After the test, the copper insert remained intact between the titanium and steel in practically the same condition as before the test, indicating no significant change through the process. Specimens B and C had the titanium and steel bonded through a copper insert at 900 or 950°C. The copper insert was almost completely eliminated from the interface. These specimens were in full accord with those showing a leaking substance at each edge. This finding substantiated the assumption that the copper would form a low-melting-point intermetallic compound with

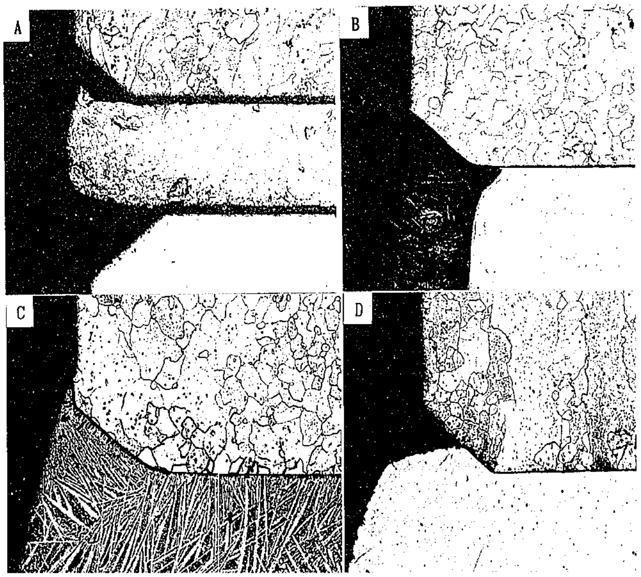


Photo 2 Optical microstructures of interface cross sections of four specimens after butt welding test
A: 850°C-0.5 h (Cu inserted) B: 900°C-0.5 h (Cu inserted)
C: 950°C-0.5 h (Cu not inserted) D: 900°C-0.5 h (Cu not inserted)

titanium as predicted from its phase diagram, and that the intermetallic compound would ooze to the side. In this test, the butt welding load was initially set at 9.8 MPa (1 kgf/mm^2), a value which is lower than the reduction stress during hot rolling, and decreased after the start of the melting of the intermetallic compound $TiCu_3$, reaching zero in a short time. Despite this situation, the liquid phase was completely squeezed out of the interface. This result suggests that the squeeze-out of the liquid phase can be expected even under light reduction.

A very thin different phase was recognized at the interface where the titanium and steel were presumed to be in contact after the elimination of copper. This phase is probably the liquid phase left without being squeezed out of the interface or a high-melting-point titanium-copper intermetallic compound. When the specimen was heated to 950°C or above and pressure welded, its peripheral titanium area indicated the formation of a phase with a microstructure composed of white acicular grains on a black matrix when etched in nital. This phase is also regarded as a titanium-copper intermetallic compound. It thickly formed in the peripheral titanium area, probably because the area was high-frequency heated to a higher temperature than the other area.

The specimens having the titanium and steel pressure welded through the copper insert formed a thin intermetallic compound layer but no oxides at the interface and had a very good bond. Optical microscopy found no special phases at the interface of the specimens heated and pressure welded in vacuum without the copper insert.

4.4 Laboratory roll bonding results of titanium-clad steel sheet

Fig. 4 shows the laboratory roll bonding results of titanium-clad steel. These results approximately agree with the interface breaking strength of specimens in the pressure welding test. Sound bonds were obtained at the heating temperature of 850 to 900°C. **Photo 3** shows the appearance of two laboratory titanium-clad steel sheets. Sheet B had the titanium and steel tightly bonded, left the cover welds saw-toothed at the edge, and had no separation or cracking. Sheet A was roll bonded under inappropriate conditions and suffered separation in the first few passes, forcing the abort of the roll bonding operation.

