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Ultra Clean Stainless Steel Tubes for Semiconductor Plants

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Abstract:

The 316L stainless steel tube called "clean tube" has been increasingly used for the high purity gas piping system in the semiconductor manufacturing plant. With advance of the semiconductor integration, requirements for the piping material are becoming stricter, for instance, a requirement to decrease nonmetallic inclusions to the utmost in order to prevent the piping material itself from becoming a pollution source, a requirement of purifying the material in order to control harmful fumes during welding joints, etc. "KS007" is a 316L stainless steel with a high purity fulfilling these requirements through the triple melting processes of VIM-ESR-ESR. Further, "KS270", having a high purity realized through the ESR melting process with applying YUS270 (20Cr-18Ni-6Mo) as the base material, can be used in an environment in which the anti-corrosion property is required.

1. Introduction

As semiconductor integration continues to progress, requirements for materials used in semiconductor manufacturing plants are becoming increasingly complex. Among these advanced requirements are ultra-clean gas piping (hereafter referred to as "clean tube") which plays an important role in semiconductor manufacturing processes. Nippon Steel has supplied seamless stainless steel tubes produced by the Hot Extrusion method, which serve as mother tubes, for Kuze Bellows Kogyosho Co., Ltd, which is a pioneer in the manufacture of clean tubes in response to market needs, recently resulting in practical use as the "KS series". Here, we consider the nature of future materials, and introduce this series with its emphasis on high purity materials.

2. Introduction of a Clean Tube (Pipe)

Various high purity gases are used in semiconductor manufacturing processes — these gases range in chemical reactivity from the inert to the corrosive. The piping material usually employed represents 316L stainless steel (18-12-2Mo steel). In considering the ease of manufacture, weldability, anti-corrosion property and other features, and furthermore, in view of the fact that it is desirable to use the same material in equipment such as joints and pressure regulators as well as piping, it is thought that the piping material has been integrated into 316L steel and that the fact has become well established. Pipe sizes include small tubes of 6.35mm (1/4") to 12.7mm (1/2") in diameter (tube size), and small and medium tubes of 13.8mm (1/4B) to 165.2mm (6B) in diameter (pipe size), and most of the wall thickness is equivalent to Schedule 5S. Everything is referred to as piping for convenience's sake. In this paper, a generally accepted designation of "clean tube" will be used.

"BA (bright annealing) tubes", which maintain their gloss mostly in a state of cold drawing, have been used for clean tubes from the beginning (before 256kbit DRAM), but it has now become common to use "EP (electro polishing) tubes", applying electro polishing to the internal surface of BA tubes, particularly in tube sizes after 1Mbit DRAM[1]. This is due to the need to improve internal surface roughness to reduce the probability of contamination from piping. This is because there are more

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chances for gas to come in contact with the internal walls of tubes near the end, which is regarded as a use point, where a small tube is used, increasing the possibility of contamination from the tube.

The guaranteed surface roughness of ordinary BA tubes is R_{max} 3.0μm or less, and that of EP tubes is R_{max} 0.5μm or less. It has become increasingly difficult to meet necessary quality requirements with only surface roughness from around the point where the integration value exceeds that required for a 4Mbit DRAM.

In other words, it was added as a new requirement to minimize nonmetallic inclusions, which may be exposed to the internal surface of the tube after electro polishing, and metallic fumes including Mn released from molten metal in the butt welding of tubes.

3. Required Characteristic Levels of Materials for Clean Tubes and Means for Achievement

Most of the newly required characteristics for clean tubes with improving semiconductor integration are associated with the materials themselves. **Fig. 1** provides a summary of required characteristics as well as the means and levels required to attain them.

The most important required characteristics in **Fig. 1** are "the reduction of nonmetallic inclusions" and "the reduction of fumes produced in welding."

3.1 Reduction of nonmetallic inclusions

Achieving the required level for "nonmetallic inclusions" requires applying the method of special remelting.

