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Development of Austenitic Stainless Steel Sheets for Micro-Fabrication

Masayoshi SAWADA* Hayato KITA
Masayuki SHIBUYA Kazuyoshi FUJISAWA

Abstract

Austenitic stainless steels "304 H-SR", "304 H-SR2" and "301L SE1" were developed for microfabrications like photoetching and laser processing. 304 H-SR and 304 H-SR2 have superior flatness, low residual stress and improved surface wettability, which are required as the materials for microfabrications. These high performances are attained mainly by Tension Leveling (T/L) process, Stress Relieving (S/R) process and Special Surface Treatment. 301L SE1 with fine grained structure has been received high reputations as a material with excellent smoothness of the fabricated surface, in addition to the above mentioned characteristics. The grain refinement has been achieved through the use of $\alpha' \rightarrow \gamma$ reverse transformation and pining effects by minute precipitates with optimization of the alloy composition and manufacturing process.

1. Introduction

Austenitic stainless steel sheets provide high mechanical properties through cold rolling, and are therefore used for mechanical and electronic parts of precision machinery in automobiles and consumer electrical appliances.[1,2] To respond to the recent trend toward further miniaturization and sophistication in apparatus performance, stainless steel must now offer more sophisticated functions to meet requirements.

Nippon Steel & Sumitomo Metal Corporation produces SUS 304 H-SR (hereinafter "304 H-SR"), SUS 304 H-SR2 ("304 H-SR2") and NSSMC-NAR-301L SE1 ("301L SE1"). 304 H-SR is a stainless steel developed for precision cutting, including photo-etching and laser processing. It is based on an austenitic stainless steel used as a thin sheet spring material of 0.6 mm or below in thickness. The development of 304 H-SR2 and 301L SE1 was based on the production technology for 304 H-SR; precision-cutting performance of them was enhanced by refining the crystal grains of the mother material. This article introduces the characteristics of austenitic stainless steel for precision cutting and the technical background guiding the development of the steel, focusing mainly on crystal grain refining technology.

2. Precision Cutting Technology

2.1 Photo-etching and laser process

The photo-etching process and laser process discussed in this article are considered as typical examples of precision-cutting methods.[3,4] They process stainless steel sheets into desired product shapes by removing unnecessary portions through chemical dissolution or thermofusion.

The photo-etching process for metallic material utilizes printing and corroding technology. It is widely used to produce the following parts: metallic parts with high dimensional accuracy; complicated figures such as precision machinery parts; precision electronics and optical apparatus parts; and decoration parts or ornaments. In the photo-etching process, desired product figures are obtained by printing the product figure pattern on the subject metallic material surface with a photo-sensitive resin (Photoresist), and then by making the exposed metallic portion dissolve selectively into a corrosive chemical solution such as ferric chlorides. This process results in a product that is free from burrs, strains, material deformation and work hardening, enabling precision cutting where dimensional accuracy in the micro-millimeter order is required. Also, since costly dies are unnecessary, the process is capable of meeting various production requirements, from small-lot trials to extensive mass production. It is also capable of etching both surfaces (perforating holes, as well as holes having different diameters on the two surfaces), and processing products that have complicated sectional shapes (by combining half etching of either surface with stepped etching).

Laser processing is a fusion-melting method used to remove un-

* Researcher, Titanium & Specialty Stainless Steel Research Lab., Steel Research Laboratories
1-8 Fuso-cho, Amagasaki City, Hyogo Pref. 660-0891

necessary portions by radiating a laser beam directly onto the surface of metallic materials that are to be processed in accordance with a CAD design drawing. Laser processing is capable of processing products having a density higher than those processed by photo-etching, and has a readiness to comply with the small lot production of many products. One example where laser processing is applied is the metal mask ("Stencil") for printing solder paste on a print circuit board.[3] The metal mask is made from a stainless sheet of 0.1 - 0.2 mm in thickness on which a circuit pattern has been printed and cut off. Conventionally, the photo-etching process is used for cutting; however, laser-processed metal masks are increasing in number to meet the requirements of printed circuit boards growing higher in density. Metal masks having more sophisticated functions have also been developed for practical use. They have sectional figures processed by a controlled combined application of the etching and laser processes, and vertical laser-processed sections. Small, thin electronic devices like smartphones and tablet PCs are rapidly become common in recent years, and to meet the demand for higher circuit density, processing that provides even higher precision is being sought. Also in demand are materials that offer higher performance, and further developments in the processing technology.