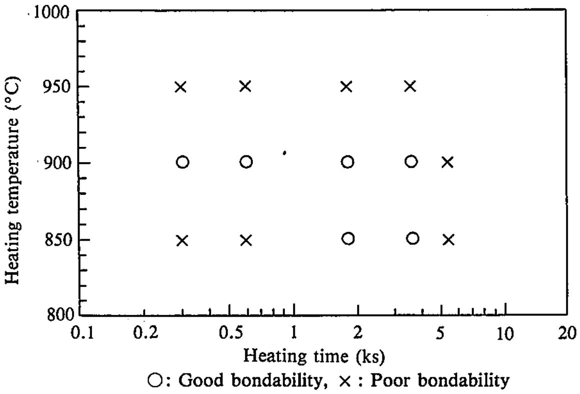


Fig. 4 Laboratory rolling test results of titanium-clad steel made by utilizing liquid phase

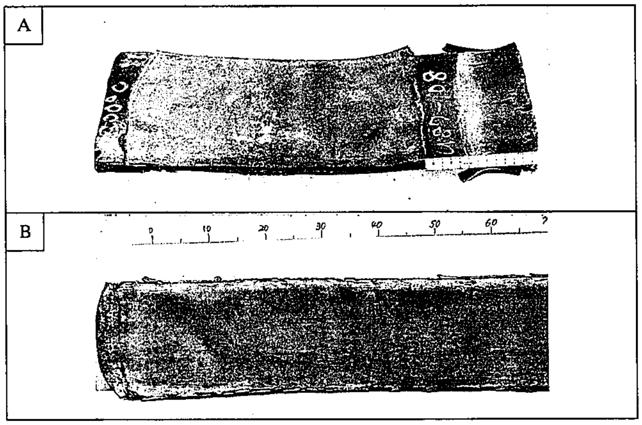


Photo 3 Appearance of laboratory rolled titanium-clad steel sheets made by utilizing liquid phase
A: 800°C-0.5h B: 900°C-0.5h

When the specimen was heated to 900°C or above and rolled in the first pass, a molten substance scattered toward the rear and sides of the mill. The scatter tendency of the molten substance showed no difference within the first-pass reduction range of 10 to 40%. The copper insert was 0.5 or 1.0 mm in thickness. The copper insert thickness had no effect on the scatter tendency of molten substance. In either case, the molten substance did not scatter in the second and subsequent passes.

The molten substance collected at the rear of the mill was lava-like and its surface exhibited such interference colors as blue, green and yellow. **Photo 4** shows the appearance, cross-sectional optical microstructure, and EDS elemental analysis of the scattered molten substance. A dendrite structure was recognized, in which titanium and copper were identified. It was thus confirmed that the scattered molten substance was a titanium-copper intermetallic compound and that it was squeezed out of the interface by rolling as predicted.

4.5 Properties of titanium-clad steel sheet produced by laboratory test rolling

Photo 5 shows the cross-sectional optical microstructure of titanium-clad steel sheet produced by hot rolling in the laboratory (after heating at 900°C for 0.5 h). As evident from the microstructure, the titanium thickness is almost constant, and

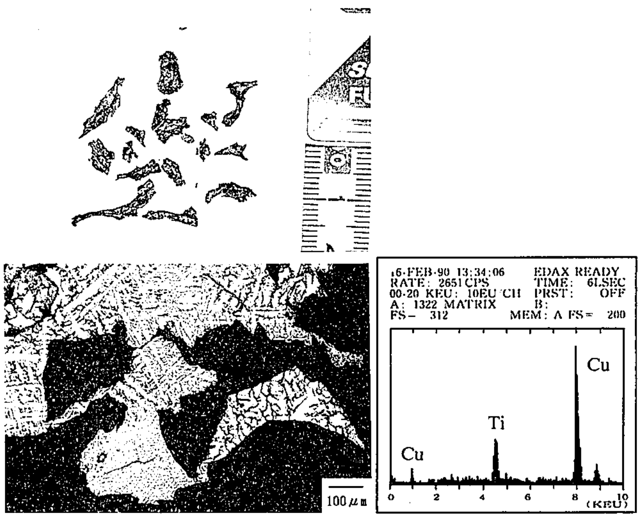


Photo 4 Appearance and cross-sectional optical microstructure of scattered molten substance (nital etch)