Possible methods of special remelting include the Electro Slug Remelting (ESR), the Vacuum Arc Remelting (AVR) and the Electron Beam Remelting (EBR). We determined that the most promising method was that of ESR, which would allow future cost reductions because the method is generally accepted in the reduction of nonmetallic inclusions and because it can handle relatively large steel ingots. **Fig. 2** shows the behavior of nonmetallic inclusions in melting material using 7t ESR equipment with 10t VIM material as the primary electrode. It is data on billets extracted from steel ingots at five charges.

Application of special slugs developed for highly clean stainless steel and furnace atmosphere control technology have indicated that applying ESR once permits the reduction of nonmetallic inclusions approximately equivalent to applying VAR once. We therefore studied applying ESR twice aiming at minimizing variations and further high cleaning.

The material was dubbed "KS007" in view of reaching a level of oxygen in steel of less than 10 ppm, which is a parameter of nonmetallic inclusions, that is, a level of a fraction of a million (7th power of 10); which is a sufficient level.

3.2 Minimizing fumes produced in welding

Butt welding of clean tubes is normally given by nonfilar TIG welding from the periphery. Metallic fumes containing constituents of low vapor pressure including Mn and S, as released from the surface of the molten metal described above, then present a problem. There may be cases where the fumes themselves agglutinate to the internal wall of the tube to form a pollution source (particles) liberated when the tube is used, and where Mn concentrates and adheres in the vicinity of the welding heat affected zone (See **Photo 1**). It may form oxides to cause local corrosion by degrading passivation of the affected area, with corrosive products forming a pollution source.

Attention is given to the latter in particular because corrosive gases such as HCl and HBr have often been used recently [2]. On the other hand, the method of minimizing areas where fumes are produced by controlling welding heat input low and controlling the low vapor pressure constituents contained in material low have been suggested [3].

First, common 316L steel contains Mn of about 1% (spec. ≦ 2.00%), while the content of Mn in KS007 is established at 0.2% or less. Mn is an important constituent for austenitic stainless steel because of the effect of desulfurization and for austenitic phase stabilization, but here, it is regarded as a harmful constituent. In view of the above, a lower content of Mn is more desirable. However, to achieve an Mn content of less than 0.05%, a special, very low manganese raw material is required at the time of primary melting VIM for ESR because it has no effect