2.2 Characteristics required for material using in precision cutting

High sheet thickness accuracy and flatness are required for photo-etching, in order to secure stabilized line threading behavior and accuracy of luminous pattern exposure. Residual stress minimization inside the material is also necessary to suppress twisting, camber and dimension change from expansion or contraction, and deformation after etching processing. Furthermore, to secure good adhesion for the photoresist, the material is also required to have excellent wettability. Product density is tending to increase considerably, and now greater attention is being paid to the sharpness of etching-processed edge surfaces and the smoothness of etching-processed surfaces.

For laser processing, the material is installed on a frame and set in a laser processing system. Therefore, if the material has poor flatness the distance between the laser head and the material surface will be uneven, and the desired finishing accuracy cannot be obtained. Also, deformation due to local heat during fusion-melting by laser occasionally becomes problematic. Accordingly, precise flatness, low residual stress, and high smoothness of processed surfaces are required for laser processing. These material criteria are similar for the photo-etching process.

3. Stainless Steel Sheets for Precision Cutting

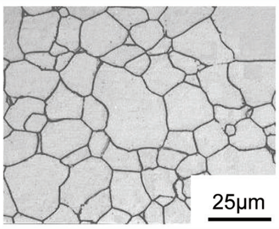
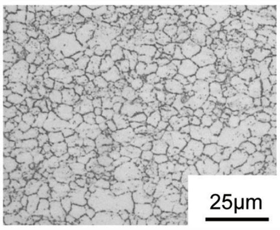
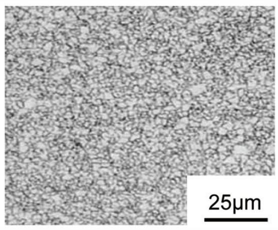
Naoetsu Works, a division of Nippon Steel & Sumitomo Metal, is working on the improvement of processing technologies and enhancing the quality of stainless steel material appropriate for above-mentioned precision cutting, such as the photo-etching and laser processes. **Table 1** shows an outline of 304 H-SR, 304 H-SR2 and 301L SE1, which have been commercialized as materials for precision cutting such as the etching and laser processes.[4-6] 304 H-SR is used for overall precision cutting purposes, while 304 H-SR2 and 301L SE1 are applied particularly to uses where high precision cutting (such as for high-density metal masks) are required.

304 H-SR2 is a fine grain steel whose development was based on 304 H-SR to meet the requirements of etching process users. Its grains are refined to an average grain size of about 5μm without changing the chemical composition, by optimizing production conditions. 301L SE1 has crystal grains refined to an average grain size of 2μm or less, by integrating a special alloy composition design and through cold rolling and annealing technologies. Furthermore, since the carbon content is made low in 301L SE1, its ability to suppress the occurrence of smut (which creates problems in etching processing) has been confirmed.[7]

Figure 1 gives an outline of the stainless steel production process for precision cutting. 304 H-SR, 304 H-SR2 and 301L SE1 are all processed to their respective specified sheet thicknesses and material strengths through hot rolling, cold rolling, annealing and subsequent temper rolling. High flatness is obtained with a tension leveler (T/L), with the material being submitted to tension and repeatedly bent and bent in the adverse direction through contact with circumferential roller surfaces. However, although the resulting sheet looks flat to the eye, the material in such a state is not appropriate for precision cutting, since a high degree of residual stress has accumulated within the material.

