NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 107 FEBRUARY 2015

Technical Report

UDC 622 . 276 . 05 : 669 . 15 - 194 . 3

Development of High-alloy Seamless OCTG and Its Manufacturing Technologies

Hideki TAKABE*
Yohei OTOME
Masayuki SAGARA
Akihito YAMANE
Yutaka NAGASE
Naoya HIRASE
Kazuhiro SHIMODA
Masaaki TERUNUMA

Abstract

In order to meet the worldwide growth in energy demand commensurate with the recent economic growth of emerging countries, developments of manufacturing technology for large-diameter (OD >178 mm) high-alloy seamless OCTG which enable high productivity of natural gas and OCTG material which safely withstand the ultra-deep gas developments have been required. In order to manufacture large-diameter high-alloy OCTG, Mannesmann mandrel mill rolling method which consists of piercing and mandrel mil processes is necessary. However, high-alloy pipes produced by the Mannesmann mandrel mill rolling method didn't have enough high quality as commercial products due to its imperfections on internal surfaces in piercing process and some rolling troubles in mandrel mill process so far. A new 3D finite element model for rotary piercing has been developed to optimize rolling conditions for high-alloy materials. An analytical model considering material property of high-alloy materials in continuous hot rolling conditions has been newly introduced for optimization of mandrel mill rolling conditions. Thus mass-production technology for large-diameter, high-alloy OCTG was established. In addition, an ultra high strength Ni alloy OCTG meant for ultra-deep gas well development applications has been developed by adding rare earth micro alloying resulted in enhancing the SCC (Stress Corrosion Cracking) resistance, as well as improving the hot workability

1. Introduction

In parallel with the big growth of world economy ever since 1990, where the newly emerging countries, such as China and India, have been playing major roles in its central part, the demand for energy on a global scale is expanding each year.[1] On the other hand, reduction of CO_2 emission has also become a great urgent matter to prevent global warming. As the amount of CO_2 gas emitted during combustion of natural gas is smaller compared with those of coal and petroleum, the demand for natural gas is rapidly increasing in order to make expansion of energy demand coexist with deterrence of global warming. A well is drilled to the depth of natural gas reservoir layer for exploitation of natural gas, and, ultimately, natural gas is mined through OCTG tubing (**Fig. 1**). Since natural gas exists in many cases in high pressure, high temperature stratum, which also contains large amount of H_2S and carbonic acid gas, OCTG tubing has been used for mining natural gas in severe, harsh corrosive environments.

Accordingly, to enhance mining efficiency and production capacity of natural gas, such highly corrosion-resistant high-alloy OCTG tubing containing many rich alloying elements such as Cr, Ni, and Mo as duplex stainless steel (20–30%Cr-4–8%Ni-2–4%Mo steel) and Ni alloy (19–30%Cr-25–60%Ni-2–14%Mo) are mainly used (**Fig. 2**).

Conventionally, products less than 7 inches (177.8 mm) in outer

* Senior Manager, Head of Dept., Dr.Eng., Seamless Pipe Material R&D Dept., Quality Control & Technical Service Div., Wakayama Works
1850 Minato, Wakayama City, Wakayama Pref. 640-8555