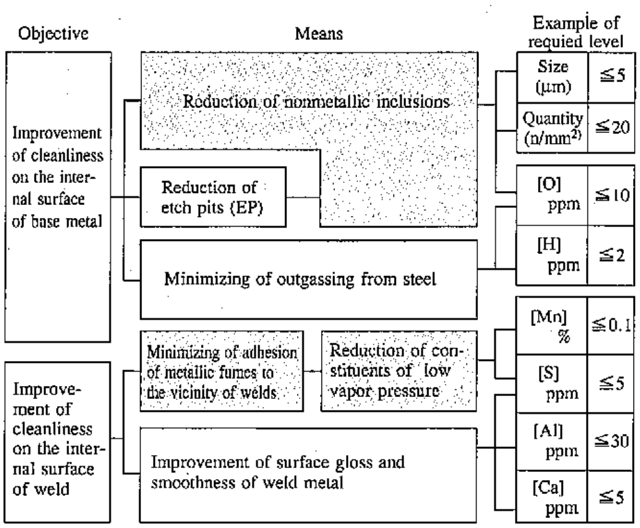


Fig. 1 Characteristics and levels required of 316L clean tube materials

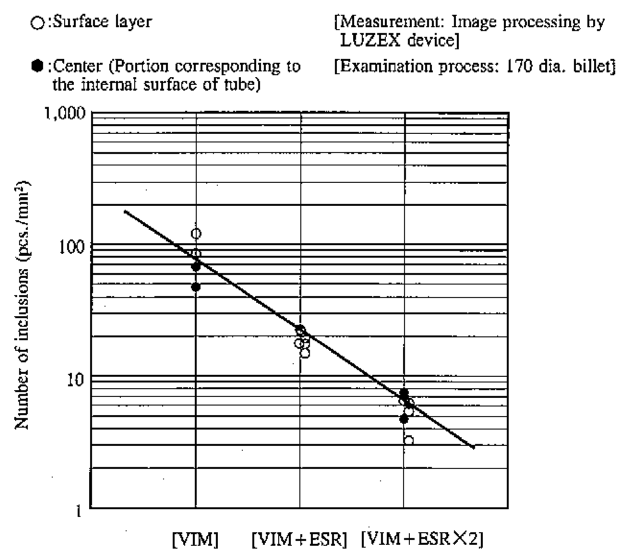


Fig. 2 Behavior of nonmetallic inclusions in SUS316L using ESR

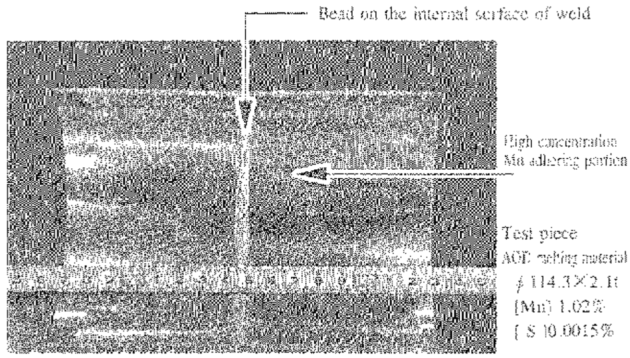


Photo 1 Mn adhering to the internal surface of weld of BA tube

on the de-Mn, and thus it is not cost efficient. Since this phenomenon of Mn concentration in the vicinity of welds was difficult to observe due to EPMA and others at Mn ≦0.25% for small tubes (tube size) when the amount of back shield gas flow was controlled properly, the above value was set.

Next, common 316L steel contains S of ten to several tens ppm, while the content of S in KS007 was reduced to around 3 ppm, due to the strong desulfurization by the action of slugs for ESR. It is observed that S produces much more fumes than Mn with respect to the content [3], thus greatly minimizing the total amount of fumes (See **Fig. 3**).

The reduction of welds is also an important measure to minimize fumes. From this point of view, KS007 has a system to supply even coiled tubes (200m maximum length), and the base metal performance is the same as straight tubes.

4. Manufacturing Processes and Quality Characteristics of Clean Tubes

4.1 Manufacturing processes

Fig. 4 shows the integrated manufacturing processes of KS007 clean tubes.

4.2 Quality characteristics

Table 1 shows examples of chemical composition analysis values.

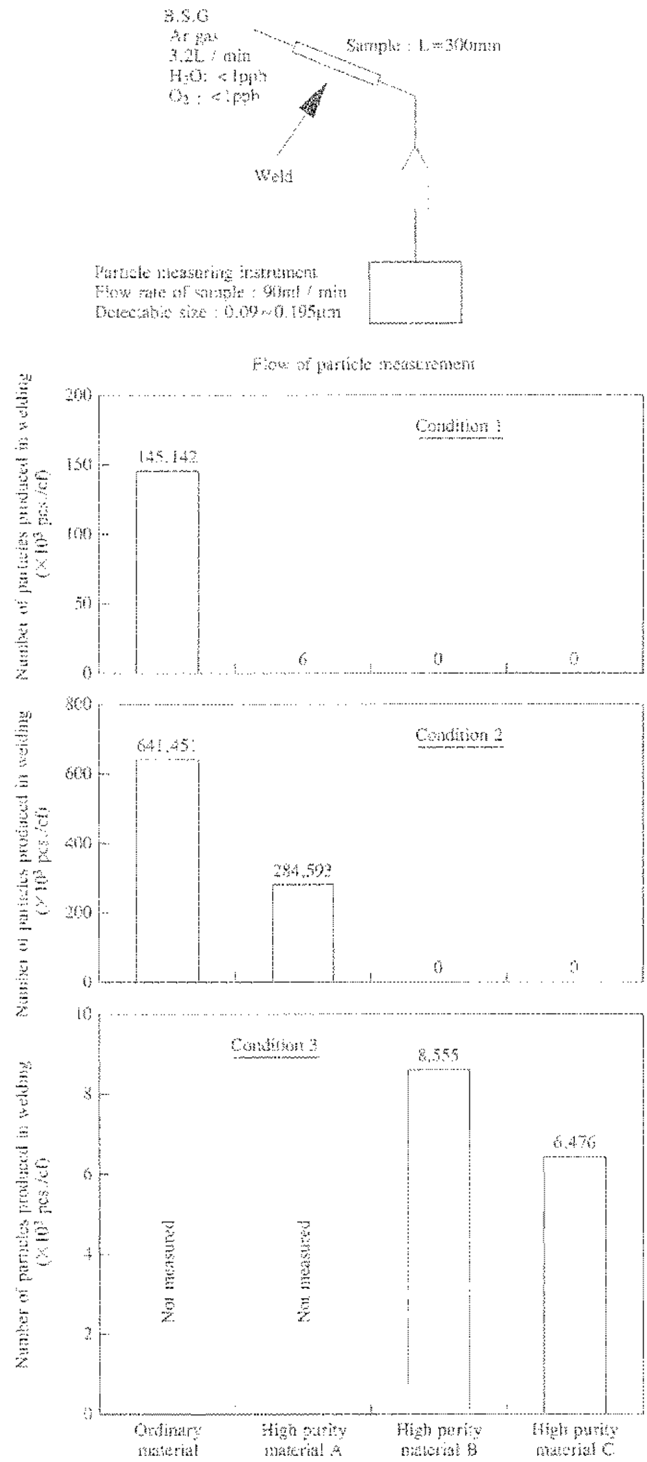
Table 2 shows the results of the distribution measurement by size for nonmetallic inclusions in tubes. Nonmetallic inclusions tend to elongate in the direction of working between hot extrusion and drawing, but no inclusion exceeding 10μm is observed.