Residual stress inside the material is alleviated by applying heat

Table 1 Chemical compositions, microstructures, average grain sizes, thickness and applications of SUS 304 H-SR, SUS 304 H-SR2 and NSSMC-NAR-301L SE1

	SUS304 H-SR	SUS304 H-SR2	NSSMC-NAR-301L SE1
Chemical Composition (mass %)	18Cr-8Ni-0.05C		17Cr-7Ni-0.02C-0.12N-0.05Nb
JIS	SUS304		SUS301L
Microstructure			
Average grain Size (μm)	20 - 30	2 - 5	-2
Thickness (mm)	0.08 - 0.60	0.08 - 0.40	0.08 - 0.25
Applications	For generic micro fabrication use	For precise etching use, Fine metal mask	

treatment at a relatively low temperature (“stress relief (S/R) treatment”). **Figure 2** shows the appearance of strip form specimens (0.2 mm × 12 mm × 100 mm) that have been etched to half their thickness on one side (”half etching”) in a solution of ferric chlorides. In Fig. 2 (a), the temper rolled specimen exhibits a camber convex with respect to the etched surface, while the T/L-treated specimen exhibits a large camber in the direction opposite to the direction of the camber of the specimen after temper rolling. The temper-rolled material is provided with tensional residual stress in the neighborhood of the surface by rolling, and flatness is maintained by a state of equilibrium between the tensional residual stress and the compressive residual stress that exists in the center area in the thickness direction of the material.

As etching reduces surface layer thickness, the stress equilibrium in the thickness direction is broken, and a camber develops. In the case of the T/L-treated material, compressive residual stress is provided close to the surface layer through repeated bending and bending in the adverse direction. Although flatness is maintained by the equilibrium of the compressive residual stress and the tensional residual stress in the thickness center area, when a surface layer is removed by etching, compressive stress near the surface is released so that a camber in the direction adverse to the temper rolled material direction is produced. On the other hand, as a result of alleviation of the entire residual stress in the plate thickness direction of the S/R treated material, the camber after half etching is remarkably suppressed. Furthermore, as shown by 304 H-SR2 in Fig. 2 (b) and 301L SE1 in Fig. 2 (c), it has been confirmed that the camber after half etching is reduced not only through S/R treatment but also further reduced by incorporating a device in the previous stage of the process.

In the production process for stainless steel sheets destined for precision cutting, wettability is improved by applying a special surface treatment after the S/R treatment, to reform the surface layer. Poor wettability deteriorates the adhesion of photoresistant material to steel sheets, and as **Fig. 3** (a) shows, percolation of an etchant between the photo-resistant barrier and the material takes place and occasionally produces a faulty product. As Fig. 3 (b) shows, wettability improvement suppresses etchant percolation. In some cases, product yield has been enhanced greatly.

As mentioned above, for stainless steel sheets destined for precision cutting, a highly balanced equilibrium is now one of the requirements for materials destined for etching processes, along with, for example, excellent flatness, low residual stress, and high surface wettability. This equilibrium can be realized through integrated process control, from the alloy composition stage to the production process stage.

4. Grain Refining Technology

4.1 Basic information on crystal grain refining technology

The crystal grain size of conventional stainless steel is about 20-30 μm. When finishing accuracy in the order of single digit micrometers is required, crystal grain size occasionally influences the finish of processed products. The finer the crystal grain, the more improved is the straightness (sharpness) of the etching-processed product edge and the smoothness of the etching-processed surface. In laser processing, too, the lower the melting point at crystal grain