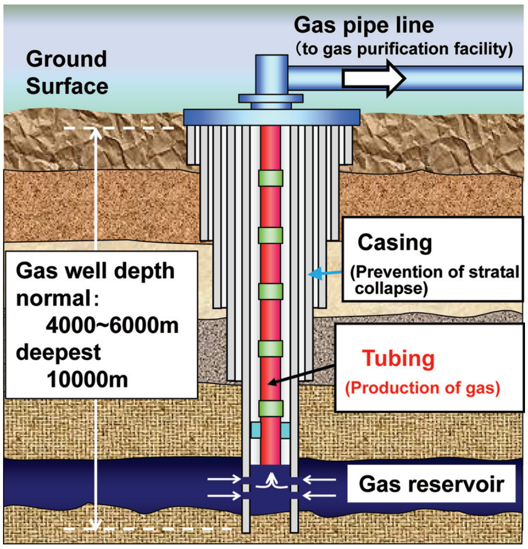


Fig. 1 Outline of mining of natural gas

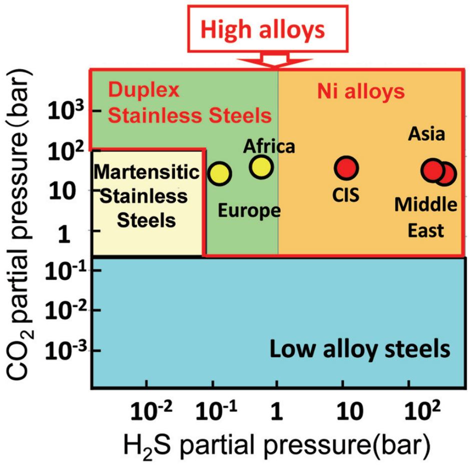


Fig. 2 Representative natural gas filed-environments and applied OCTG materials

diameter have been mainly used as high-alloy OCTG tubing. In recent years, the need for development of large-diameter and long-length OCTG has grown from the viewpoint of improving natural gas production efficiency and the development cost reduction in natural gas wells.

Moreover, to further increase the production capacity of natural gas, developments of ultra-deep gas fields, which could have never been developed before, has become necessary. In such ultra-deep gas fields, the pressure and temperature of the environments to which OCTG tubing is exposed are growing higher and higher year by year. In order to develop gas fields in very harsh environments of high pressure and high temperature, the demand for ultrahigh strength OCTG having 0.2% offset yield strength higher than 140 ksi is growing strongly in natural gas mining industry.

Therefore, development of production technologies of large-diameter and long-length high-alloy OCTG having ultrahigh strength has been conducted. This study describes the contents of the developed technology.

2. Contents of the Developed Technology

2.1 Mass production technology of large-diameter and long-length high-alloy OCTG

In many cases, the production efficiency of natural gas can be improved by applying large outer diameter pipe that allows to secure the large cross-sectional area of OCTG tubing and that makes development cost of gas fields lower. For instance, there is a trial estimation that suggests the possibility of 30% reduction of development cost by increasing the outer diameter of OCTG tubing from 7 inches (177.8 mm) to 9.6 inches (244.5 mm). The authors investigated the production of large-diameter high-alloy OCTG (outer diameter exceeding 178 mm), which had not been commercialized as mass-produced merchandise before.

Conventionally, high-alloy OCTG tubing up to 7 inches in outer diameter is in the mainstream and is produced by the hot extrusion method. As **Fig. 3** shows, in the hot extrusion method, a heated billet having pre-machined small hole inside is vertically expanded, then a mother pipe is extruded subsequently, and finally plural cold workings are applied to the mother pipe and OCTG is produced. However, in this method, due to the restriction in the production equipment and the process, it is difficult to secure large-diameter and long-length required simultaneously. Therefore, development of production technology of large-diameter and long-length pipes was carried out according to the Mannesmann mandrel mill rolling method (piercing and rolling method) that is usually used for the production of OCTG of carbon steel, stainless steel, and so on.

Piercing and rolling method is a process of producing OCTG in which, as shown in **Fig. 4**, a heated billet is pierced and rolled by the piercer, then the material is rolled, and the wall thickness is reduced by the mandrel mill and squeezed on its external side by the sizing mill to desired dimensions. Compared to the hot extrusion method, the material undergoes very harsh and complicated deformation. In the case of the high-alloy material, as surface defects occur on the internal surface of the pipe by the plug in piercing/rolling process and rolling troubles in extracting internal mandrel tool in mandrel mill rolling take place, application of piercing and rolling method has been considered difficult.

However, mass production technology of large-diameter and long-length high-alloy OCTG by the piercing and rolling method has been established for the first time in the world.