Table 3 shows the mechanical properties of tubes. Low strength elements such as C provides lower proof stress and softness than ordinary material, but they fulfill the JIS (Japanese Industrial Standards) and other similar standards.

Photos 2 and **3** show the results of photographing the internal surface of an EP tube with an optical microscope (polarization) and observing the internal SEM of the EP tube respectively. Photographed portions are specific areas in examined surfaces. They indicate that the difference in the distribution of nonmetallic inclusions has a great effect on the difference in the internal smoothness of ordinary material and KS007.

Photo 4 shows the internal appearance of TIG welded joints. Ripples are observed on the internal bead surface of ordinary material, while KS007 provides smoothness.

Fig. 5 shows the test results on pitting (JIS ferric chloride) with test pieces including tube welded joints. From **Fig. 5** and the results of the measurement of pitting potential, which is not



Test material	Chemical composition (%)		Amount of welding heat input (J/cm)		
	Mn	S	Condition 1 (Proper)	Condition 2 (Excessive)	Condition 3 (Excessive)
Ordinary material	1.07	0.0013	731	906	–
High purity material A	0.64	0.0009	761	956	–
High purity material B	0.02	0.0002	630	814	989
High purity material C	0.17	0.0003	729	904	1,079

Fig. 3 Effect of Mn and S on the amount of particles produced in welding (Derived from data measured by Nippon Sanso Co.)