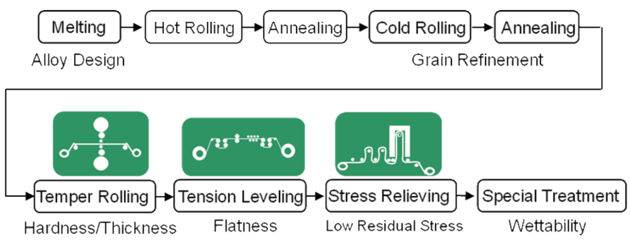


Fig. 1 Schematic illustration of manufacturing process for developed Steel

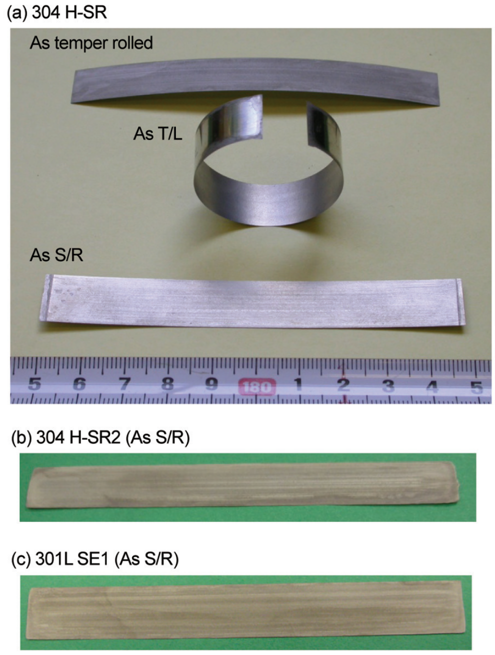


Fig. 2 Appearance of the half etched specimens

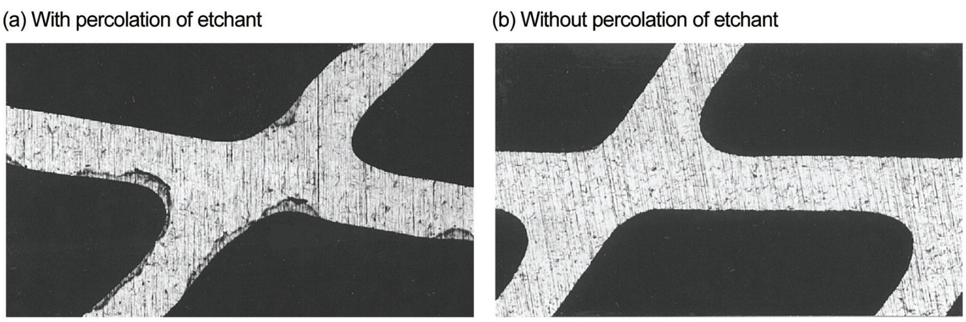


Fig. 3 Appearance of specimens after stripping photo resist
(a) With percolation of etchant between resist and materials and (b) Without percolation of etchant

boundaries, compared with within crystal grains (with crystal grains melting earlier at their boundaries),[8] the finer is the crystal grain, and the smaller is the roughness of etching-processed surfaces. This means that, in both etching processing and laser processing, refining the crystal grains of a material is very effective in improving the smoothness of processed surfaces. Furthermore, refining crystal grains is also effective in improving smoothness at the bent portion of the material, and improving the strength-elongation relationship. Therefore, crystal grain size is the most important factor to be studied in the development of stainless steel for precision cutting.

Prior to the development of 301L SE1 for precision cutting uses, the austenitic stainless steel NSSMC-NAR-301L HS1, which was crystal-grain-refined to improve fatigue strength, was developed.[9, 10] This grade has been employed by a number of car manufacturers as engine cylinder head gasket material, and has obtained an excellent reputation. 301L SE1 provides high straightness for etching-processed edges, high smoothness for etching-processed surfaces, a high degree of flatness, and low residual stress. The material was realized through integrated controlling. As **Fig. 4** shows, the entire process, from alloy design to optimization of production conditions for cold rolling and hot rolling (covering and combining crystal-grain-refining techniques developed for 301L HS1, with specific production technologies developed for precision-cutting), is used for 304 H-SR, including T/L treatment, S/R treatment, and special surface treatment. Examples of research done on crystal-grain-refining and effects of refined crystal grains on precision cutting performance are given hereunder.

4.2 Crystal grain refining mechanism

It is known that in metastable austenitic (γ) stainless steels, such as SUS304 and SUS301L, fine crystal grains can be obtained through the use of reverse transformation from deformation-induced martensite (α') formed in cold rolling to γ by heat treatment.[11] However, if the heat-treatment temperature is lower than required, the structure becomes uneven and large amounts of untransformed crystal structure remain. On the other hand, if the heat-treatment temperature is higher than warranted, the crystal grains become coarse. Therefore, stainless steel with refined crystal grains had never previously been produced on a large scale at an actual production line. Nippon Steel & Sumitomo Metal now consistently mass-produces fine grain material, using a process that suppresses crystal grain growth through the use of minute carbides and nitrides which precipitate during heat treatment,[12] in addition to the reverse transformation of work-induced α' to γ.