Compared to carbon steel and stainless steel, the deformation re-

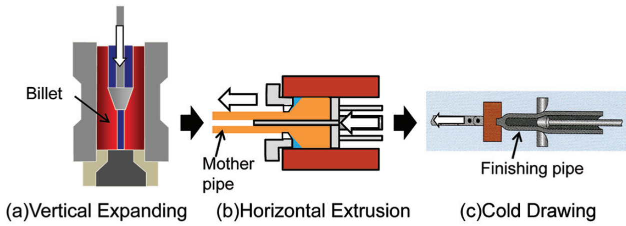


Fig. 3 Hot extrusion method

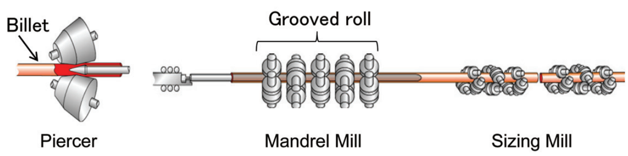


Fig. 4 Piercing and rolling method (Mannesmann mandrel mill rolling method)

sistance of high-alloy material is higher and the hot workability is lower, internal defects, as shown in **Fig. 5**, which are utterly unacceptable for products are occurred. To achieve effective suppression of the internal defects on high-alloy material, it is necessary to predict the deformation behavior of the material during piercing/rolling and to apply piercing/rolling under the appropriate conditions where hot workability is not deteriorated.

However, in the past, the piercing/rolling conditions were conventionally predetermined based on only the dimensional change from the billet dimension before piercing/rolling to the dimension of the material after rolling, and the process of deformation during piercing/rolling was not taken into consideration at all. Therefore, optimization of the piercing/rolling conditions had been difficult and defects on the internal surface could not be prevented. Then, based on the behavior and process of deformation of the material obtained from the piercing/rolling-halted portion of a material in model piercing/rolling, the three-dimensional numerical analysis technology that predicts the deformation behavior of the material during piercing/rolling with high accuracy has been developed and put into practical use.[2, 3)]

Authors tackled the development of a three-dimensional analysis model with finite element method and optimization of the boundary condition for calculation, and thereby predicting deformation of material during piercing/rolling with high accuracy, by maximum utilization of the experimental result of halting piercing/rolling. **Figure 6** shows the comparison of the calculated result of the analysis model developed with the result obtained on the sections of piecing/rolling-halted portion of the material in the model piercing/rolling (experimental rolling). The calculation result of the process of deforming in the material (external dimension) shows good agreement with that of the physical experiment of experimental piecing/rolling. Furthermore, pins were previously tapped into the billet at its end surface for the experimental piercing/rolling in order to examine the behavior of the shearing deformation during piercing/rolling process. The process of the shearing deformation during piercing/rolling was also studied and the result of the analysis showed good agreement with that of the physical experiment of experimental piercing/rolling. With the analysis technology developed as abovementioned, correct prediction of the process of deformation in piercing/rolling has become possible. By utilizing the developed piercing/rolling analysis model, piercing/rolling conditions, including designing of tools, have been optimized. The rolling condition was

Fig. 5 Example of defect on internal surface

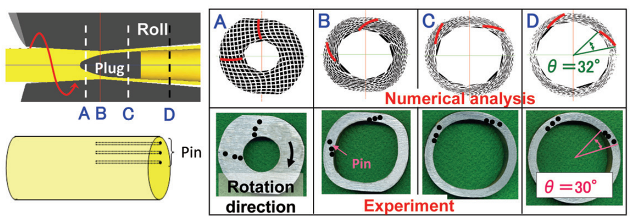


Fig. 6 Comparison between analysis and experimental results on piercing process

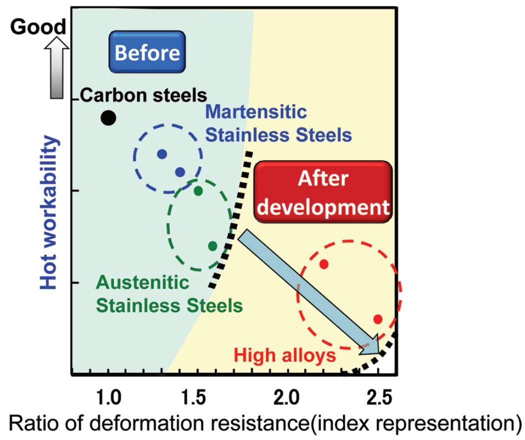


Fig. 7 Expansion of manufacturable material

proved to be effective as the defects, which used to customarily and inevitably occur on the internal surface in the piercing/rolling of high-alloy material, have reduced drastically.

