Development of High-performance Titanium Alloys for Automotive Exhaust Systems

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Nippon Steel Corporation
Nippon Steel’s Activities for Automotive Applications

Applications of conventional materials

Engine valve (Intake, Exhaust) ; Ti-6Al-4V, Timetal® 1100
Suspension spring ; Timetal® LCB
Muffler ; CP titanium

Original alloys developed by NSC

Super-TIX® 800(Ti-1Fe-0.35O-0.01N),
Super-TIX® 51AF(Ti-5Al-1Fe),
Super-TIX® 523AFM(Ti-5Al-2Fe-3M), etc.
Application of CP Titanium to Automotive Exhaust Systems

More than 1,000 ton/year is produced in Japan for mufflers in motorcycles.

The application range is expanding to four wheeled vehicles.

Strong requirement of materials having higher performance at elevated temperature with keeping good formability.

To properly respond to this issue, NSC has developed new alloys.
1. **Alloy Design**

2. Sheet Manufacturing Process

3. Formability

4. High Temperature Properties

5. Summary
Properties of Titanium Alloys
Required for Automotive Exhaust Systems

• **High Strength at Elevated Temperature**
  - Especially at temperatures **above 600°C**
  - Limited degradation during long term use

• **High Oxidation Resistance**
  - Small thickness loss during long term use
  at high temperatures, especially **above 700°C**

• **Good Formability**
  - Bendability, Stretch-expansion formability,
  Drawability, etc. equivalent to or better than those of
  Gr.2 CP titanium
Questions in the Conventional Concept of Alloy Design for Heat Resistant Alloys

General concept
- Strengthening at elevated temperature
  - Solid solution hardening by Al, Sn and Si
- High oxidation resistance
  - Addition of Si and Nb

Questions
- Many of those elements also increase strength and degrade formability at R.T.
- Especially Al has an effect of increasing S.F.E. and suppresses twinning deformation
Our Solution: Concept of Alloy Design

Solid solution hardening by Cu and low oxygen content

High strength at elevated temperature

 Addition of Cu which can be contained up to 1.5% in the form of solid solution at 790°C

Sluggish Ti$_2$Cu precipitation

Excellent cold formability

 Cu does not suppress twinning deformation, resulting in good formability at R.T.

Higher oxidation resistance

 Nb enhances oxidation resistance at temperature up to 800°C

 Nb addition is not harmful for cold formability

Ti-1Cu up to 700°C

Ti-1Cu-0.5Nb up to 800°C

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# Twin Formation in Ti-1Cu

<table>
<thead>
<tr>
<th>Strain Elongation</th>
<th>Ti-1Cu</th>
<th>Gr.1</th>
<th>Gr.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td><img src="twin.jpg" alt="Image" /></td>
<td><img src="twin_gr1.jpg" alt="Image" /></td>
<td><img src="twin_gr2.jpg" alt="Image" /></td>
</tr>
<tr>
<td>5.5%</td>
<td><img src="twin.jpg" alt="Image" /></td>
<td><img src="twin_gr1.jpg" alt="Image" /></td>
<td><img src="twin_gr2.jpg" alt="Image" /></td>
</tr>
</tbody>
</table>

Cu does not suppress twinning deformation at R.T.
1. Alloy Design

2. Sheet Manufacturing Process

3. Formability

4. High Temperature Properties

5. Summary
Sheet Manufacturing Process at NSC Mills

Ingot(VAR) → Slab forging → Hot rolling

at Hirohata mill

→ Descaling → Cold rolling → Annealing

at Hikari mill

Photo; Ti-1Cu Hot rolled coil manufactured from 3.7ton ingot
1. Alloy Design

2. Sheet Manufacturing Process

3. Formability

4. High Temperature Properties

5. Summary
# Mechanical Properties at Room Temperature

<table>
<thead>
<tr>
<th>Direction</th>
<th>0.2%PS [MPa]</th>
<th>TS [MPa]</th>
<th>elongation [%]</th>
<th>r&lt;sub&gt;L&lt;/sub&gt;-value at 5% elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>195</td>
<td>408</td>
<td>45.2</td>
<td>1.47</td>
</tr>
<tr>
<td>Ti-1Cu*&lt;sup&gt;1&lt;/sup&gt;</td>
<td>T</td>
<td>273</td>
<td>366</td>
<td>36.5</td>
</tr>
<tr>
<td>L</td>
<td>256</td>
<td>387</td>
<td>41.7</td>
<td>2.39</td>
</tr>
<tr>
<td>Ti-1Cu*&lt;sup&gt;1&lt;/sup&gt;-0.5Nb</td>
<td>T</td>
<td>316</td>
<td>383</td>
<td>33.8</td>
</tr>
<tr>
<td>L</td>
<td>251</td>
<td>383</td>
<td>36.3</td>
<td>2.50</td>
</tr>
<tr>
<td>Gr.2</td>
<td>L</td>
<td>279</td>
<td>368</td>
<td>32.2</td>
</tr>
</tbody>
</table>