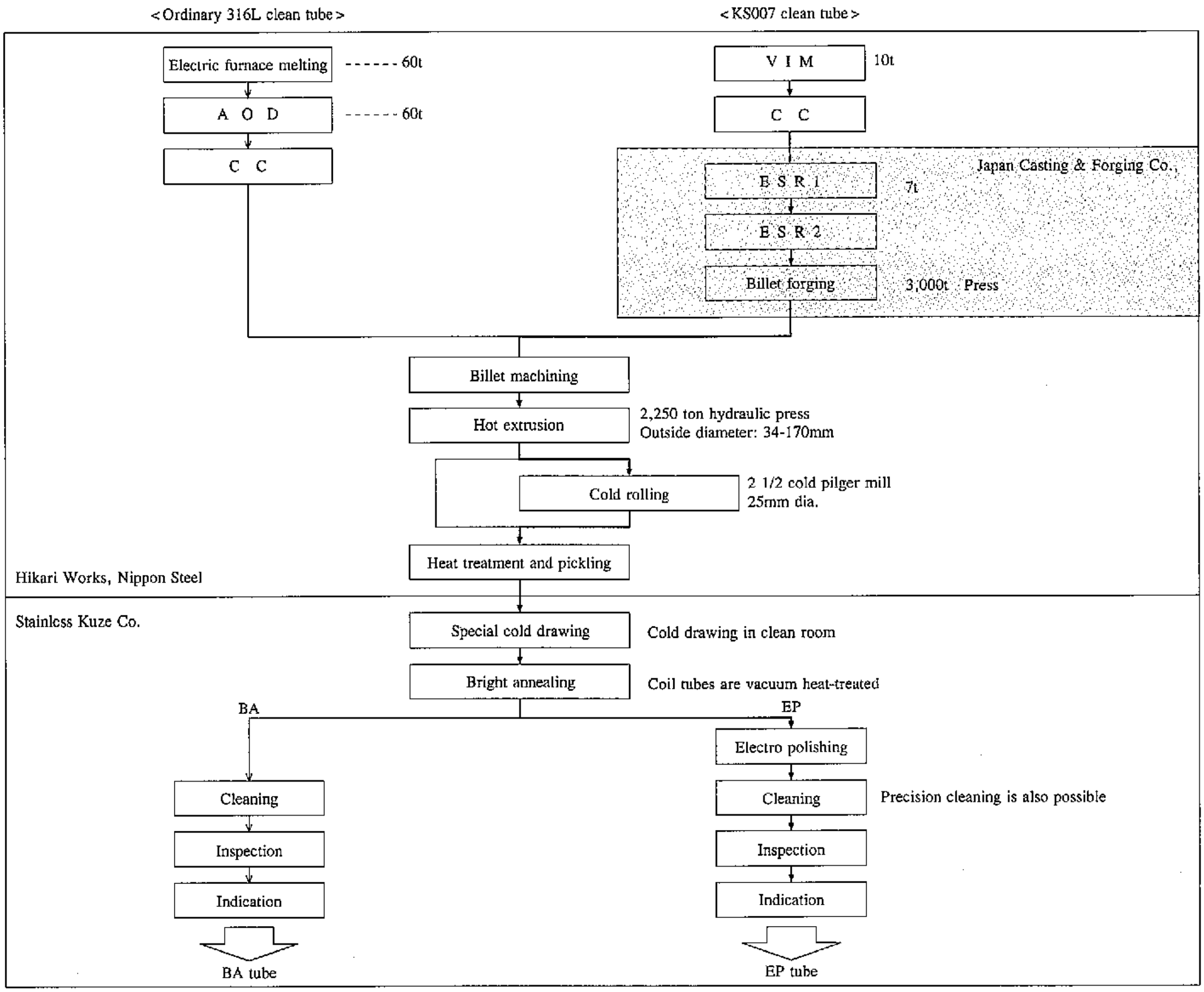


Fig. 4 Manufacturing processes of clean tubes

Table 1 Examples of KS007 chemical composition analysis

		C	Si	Mn	P	S	Ni	Cr	Mo	Al	Ca	O	N
Specification	SUS316L	Max 0.030	Max 1.00	Max 2.00	Max 0.040	Max 0.030	12.00 ~16.00	16.00 ~18.00	2.00 ~3.00	–	–	–	–
	TP316L	Max 0.035	Max 0.75	Max 2.00	Max 0.040	Max 0.030	10.00 ~15.00	16.00 ~18.00	2.00 ~3.00	–	–	–	–
Example of actual results	Ordinary (1)	0.020	0.36	0.81	0.025	0.002	12.72	17.75	2.26	30	10	50	340
	material (2)	0.018	0.34	0.79	0.025	0.002	12.52	17.84	2.29	20	10	46	330
	KS007 (1)	0.005	0.28	0.18	0.013	0.0003	14.07	16.87	2.26	20	2	7	192
	KS007 (2)	0.006	0.23	0.13	0.016	0.0003	14.22	16.72	2.29	20	2	8	174