Furthermore, to solve rolling troubles, deformation characteristics of high-alloy material in continuous hot rolling was studied in detail, and the analysis model incorporating material characteristics during continuous rolling was newly introduced. As a result, optimization of roll-pass designing and rolling condition could be successfully achieved, and troubles in extracting the mandrel and the rolling defects could be prevented, and stable rolling of high-alloy material has become possible.

As abovementioned, owing to the developments of piercing/rolling technology and rolling technology for high-alloy and high quality, the limit of the range of steel quality producible has been successfully expanded greatly from austenitic stainless steels to high-alloy materials, and the mass production technology of large-diameter and long-length high-alloy OCTG based on piercing/rolling pipe manufacturing process has been established and realized (**Fig. 7**).

2.2 Development of ultrahigh strength high-alloy OCTG

In order to increase the production amount of natural gas to meet the expanding global demand for energy, as shown in **Fig. 8**, the environments of natural gas fields under development are becoming far high pressure high temperature (HPHT) each year, and developments of natural gas fields under the environments of ultra HPHT (stratum pressure being higher than 20000 psi (138 MPa) and stratum temperature being higher than 400°F (204°C)) have started in recent years.[4)] 0.2% offset yield strength of 110 ksi (758 MPa) or

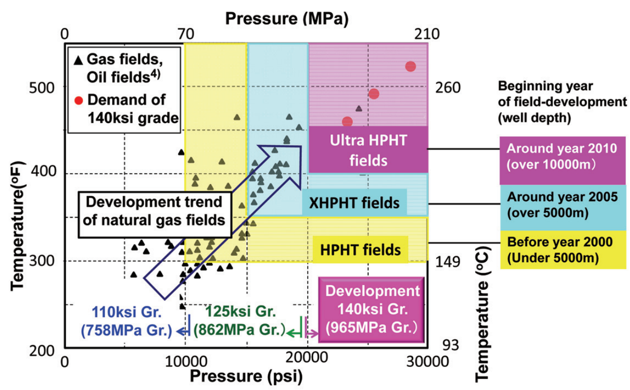


Fig. 8 Relationship among temperature and pressure of main natural gas and oil fields and strength of high-alloys

above and of 125 ksi (862 MPa) or above were mainly the strength grades of conventional high-alloy OCTG. However, for the development of ultra-deep natural gas fields, OCTG to be used has to withstand high internal pressure exerted by the natural gas produced and is required to have corrosion resistance. Therefore, high-alloy OCTG having ultrahigh 0.2% offset yield strength of 140 ksi (965 MPa) or above, together with high corrosion resistance was required. The authors researched on enhancing the strength of Ni alloy (compositions: 25%Cr-32%Ni-3%Mo).

For enhancing the strength, inexpensively available N element, having excellent solid-solution hardenability and work-hardenability was used. However, in enhancing strength by adding N, as **Fig. 9** shows, there existed problems of deterioration in stress corrosion cracking resistance (SCC) and hot workability. But an independent technology of improving the corrosion resistance and hot workability by addition of rare earth metal (REM) has been developed and these problems have been solved. Thus, we succeeded in developing the Ni alloy having ultrahigh 0.2% offset yielding strength of 140 ksi (965 MPa) grade.

2.2.1 Development of technology for improving SCC resistance

As a means for improving the SCC resistance of stainless steel and high-alloy steel, the general method to strengthen the corrosion resistance and repairability of the passivation film formed on the material surface is adding rich alloying elements such as Cr, Ni, and Mo.[5-7] However, authors have succeeded in the development of new material based on an entirely new technical concept of improving SCC resistance by controlling the dislocation structure within the material structure.

