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Production of High Grade Stainless Steels

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Synopsis :

On the basis of fundamental experiments, optimum condition in steelmaking and continuous casting for the production of high quality stainless steels have been determined. The amounts of impurity contents were decreased by adopting K-BOP and SS-VOD process and the secondary cooling conditions in continuous casting were optimized. With these countermeasures, all kinds of stainless steel have been produced by continuous casting without problems. For the dualphase stainless steel, hot ductility was remarkably improved by heat treatment of slab soaking. Thus the system for the stable production of all high quality stainless steels has now been established.

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Production of High Grade Stainless Steels*



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1 Introduction

At Kawasaki Steel all the processes for stainless steel manufacture from refining to hot rolling were integrated at its Chiba Works in 1981. Since then both steelmaking and hot rolling departments achieved a marked progress as the main line of stock material making by adopting new techniques. Noteworthy among all include a refining technique using MF-K-BOP-RH method, a technique for using pretreated hot metal, and a technique for making high grade stainless steels such as high purity ferritic stainless steels and duplex stainless steels. All these have been established as the basis for stable production at the company's stainless steel manufacture.

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of stainless steels was aimed at, and mechanical properties at high temperatures, which are the basis of all the processes were investigated. At this stage, chemical compositions necessary for making each type of stainless steel of stable quality were determined, and points on the production of commercial scale manufacturing were described.

In establishing production systems in the commercial scale production line, the techniques of refining, continuous casting, and hot rolling processes were improved, using the results of the fundamental investigations stated above. For stable manufacturing of high alloy steels, it is essential to reduce [S], [P], [O], [N], and [C], that is, to make steels highly pure. To this end strong stirring technique was used effectively. Hot workability and slab temperature simulation for each secondary cooling pattern were used to determine casting conditions for continuous casting processes. In the improvement of casting conditions, it was effective to optimize mold powder by taking advantage of the knowledges for carbon steels. On the other hand, for steels containing much δ -ferrite phase in the temperature range of hot rolling, it is important not only to make sound slabs but also to prevent hot rolling cracking. Improving slab's microstructure by slabbing mill is found to be effective to prevent cracking during hot rolling, with resultant remarkable improvements in production yield and quality.

As mentioned above, various fundamental techniques that have been developed have made possible stable production of high grade stainless steels. In this

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report, the essential points of these techniques are introduced.

2 Manufacturing Processes and Types of High Grade Stainless Steels

2.1 Manufacturing Processes

The refining and casting of stainless steels were performed in the No. 1 Steel Making Shop of Chiba Works. When the improvement of cast slab microstructure was necessary, soaking pit and slabbing mill in the No. 3 Slabbing Mill were used. **Table 1** shows the specifications for main facilities. The refining process is selected according to the heat size and the levels of chemical composition to be attained. The refining of austenitic steels was carried out by mainly using MF-K-BOP-RH process, and that of ferritic and martensitic steels was carried out by using hot-metal-pretreatment-K-BOP-RH process. In the refining of high Cr ferritic steels, the SS-VOD facility, which makes strong stirring possible, was also used.

The continuous casting of all types of stainless steels was realized, but the slabs were treated differently

depending on their steel grades, especially crack sensibility. The steels, which transform into martensite at normal cooling rate or which are brittle at normal temperature, need special considerations for slab treatment, and temperature control of slabs was performed. The steels easy to crack during hot rolling were pretreated with sizing and soaking prior to rolling.

2.2 Manufactured Steels

The integration of stainless steel manufacturing processes at Chiba Works has made it possible to establish a production system capable of making all types of stainless steels from austenitic type high alloy steels to martensitic type 13% Cr steels.

Table 2 shows examples of typical steels manufactured. Among all, SUS 447 J1 (extremely low carbon and nitrogen 30 Cr-2 Mo steel) is made highly pure by effectively using the ladle refining technique and has high corrosion resistance. Therefore, this steel is widely used in various fields. The duplex structure stainless steels in KWB series applicable to nuclear power plants manufacture with Magley welding method, and R 434 LN-2 materials for solar collectors are representative high grade stainless steels of Kawasaki Steel. **Figure 1** classifies these steels according to their microstructures.