Upon utilizing minute carbides and nitrides, a thermo dynamic calculation was carried out. **Figure 5** shows the phase diagram of SUS 301L calculated with the thermo dynamic software Thermo-Calc.[13] It is found from the diagram that in the case of SUS301L added with 0.05mass% Nb, for example, Nb is solid-soluted to γ phase at a high temperature above 1,100°C, and precipitates as Nb(C, N) at a lower temperature. Accordingly, after solid-solution heat treatment, minute Nb(C, N) precipitates in finishing annealing at a temperature lower than in solid-solution heat treatment, and the precipitate hinders the movement of crystal grain boundaries ("pinning effect"), thereby suppressing crystal grain growth.

Figs. 6 and **7** are TEM images of thin films and extraction replicas of conventional SUS301L and SUS301L containing 0.1mass% Nb.

These samples were taken from sheets cold-rolled with a cold reduction ratio of 67% from sheets made from small ingots for trial purposes, then heat-treated at 1,150°C for solid-solution. The cold-

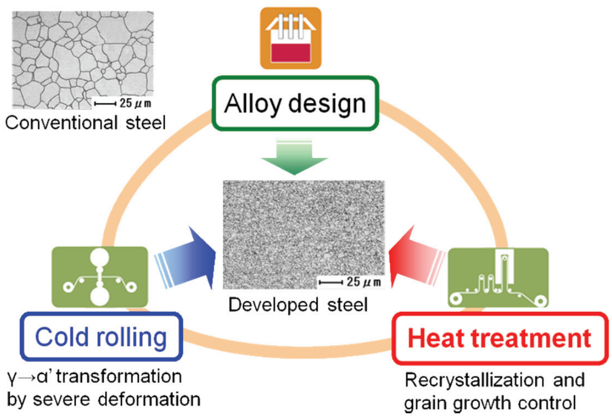


Fig. 4 Schematic illustration showing our philosophy for producing fine-grained stainless steels