Authors clarified for the first time that the dislocation structure can be controlled by addition of REM in the Ni alloy having the strength of 140 ksi grade enhanced by addition of high amount of N. As the result of study on the effect of added elements, the change on dislocation structure had been found through close observation of the structure of the material with a transmission electron microscope. **Figure 10** shows the result of observation with a transmission electron microscope. In the Ni alloy having high strength of 140 ksi grade enhanced by the addition of high amount of N, planar structure could be changed to non-planar structure in dislocation structure by addition of REM. As mentioned later, with non-planar structure, corrosion resistance can be improved.

The SCC resistance of the Ni alloy of high amount of N added with REM was investigated in a H_2S environment by the slow strain rate test (SSRT) method.[8] In this method, tensile tests are conducted with constant strain being applied at low rate (e.g., $4.0 \times 10^{-6}s^{-1}$) in a corrosive environment in test equipment. Generally, in the SSRT method, SCC does not take place in the corrosive environment if the area of reduction in the tensile test in the corrosive environment is above 0.8 in ratio of that of the tensile test in non-corrosive atmospheric environment.[8]

As **Fig. 11** shows, SCC resistance in H_2S environment of the REM-added Ni alloy having strength of 140 ksi grade has been improved compared with that of the Ni alloy without the addition of REM.

The mechanism how SCC resistance of the REM-added ultrahigh strength Ni alloy has been improved is assumed as shown in **Fig. 12** based on the relationship between the dislocation structure and corrosion-active planes at the time of fracture of the film.[9, 10] Namely, in the process from the rudiment to the restoration of the passivation film formed in the corrosive environment, dislocation in the material without addition of REM takes place on a plane, meaning that slip deformation takes only on a specific slip plane in a concentrated manner, tending to cause a large corrosion-active surface at the rudiment of the fracture of the film. For this reason, repairing and restoring of passivation are not easy and SCC tends to occur. On the other hand, in the REM-added Ni alloy, deformation takes place on any planes in a dispersed manner, and the total area of

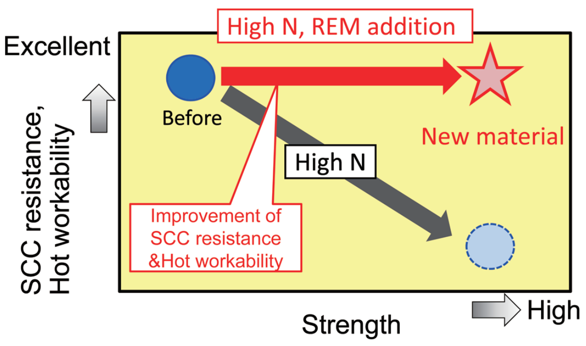
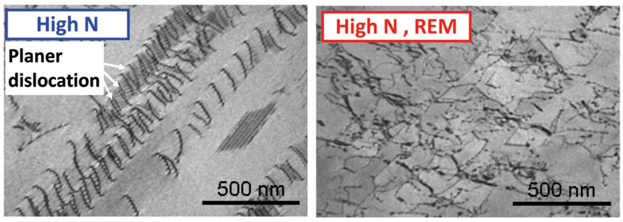


Fig. 9 Development concept of ultra high strength Ni alloy



(a)Planer dislocation (b)Non planer dislocation

Fig. 10 Effect of REM addition on dislocation structure

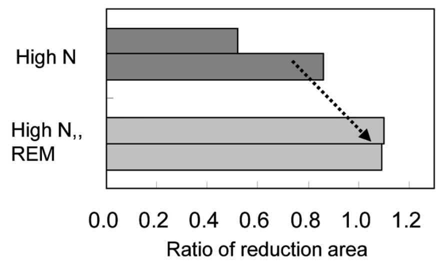


Fig. 11 Effect of REM addition on SCC resistance (SSRT, 0.7MPa H_2S, 25%NaCl+0.5%CH_3COOH, 175°C)