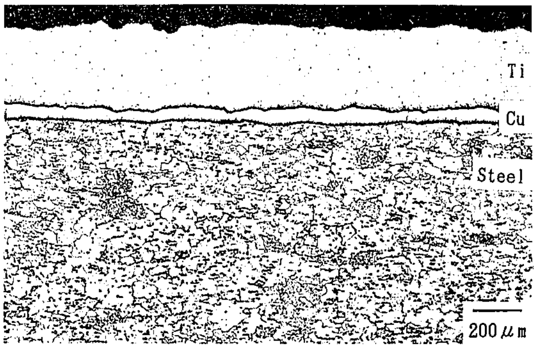


Photo 5 Cross-sectional optical microstructure of laboratory hot roll-bonded titanium-clad steel (after heating at 900°C for 0.5 h)

no oxides are observed at the interface.

Fig. 5 shows the hardness distribution of the titanium-clad steel sheet across the bond interface. The titanium-copper interface was slightly harder than the bulk of the base metal and the cladding metal, suggesting the presence of an intermetallic compound. **Fig. 6** shows the CMA composition line analysis of the interface. The region where titanium and copper overlap was detected over a width of 1 μm or less at the titanium-copper interface, and the presence of a presumably intermetallic compound layer was confirmed. The CMA failed to detect oxygen at the titanium-copper interface. This finding supports the removal of oxides and residual air from the interface as foreseen.

Fig. 7 shows the Weibull distribution of the shear strength of titanium-clad steel. For comparison purposes it includes the data of 3-mm thick titanium-clad steel with a cladding ratio of 10 to 15% produced by the vacuum rolling process in the laboratory and of commercially available 2.2-mm thick laminated steel. The shear strength of the titanium-clad steel sheet made by the new process is about 180 MPa, which is higher than the value specified in JIS G 3603. The shear strength of about 180 MPa is lower than that of the titanium-clad steel sheet made by the conventional vacuum rolling process, higher by approximately one magnitude than that of the laminated steel, and much higher than that of linings with service performance as corrosion-resistant materials and adhesives. **Table 2** gives the mechanical properties of 3-mm thick hot roll-bonded titanium-clad steel (with a measured cladding ratio of 12%) made by the new process in the laboratory.

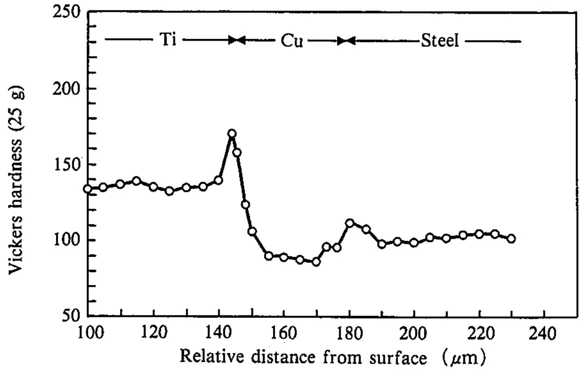


Fig. 5 Hardness distribution across interface of titanium-clad steel made by rolling in laboratory by utilizing molten substance layer

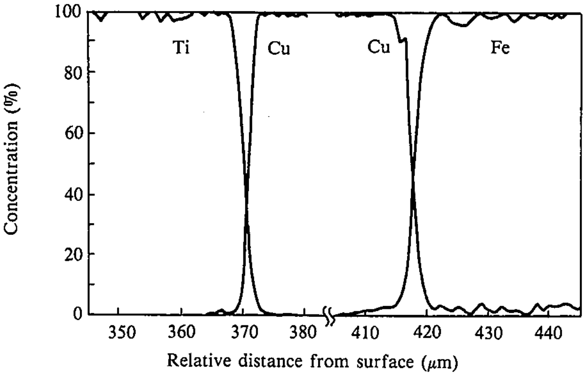


Fig. 6 Composition distribution across interface of titanium-clad steel made by rolling in laboratory by utilizing molten substance layer