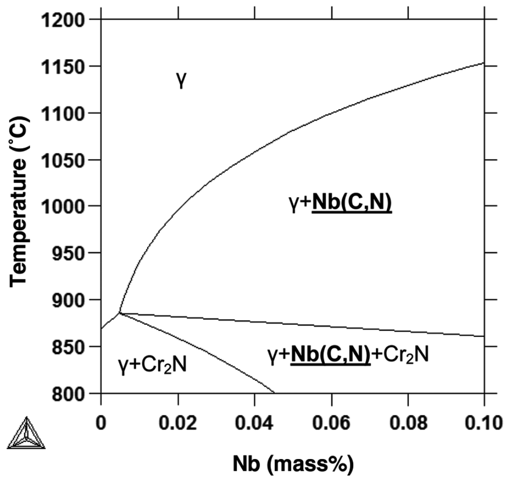


Fig. 5 Calculated phase diagram of SUS301L containing Nb

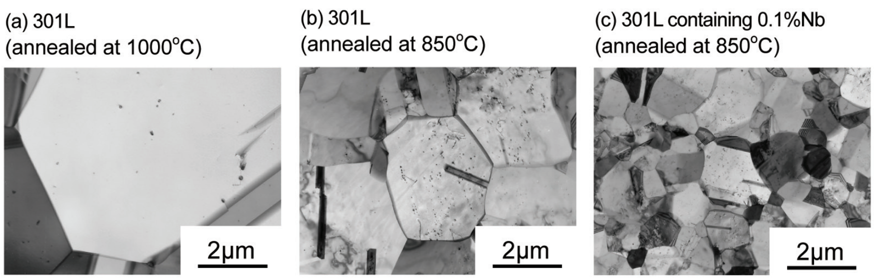


Fig. 6 TEM images of thin film prepared from annealed specimen

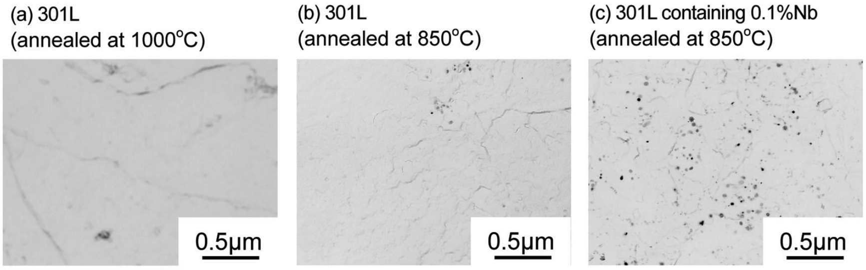


Fig. 7 TEM images of the extraction replica prepared from annealed specimen

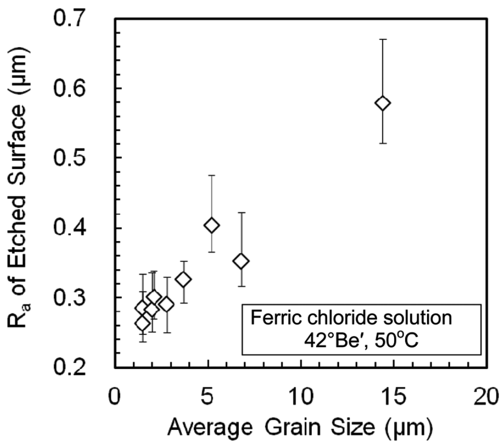


Fig. 8 Relationship between calculated average roughness R_a of etched surface and average crystal grain size

rolled sheets were annealed at 1,000°C (a) or at 850°C (b, c). The average crystal grain size of SUS301L without Nb annealed at 1,000°C is about 10 μm, and about 4 μm when annealed at 850°C. However, grain-refining in this case is due to the weak grain growing force because of the low annealing temperature. If the annealing temperature is lowered excessively, the structure becomes uneven, retaining great quantities of untransformed grains that had previously developed under the influence of cold working, and resulting in a variation in characteristics. On the other hand, when Nb is added in small amounts, the added Nb precipitates as minute Nb(C, N) of about 20 nm when annealed. As a result of the pinning effect of the Nb(C, N), and as a result also of the resulting suppression of crystal grain growth, a structure with very fine crystal grain size around 1 μm on average can be obtained after annealing.

4.3 Effect of crystal grain refining on precision cutting performance

This section introduces the effect of crystal grain refining on smoothness of the photo-etching-, - laser- and other processed surfaces. **Figure 8** shows the relationship between the roughness of the etched surface of the material and the average crystal grain size that is varied by controlled changes in the compositions and heat-treatment conditions of SUS304, which was used as the base for the study. The etchant used was a ferric chloride solution of 42° Be' at 50°C. The finer the crystal grains of the mother materials, the more enhanced is the smoothness of the etched surface. This is presumed to be due to the fact that, since the etching rate depends on crystal orientation,[14] as the crystal grains become finer, the rate of etching becomes more level.

Figure 9 is an electron microscope image of the walls of holes conically perforated by the etching method used on 301L SE1, and

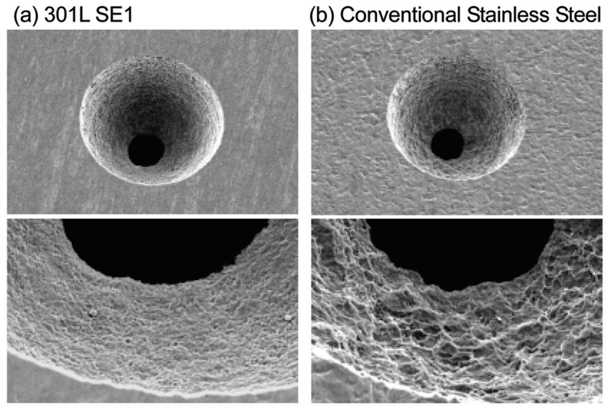


Fig. 9 Appearance of stainless steel sheets perforated by photoetching (a) 301L SE1, (b) Conventional stainless steel