Table 1 Main specifications of steel making shop and slabbing mill

	Specifications
UHP melting furnace	Heat size : 85 t Transformer capacity : 65 MVA Clean-house Inner volume: 5 300 m ³
Hot metal treatment	Torpedo car : 350 t Flux : CaO-Fe ₂ O ₃ -CaF ₂ Injection rate: 350-500 kg/min Flux/gas : 80-130 kg/Nm ³
K-BOP	Heat size : 85 t Process gas: O ₂ , N ₂ , Ar Top blowing lance and sub lance
Ladle refining	RH degasser SS-VOD
Continuous casting	Curved mold slab caster Sumitomo-Concast one strand machine
Soaking pit	Top one way type with variable flame type burner Capacity: 230 t/hole Pit size : 5 400 × 8 000 × 5 000 mm
Mill	Universal type H mill: 1 320φ × 2 700 mm V mill: 1 050φ × 2 400 mm

Table 2 Stainless steel grades cast at Chiba No. 1 caster

Classification	Steel grade
Ferritic	SUS 430, SUS 434, SUS 444, SUS XM27, SUS 447J ₁
Martensitic	SUS 410, SUS 420J ₁ , SUS 420J ₂ , R 409 SR, SUS 409, R 410 DB, R 410 DH
Austenitic	SUS 304(L), SUS 301(L), SUS 316(L), SUS 317(L), SUS 321, SUS 347, SUS 309S, SUS 310S, KWB 308L, SUS 631, SUS 329J ₁

3 Manufacturing Technique Establishment

3.1 Mechanical Properties at Elevated Temperatures

Continuous casting of high grade stainless steels is important to improve slab quality and yield. Also, it is needless to say that the background of the integration program for stainless steel manufacture at Chiba Works was a drastic cost reduction aimed at by way of continuous casting of various types of stainless steels utilizing the existing casters.