Table 2 Nonmetallic inclusions in KS007

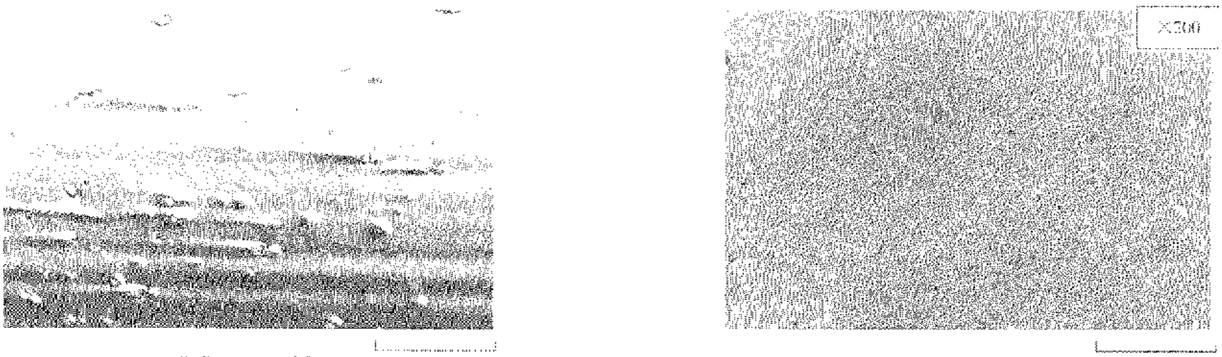
Measurement results by image processing (Conforming to the method of JIS/x200, 63 field of view = LUZEX device)

Unit: % (Area)

		Type A	Type B	Type C	Total
KS007	6.34 ϕ ×1.0t	0.0003	0	0.0015	0.0018
	9.53 ϕ ×1.0t	0.0001	0	0.0012	0.0013
	12.7 ϕ ×1.0t	0.0001	0	0.0005	0.0006
Comparison ordinary material	9.53 ϕ ×1.0t	0.0003	0	0.0507	0.0510

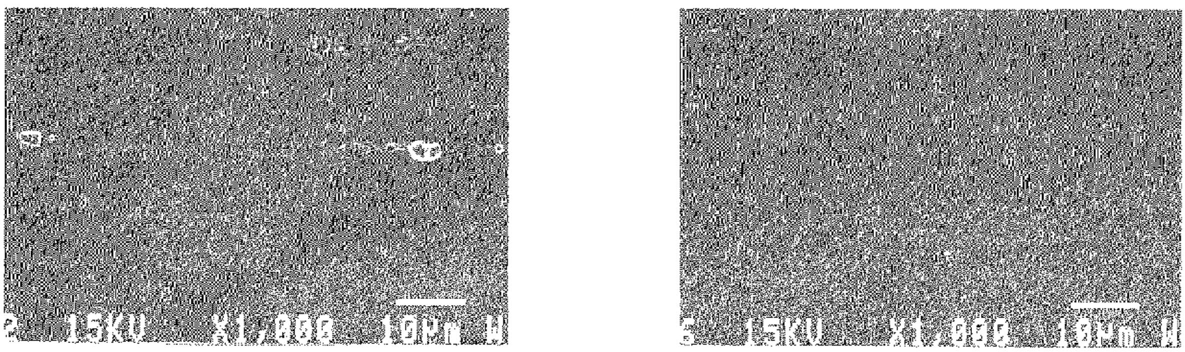
Table 3 Mechanical properties of KS007 (Test material 9.53 dia.×1.0 EP tube)

		Tensile strength N/mm²	Proof stress N/mm²	Elongation %	Hardness Hv
Specification	SUS316L	Min 480	Min 175	Min 35	–
Example of actual results	Ordinary (1)	596	269	53	143
	material (2)	598	276	53	154
	KS007 (1)	542	238	57	135
	KS007 (2)	556	233	61	136