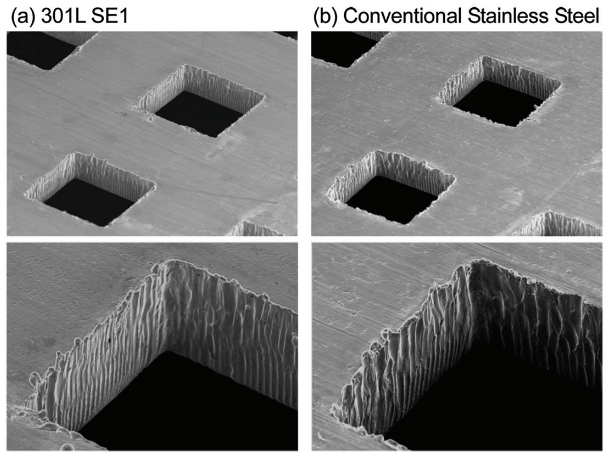


Fig. 10 Appearance of stainless steel sheets perforated by laser processing, (a) 301L SE1, (b) Conventional stainless steel

on general-use material (SUS304) for comparison. As is obvious from the image, the smoothness of the finish of the processed wall of 301L SE1 is superior to that of the general-use material. Enhanced smoothness of the etching-processed surface, or sharpness at the cut edge, greatly contributes to cutting accuracy. Furthermore, the use of 301L SE1 could in certain cases eliminate the need for electrolytic grinding, which is conventionally performed after the etching process.

Refining crystal grains contributes to the enhancement of surface smoothness after laser processing. **Figure 10** shows the appearance of 301L SE1 sheets and a conventional material after laser processing. It is found that, similar to the case of the etching-processed sur-

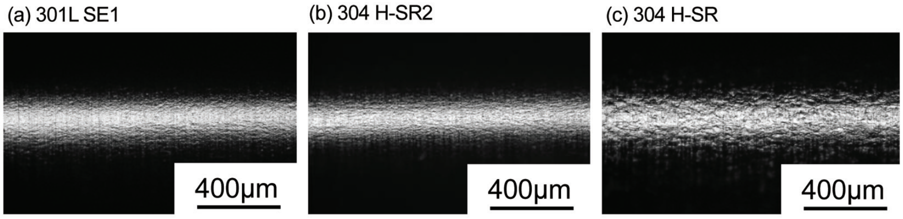


Fig. 11 Appearance of specimens after V-block bend tests with 90° bending angle and 0 mm inside radius

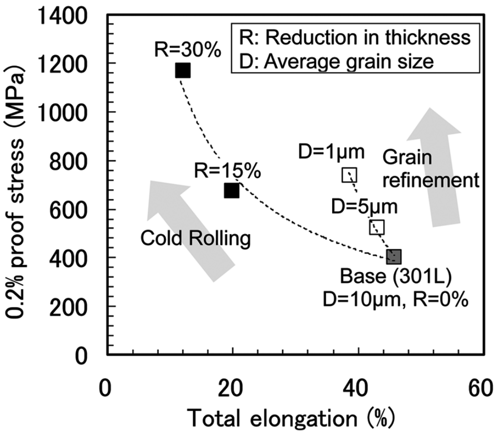


Fig. 12 Effect of cold rolling and grain refinement on balance of strength and elongation

face, the roughness of the laser-processed surface is reduced by refining the crystal grains of the subject material. Along with enhancement of the smoothness of the processed surface, the refinement of crystal grains contributes to the suppression of foreign substance adhesion on processed surfaces, and to the improvement of dimensional accuracy, thereby contributing to the enhancement of stability in operations when the material is used as a metal mask. It also contributes to eliminating subsequent processes involving chemical grinding or electrolytic grinding, due to the reduction of burrs made from molten metal during laser processing. In certain cases, such elimination has contributed to overall cost reduction.

With regard to the effect of refining crystal grains on bending work, the photos in **Fig. 11** show the ridge lines on specimens of the three types of austenitic stainless steel sheets when bent by 90 deg. Surface roughness before bending is almost the same. It is confirmed that when the smoothness of the ridges is compared, a remarkable improvement in smoothness is recognized in both 304 H-SR2 and 301L SE1 (both having fine crystal grains), in comparison with 304 H-SR which has conventional crystal grain size and which exhibits a rough skin with the appearance of protruded crystal grains.