NIPPOON STEEL
Ti-1Cu and Ti-1Cu-0.5Nb have also very excellent bendability.
Rectangular Cup Drawing of Ti-1Cu sheet

0.5mm, Blank ; 170mmΦ

Corner radius ; 1mm
1. Alloy Design

2. Sheet Manufacturing Process

3. Formability

4. High Temperature Properties

5. Summary
0.2\%PS at Elevated Temperatures

Ti-1Cu has twice higher 0.2\% proof stress than Gr.2 at 500-700\°C
0.2%PS at R.T. and Elevated Temperatures

Ti-1Cu has small temperature dependence of strength
Variation of 0.2% proof stress at elevated temperature during long term exposure at the same temperatures at which tensile tests were conducted.

Influence of Long Term Exposure

Exposure and test temperature / ºC

0.2% proof stress / MPa

Before exposure
After exposure

Exposure time ;
500ºC, 2000h
600ºC, 2000h
700ºC, 1000h

Ti-1Cu
Gr.2

Variation of 0.2% proof stress at elevated temperature during long term exposure at the same temperatures at which tensile tests were conducted.
Fatigue Properties at 700°C

Ti-1Cu has about twice as high fatigue strength as Gr.2 at 700°C
TIG Weldability

1.0mm, 38.1mmΦ

Combination of excellent TIG weldability and cold formability

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Oxidation Properties at Elevated Temperature

Exposed at 700 and 800ºC for 200h in air

Exposure temperature

700 ºC
800 ºC

Weight gain / mg.cm⁻²

Gr.2
Ti-3Al-2.5V
Ti-1Cu
Ti-1Cu-0.5Nb

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Oxidation Properties at Elevated Temperature

Cross section of surface layer
(exposed at 800ºC for 100h)
1. Alloy Design

2. Sheet Manufacturing Process at NSC Mills

3. Formability

4. High Temperature Properties

5. Summary
Summary
We have developed new high performance alloys for automotive exhaust systems.

Addition of Al, Sn, Si suppresses twinning deformation.

Higher oxidation resistance by Nb.

Solid solution hardening by Cu and low oxygen content.

We have developed new high performance alloys for automotive exhaust systems.

Gr.2 CP Ti
Solid solution hardening by Cu and low oxygen content.

Ti-1Cu
Higher oxidation resistance by Nb.

Ti-1Cu
Addition of Al, Sn, Si suppresses twinning deformation.

e.g. Ti-3Al-2.5V

Formability at R.T.
Thank you for your kind attention
Development of High-performance Titanium Alloys for Automotive Exhaust Systems
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Slide-2 Over the years the application range of titanium has been more and more expanded in the field of automobiles. NSC has successfully applied conventional alloys Ti-6Al-4V and Timetal 1100 for commercial motorcycle engine valves, not to speak of the CP titanium for muffler application. We also developed some original alloys called “Super-TIX”, such as Super-TIX800, Super-TIX51AF, and Super-TIX523AFM. They are now under investigation to be used for some automobile parts.

Slide-3 CP titanium more than 1,000 ton/year is now used globally for mufflers and exhaust pipes in motorcycles and the application range of titanium is now expanding to four wheeled vehicles. However, there is a strong requirement of materials having higher performance at elevated temperature with keeping good formability from the view point of rising operation temperature and manufacturing cost. To properly respond to this tough issue, Nippon Steel has developed new alloys.

Slide-5 Properties of Titanium alloys especially required for automotive exhaust systems are as follows.
First, high strength at elevated temperature is required at temperatures above 600°C, and small degradation during long term use is also needed.
Second, high oxidation resistance, specifically small thickness loss during long term use at high temperature especially above 700°C is required.
Third; this is most important, good formability is taken account especially, such as bendability, stretch-expansion formability, drawability, etc. equivalent to or better than those of Gr.2 CP titanium.