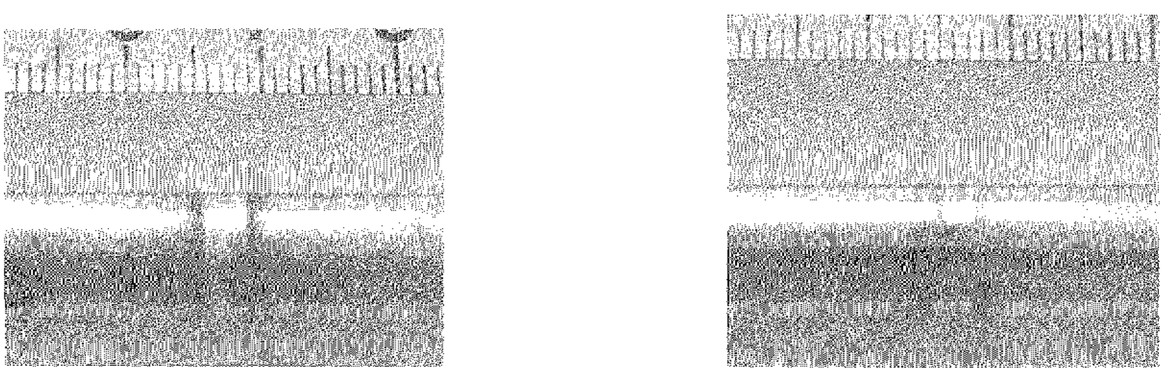
Ordinary material KS007

Photo 2 Photos of the internal surface of EP tube with an optical microscope (Polarization) (Size: 9.53 dia.×1.0)

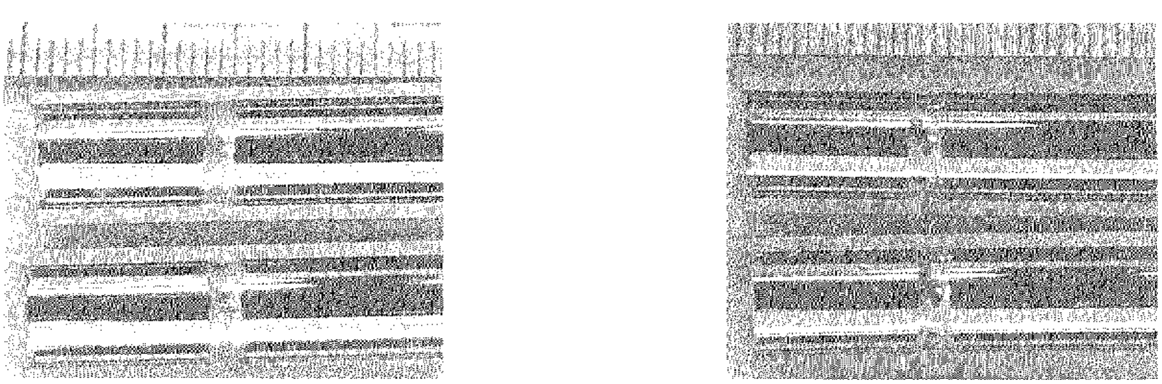


Ordinary material KS007

Photo 3 Photos of the internal SEM of EP tube (Size: 9.53 dia.×1.0)



External surface of ordinary material External surface of KS007



Internal surface of ordinary material Internal surface of KS007

Photo 4 Photos of the appearance of TIG welded joints (Size: 9.53 dia.×1.0 EP tube) illustrated, the weld metal and heat affected zones are not as prone to corrosion as the base metal. No great difference was observed in pitting resistance between ordinary material and KS007. This may be because the factors determining anti-corrosion property are mainly the concentration state of Cr on the surface layer interface after EP working and the contents of Cr and Mo of base metal; they are little affected by high cleanliness and high purity.

5. High Corrosion Resistant Clean Tubes

316L steel as described above is completely acceptable as a clean tube material. This steel will be able to satisfactorily address various problems which may be encountered in future, but it may have limitations in some environments from the viewpoint of anti-corrosion property. With this problem in mind, Hastelloy C-22, a high purity ferritic stainless steel FS9 (26Cr-1Mo)[4] and other similar materials have been suggested from a materials viewpoint, and the development of them is in progress. Here, we considered austenitic stainless steel KS270, which is a direct extension of 316L steel. KS270 is based on Nippon Steel YUS270 (20Cr-18Ni-6Mo) which is highly valued as a pit-resistant steel, and is highly purified and cleaned for clean tubes.

The reason KS270 is based on YUS270 is that the shift to austenitic stainless steel from 316L steel may be done most smoothly in view of tube manufacturability (manufacturing costs) and working convenience (weldability with 316L material, etc.), and that YUS270 shows highest pitting resistance in practical austenitic steel types.

5.1 Quality characteristics of KS270

Table 4 shows some examples of KS270 composition analysis.