Furthermore, since refining crystal grains is the method among steel-strengthening methods that realizes the least deterioration in ductility, it is effective in improving the strength vs. ductility relationship. **Figure 12** shows the effects of the cold rolling reduction ratio and crystal grain size on 0.2% yield strength vs. the elongation relationship, in SUS301L. When the annealed base SUS301L having an average grain size of 10μm is cold rolled, 0.2% yield strength increases along with an increase in the reduction ratio, and elongation decreases. On the other hand, if the crystal grains of the base steel are refined by low temperature annealing, or by the addition of a very small amount of Nb, 0.2% yield strength increases, although elongation decreases slightly. However, the extent of the decrease in elongation is smaller than the increase in strength. Accordingly, when compared at a same strength level, it is found that the grain-refined material exhibits a greater elongation than the material high-strengthened by cold rolling, and is superior with respect to the strength vs. ductility relationship. These characteristics, smoothness of the bent portion and excellent strength vs. ductility relationship, are very effective in the application of the material where post-etching press forming and bending forming are applied, and the improvement in squeegee durability, in the case of metal mask use.

5. Conclusion

Austenitic stainless steel sheets 304 H-SR, 304 H-SR2 and 301L SE1 produced by Nippon Steel & Sumitomo Metal are suitable for precision cutting processes, such as the photo-etching process and the laser process. They are used by a number of domestic and foreign customers as materials for precision parts and metal masks, and are high regarded. Nippon Steel & Sumitomo Metal is now able to consistently produce these stainless steels for precision cutting uses, through integrated control of the entire process from alloy composition to the application of production conditions such as cold rolling and heat treatment. The company plans to apply its proprietary crystal grain refining technology for 301L SE1 to other steel materials as well.

References

1) Hosoi, Y.: Stainless Steel no Kagaku to Saishin Gijutsu. First Edition. Tokyo, Japan Stainless Steel Association, 2011, 217p (in Japanese)
2) Japan Stainless Steel Association: Stainless Steel Handbook. Third Edition. Tokyo, Nikkan Kogyo Shinbun-sha , 1995, 1173p
3) Shibuya, M.: Materia. 34 (9), 1068 (1995)
4) Shibuya, M.: Convertech. 40 (7), 75 (2012)
5) Fujisawa, K.: Sokeizai. 53 (1), 33 (2012)
6) Hirahara, K.: Sokeizai. 49 (1), 19 (2008)
7) Allen, D.M. et al.: CIRP Annals - Manufacturing Technology. 54 (1), 187 (2005)
8) Heish, T.R. et al.: Acta Metall. 37 (6), 1637 (1989)
9) Adachi, K. et al.: Materia. 47 (1), 36 (2008)
10) Katsurai, T.: Honda R&D Technical Review. 12, 151 (2000)
11) Takaki, S. et al.: Tetsu-to-Hagané. 74 (6), 1052 (1988)
12) Sawada, M. et al.: ISIJ Inter. 51 (6), 991 (2011)
13) Thermo-Calc Software: http://www.thermocalc.com
14) Sato, A. et al.: The Japan Society of Mechanical Engineers, Tohoku Branch Autumn Lecture Meeting, Proceedings. 2007 (43), 1213 (2007)

Masayoshi SAWADA
Researcher
Titanium & Specialty Stainless Steel Research Lab.
Steel Research Laboratories
1-8 Fuso-cho, Amagasaki City, Hyogo Pref. 660-0891

Masayuki SHIBUYA
Senior Manager, Head of Dept.
Specialty Stainless Steel Technical Service &
Solution Dept.
Titanium & Specialty Stainless Steel Unit

Hayato KITA
Senior Manager
Specialty Stainless Steel Technical Service &
Solution Dept.
Titanium & Specialty Stainless Steel Unit

Kazuyoshi FUJISAWA
Manager
Production & Technical Control Dept.
Production Div., Naoetsu Works
Titanium & Specialty Stainless Steel Unit