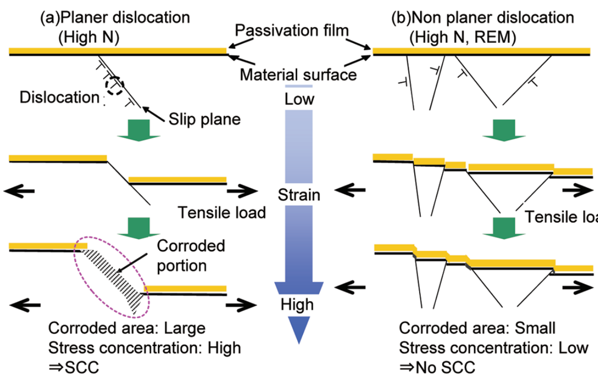


Fig. 12 Mechanism of SCC resistance improvement by dislocation control technique

Table 1 SCC test results of newly developed Ni alloy (4 point bent beam test)

No.	YS (ksi)	Macro observation (monthly) 1	2	3	4	5	6	Micro observation
1-1	151	○	○	○	○	○	○	No cracking
		○	○	○	○	○	○	
1-2	166	○	○	○	○	○	○	No cracking
		○	○	○	○	○	○	

○: No cracking by macro observation

newly developed corrosion-active planes are relatively small. Therefore, restoration of passivation is easy and SCC occurrence becomes hard.

Furthermore, a long-term stress corrosion cracking test was carried out to confirm the SCC resistance of the developed material. Susceptibility of SCC was evaluated by four-point-bent beam test [11] in which equivalent stress to 100% of actual 0.2% offset yield strength was loaded to the material in the environment contains solution of 25mass%NaCl + 0.5mass%CH_3COOH, with the gas atmosphere of 0.7 MPa H_2S at elevated temperature of 150°C, which simulates an actual typical natural gas well environment. Stress corrosion cracking was evaluated by macroscopic observation for every month and after the whole test term of six months. Final judgment as to the cracking was made through microscopic observation of the section. **Table 1** shows the result. It was confirmed that despite having ultrahigh 0.2% offset yield strength of higher than 140 ksi, the developed material shows sufficient SCC resistance even in a H_2S-gas-containing environment.

2.2.2 Technology for improving hot workability

It was found that in the Ni alloy with enhanced strength by addition of N, slight segregation of the S element at grain boundaries deteriorates hot workability. Hot workability was secured by utilizing an REM having strong affinity with S. **Figure 13** shows the relationship between hot workability and the amount of N contained in the Ni alloy. In the material without REM addition, reduction of area at elevated temperature is deteriorated, while reduction of area is recovered in the material with addition of REM, and excellent hot workability is obtained. This was caused by the S element reaction that precipitates in the matrix as non-metallic inclusions by addition of REM, instead of being S enriched at the grain boundaries that deteriorates hot workability (**Fig. 14**).

2.2.3 Result of development of ultrahigh strength high-alloy OCTG

Authors have succeeded in improving SCC resistance and hot workability by adding REM. As the result, high-alloy OCTG material of 140 ksi (965 MPa) grade applicable to natural gas development containing H_2S and CO_2 gases has been developed.

With the development of this technology, production at ultra-deep gas wells in ultra HPHT environment, which had been difficult to be developed before, has become possible. Furthermore, the pipe thickness can be reduced in the natural gas fields where environment is not as harsh as HPHT by applying ultrahigh strength grade that is expected to make well designing reasonable with weight reduction of pipes and reduction in development cost of natural gas fields. Therefore, this material will greatly contribute to expansion in production and stable supply of natural gas in future.

Furthermore, for practical use, products were shipped for the development of such ultra-deep gas well in ultra HPHT environment in the Gulf of Mexico. In addition, as this material is applicable to natural gas wells and oil wells, it is expected it will be utilized in a far deeper natural gas field and oil field developments.