Table 5 shows the test results on ferric chloride pitting with test pieces exposing only the internal surface of an EP tube. The amount of corrosion of KS270 was 0 under the test conditions.

6. Conclusion

We described the characteristics required for gas piping materials in semiconductor manufacturing plants showing the need for rapid progress, and the way these have been addressed at Nippon Steel.

There are a number of ways in which requirements differ from general requirements for metallic materials in the field, such as "no impurities must be contained" and "no corrosion must occur", rather than simply aiming at fewer impurities and less corrosion. 316L steel has been improved in line with these demands; however, the steel has limitations as demands increase, and various characteristic materials having been proposed. However, costs can never be neglected, and plant construction costs are becoming an increasingly important factor also in the field in recent years.

Austenitic stainless steel is thus best suited to satisfying demands for low costs when integrated costs up to melting, manufacturing and piping work are taken into account. Further developments and improvements, taking advantage of the characteristic features of the steel, are desirable.

We described KS007 as an ultra clean 316L steel and high anti-corrosion austenitic stainless steel KS270. The KS series includes KS005 of AOD melting material minimizing Mn fumes at an optimum ratio, and grades for various needs are being prepared. We will continue to meet customer expectations in the semiconductor field in the future.

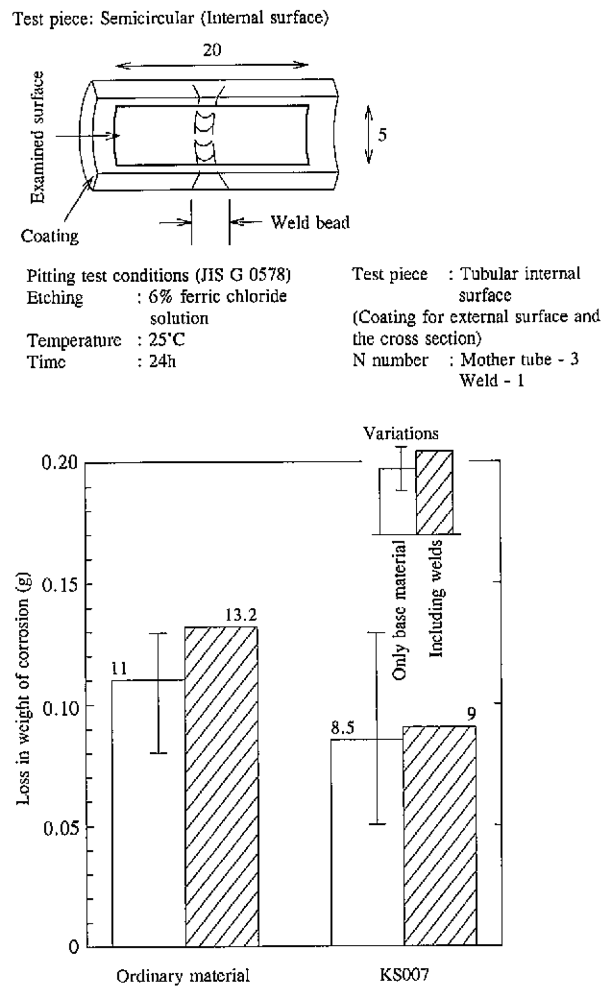


Fig. 5 Test results on ferric chloride pitting

Table 5 Test results on KS270 ferric chloride pitting

	Loss in weight of corrosion ($g/m^2 \cdot h$)	Test conditions
KS270	0.000(n=7)	Size : φ9.53×1.0 (mm) Solution : 6% ferric chloride Temperature : 25°C Time : 24h
SUS316L (Comparison material)	1,200(n=3)	

Table 4 Examples of KS270 composition analysis values

(mass%) (ppm)

Composition	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Al	H	O	N
Specification	≦0.020	≦0.80	≦1.00	≦0.030	≦0.010	17.50 ~18.50	19.50 ~20.50	6.0 ~6.50	0.50 ~1.00	–	–	–	1,800 ~2,200
Example of KS270	0.015	0.47	0.44	0.023	0.0003	17.90	20.10	6.15	0.52	0.053	1.2	9	2,170

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