Slide-6 It is generally thought that the alloying element Al, Sn and Si contribute to increase strength at elevated temperature. But these elements also increase the strength at room temperature and deteriorate formability at room temperature. Especially Al has an effect of increasing the stacking fault energy and suppresses twinning deformation which is a source of excellent cold formability of titanium.

Slide-7 We, Nippon Steel, have developed a new alloy which has 1 mass% of alloying element Cu. Titanium can contain up to 1.5% copper in the form of solid solution at 790°C. Considerable amount of solid solution Cu can be contained in the α matrix at R.T. by quite sluggish Ti2Cu precipitation kinetics. Copper has a strong solid solution hardening effect at elevated temperature. However it does not suppress twinning deformation resulting in good formability at R.T. Low oxygen content also contributes to twinning deformation at R.T.
In the case that higher oxidation resistance is required such as at temperature up to 800°C, Nb addition is quite effective, which is not harmful for cold formability.

Slide-8 Deformation twinning plays an important roll in Gr.1, Gr2 CP titanium and also Ti-1Cu. When they are subjected to tensile deformation by 3%, more amount of twin is introduced in Ti-1Cu than in Gr.2 and almost the same amount of twin can be observed in Gr.1 CP titanium. This shows Cu does not suppress twinning deformation at R.T.

Slide-9 The schematic view of new alloys for automotive exhaust systems described above is shown. Repeatedly insisted, we have designed the Ti-Cu alloy system which has high performance at elevated temperature with keeping excellent formability at R.T.

Slide-11 Specimens of Ti-1Cu and Ti-1Cu-0.5Nb are prepared by the similar process to CP titanium. Ti-1Cu is produced through the proper process at Hirohata mill (hot rolling) and at Hikari mill (descaling, cold rolling and annealing) etc.

Slide-13 Tensile properties can be adjusted by final heat treatment. This is also one of the features of
the alloy. For example, annealing at 750°C for 1h gives high ductility in both L and T direction, while annealing at 670°C for 10h bears high $r_t$ value with keeping high elongation equivalent to that of Gr.2 CP titanium, resulting in good deep drawability.

Slide-14 Ti-1Cu sheet annealed at 750°C has higher stretch-expansion property than Gr.2 and equivalent to Gr.1 CP titanium. Meanwhile, Ericsen number of a sheet annealed at 670°C for 10h is a little bit lower than that annealed at 750°C. However, it is still at high level, equivalent to Gr.2 CP titanium.

Slide-15 Ti-1Cu sheet annealed at 750°C has such an excellent bendability that it can be completely folded. Meanwhile, minimum bendable radius without cracking of a sheet annealed at 670°C for 10h is a little bit lower than that annealed at 750°C. However, it is still at high level.

Slide-17 Ti-1Cu has twice higher 0.2% proof stress than that of Gr.2 CP titanium at 500-700°C. This is caused by solid solution hardening effect of Cu at elevated temperature.

Slide-18 Ti-1Cu has twice higher tensile strength than Gr.2 CP titanium at 500-700°C. It should be noted that twinning is not occurred in this temperature range and slip governs total deformation.

Slide-19 Our new alloy has small temperature dependence of strength, which enables us to obtain both low strength at R.T.(good formability) and high strength at high temperature.

Slide-20 When Gr.2 CP titanium is exposed at operation temperature for long time, 0.2% PS at elevated temperature decreased due to grain growth. In Ti-1Cu, similar phenomenon is observed, although the drop of 0.2% PS is caused Ti2Cu precipitation, which reduces solid-solution Cu content. However, it should be noted that 0.2% PS of Ti-1Cu is still high, twice higher than Gr.2 CP, and clear 0.2% PS drop is not recognized at 700°C, at which temperature Ti2Cu precipitation is limited, and small amount of Ti2Cu rather contribute to the suppression of grain growth.

Slide-21 Plane bending fatigue test is conducted at 30Hz where the ratio of stress amplitude equal to minus one. Ti-1Cu has about twice as high fatigue strength as Gr.2 CP titanium at 600°C.

Slide-22 Ti-Cu is fully weldable with similar welding parameters to those of CP titanium. Weld joint also has excellent formability. TIG weld tube can be manufactured and supplied.

Slide-23 Ti-1Cu has similar oxidation properties in air to Gr.2 CP titanium at 500-800°C. In the case where higher oxidation resistance is required at temperature over 700°C, addition of alloying element 0.5%Nb is quite effective. Meanwhile Nb addition does not influence cold formability and mechanical properties at elevated temperature.