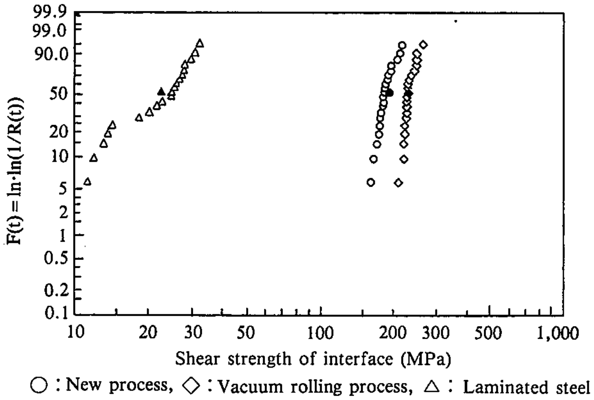


Fig. 7 Weibull distribution of shear strength of titanium-clad steel made by rolling in laboratory by utilizing molten substance layer

Table 2 Tensile properties of titanium-clad steel made in laboratory

σ_B (MPa)	$\sigma_{0.2}$ (MPa)	T-El. (%)	El_{Ti} (%)	σ_S (MPa)
345.2	222.6	44.5	42.3	185.3

σ_B: Tensile strength, $\sigma_{0.2}$: 0.2% offset yield strength, T-El.: Total elongation, El_{Ti}: Elongation at break of titanium, σ_S: Shear strength of interface

The above results demonstrated the feasibility of bonding titanium and steel by introducing a molten substance layer in their interface and squeezing it out of interface together with oxides and residual air through the process of rolling. It was also confirmed by laboratory research based on this idea, that titanium-clad steel sheet can be made in air by utilizing a titanium-copper intermetallic compound.

5. Conclusions

Technology of bonding titanium and steel in air was studied in an exploratory manner, and titanium-clad steel sheet was made by rolling in air in the laboratory. The basic concept of bonding, optimum manufacturing conditions, and properties of titanium-clad steel made on a trial basis may be summarized as follows:

1) A new bonding method was conceived whereby a melt is formed to fill the interface between two metals and is squeezed out of the interface to bond the metals. Titanium and steel can be bonded in air by inserting a copper sheet between them, forming a molten titanium-copper intermetallic compound through solid-phase reaction between the titanium and copper, and squeezing the molten intermetallic compound together with oxides and residual air out of the interface.
2) The optimum heating temperature and time for bonding titanium and steel in air are 850 to 900°C and 300 to 1,800 s, respectively.
3) The effectiveness of the molten titanium-copper intermetallic compound as a sort of carrier for oxides and residual air does not widely differ when the first-pass reduction ranges from 10 to 40% and the copper thickness ranges from 0.5 to 1 mm.
4) The bond strength of titanium-clad steel sheet made by using the molten titanium-copper intermetallic compound is lower than that of titanium-clad steel sheet made by directly pressure welding titanium and steel in vacuum, but is practically high enough for a rolled sheet.
5) An intermetallic compound layer of 1 μm or less in thickness remained at the titanium-copper interface of hot roll-bonded titanium-clad steel sheet. Its hardness was slightly higher than the bulk of the base metal and the cladding metal. No oxides were recognized at the titanium-copper interface.

By this technology, hot-rolled coils of titanium-clad steel sheet were successfully produced at the hot strip mill of Muroran Works for the first time in the world. The titanium-clad steel sheet is used for the corrosion protection of steel bridge piers for the Trans-Tokyo Bay Highway now under construction.

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