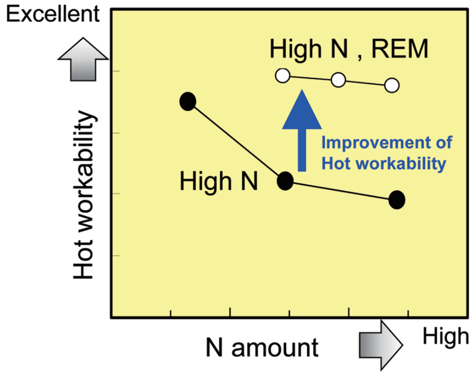
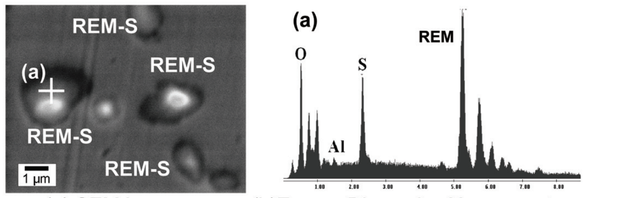


Fig. 13 Relationship between hot workability of Ni alloys and N amount



(a) SEM image (b)Energy Dispersive X-ray spectroscopy

Fig. 14 Non-metalic inclusion in high N and REM added Ni alloy

3. Conclusion

The high-alloy OCTG produced by the developed technologies of "Production technology of large-diameter and long-length high-alloy OCTG (new product)" and "Development of 140 ksi grade ultrahigh strength high-alloy OCTG (new product)" is playing far more important roles in the development in a harsh corrosive environment and ultra-deep natural gas fields. Therefore, it is believed that the products will contribute to the expansion of demand for energy on global scale and prevention of global warming.

References

1) BP Energy Outlook 2030. 2012
2) Yamane, Y., Shimoda, K., Inoue, Y.: Three-Dimensional Deformation Analysis of Piercing and Rolling. The Iron and Steel Institute of Japan, 2012
3) Inoue, Y., Shimoda, K., Yamane, Y.: Speed Analysis of Material and Plug during Piercing and Rolling at Piercer. The Iron and Steel Institute of Japan, 2012
4) Journal of the Japanese Association of Petroleum Technology. 76 (5), 415-424 (2011)
5) Ueda, M., Amaya, H., Okamoto, H.: Proceedings of Corrosion 97. Paper No. 25, Houston, 1977, TX: NACE International
6) Murayama, J., Miyuki, H., Kudo, T., Fujino, N., Terasaki, F.: Proceedings of TMS of AIME Meeting. Paper No. A84-45, 1984
7) Ueda, M., Kudo, T.: Proceedings of Corrosion 94. Paper No. 69, Houston, 1994, TX: NACE International
8) NACE Standard TM0198-2004 Item No. 21232. NACE International, 2004
9) Otome, Y., Okada, H., Amaya, H., Igarashi, M.: Proceedings of the 2nd International Symposium on Steel Science (ISSS 2009). Kyoto, Japan, Oct. 21-24, 2009, ISIJ
10) Sagara, M., Otome, Y., Sawado, N., Amaya, N., Igarashi M.: Materia. 51 (3), 117 (2012)
11) European Federation of Corrosion. Publications No. 17 Second Edition. The Institute of Materials, 2002


Hideki TAKABE
Senior Manager, Head of Dept., Dr.Eng.
Seamless Pipe Material R&D Dept.
Quality Control & Technical Service Div.
Wakayama Works
1850 Minato, Wakayama City, Wakayama Pref. 640-8555


Yutaka NAGASE
General Manager, Head of Div., Ph.D.
Quality Control & Technical Service Div.
Wakayama Works


Yohei OTOME
Manager
Seamless Pipe Material R&D Dept.
Quality Control & Technical Service Div.
Wakayama Works


Naoya HIRASE
Manager, Head of Section
Small Size Seamless Pipe & Tube Making Plant
Tool Management & Production Planning Section
Pipe & Tube Div.
Wakayama Works


Masayuki SAGARA
Senior Researcher, Dr.Eng.
Pipe & Tube Research Lab.
Steel Research Laboratories


Kazuhiro SHIMODA
Senior Researcher
Steel Rolling R&D Div.
Process Research Laboratories


Akihito YAMANE
Senior Researcher
Steel Rolling R&D Div.
Process Research Laboratories


Masaaki TERUNUMA
Senior Manager, Head of Dept.
Specification & Quality Control Dept.
Quality Control & Technical Service Div.
Amagasaki Works