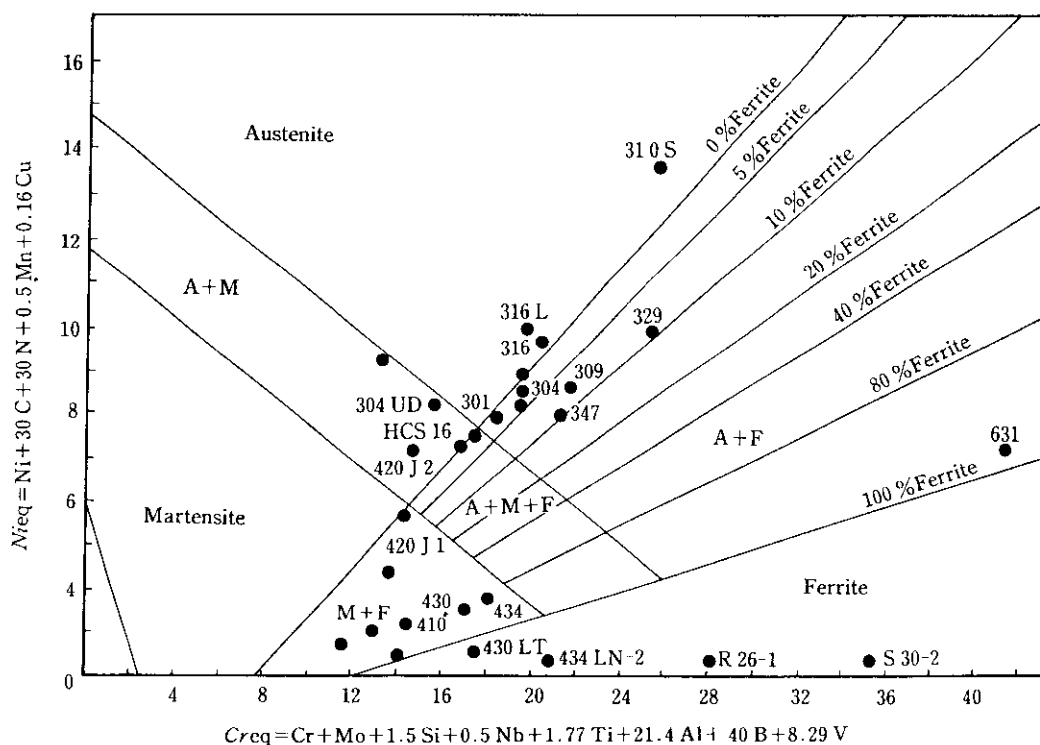


Fig. 1 Schaeffler diagram

Before the first trial of continuous casting, it is very important to determine its chemical compositions, casting temperatures, and cooling conditions, on all of which the embrittlement characteristics of the steel depend.¹⁾ In the subject investigation, mechanical properties of various types of stainless steels have been studied. The specimens were made from the materials whose compositions were adjusted to the predetermined levels in the test melting furnace. Tensile tests were performed on these specimens using an Instron type tensile test machine. Argon gas was used as testing atmosphere, with temperature controlled within $\pm 2^\circ\text{C}$. Specimens were heated to 1350°C before the test and cooled to the testing temperature at the rate of 10°C/s . **Figure 2** shows the results of tensile strength and reduction of area. These steels have very small values of reduction of area below 1150°C , therefore it is presumed that these have high crack sensibility.

The effects of impurity elements on crack sensibility have been reported on austenitic single-phase SUS 310S steel,^{2,3)} and it has been shown that the reduction of [P] and [S] in molten steel strengthens the grain boundary and lowers the crack sensibility. In the subject investigation, these results were taken into consideration and effects of high purity on duplex structure stainless steels SUS 329, SUS 631, etc. were studied. **Figure 3** shows the

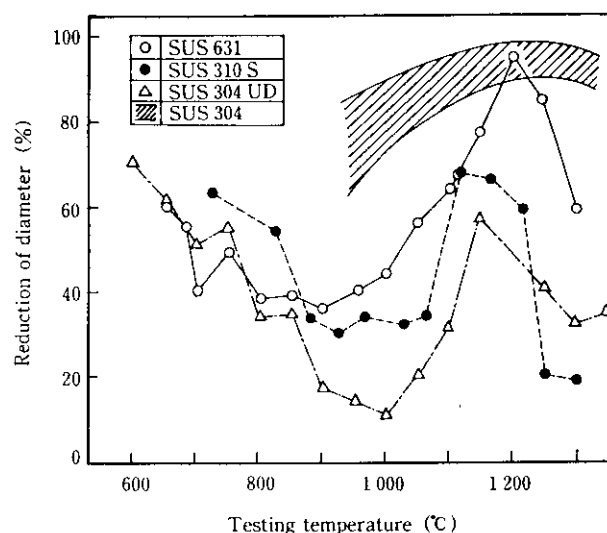


Fig. 2 Hot workability of stainless steel

relation between [S] and the reduction of area for SUS 329. The reduction of [S] markedly increases hot ductility. Also, an addition of small amounts of Ca and REM to an extremely low sulfur molten steel further improves its hot ductility. With the composition design based on these results, a stable casting of high grade stainless steels has been attained.

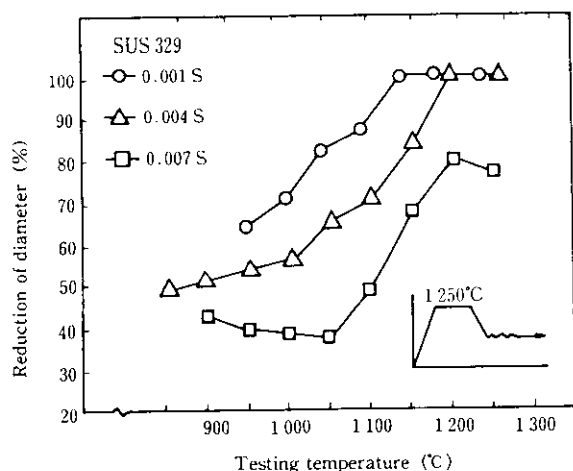


Fig. 3 Effect of S content on hot workability of stainless steel

3.2 Application to Production Line

3.2.1 Refining techniques

The refining section of stainless steels consists mainly of the combined-blown oxygen converters⁴⁾ capable of strong stirring and the SS-VOD facility⁵⁾ which is a ladle refining system having the largest stirring capability.

These facilities are effectively used for making high grade stainless steels in order to reduce impurity elements such as [S], [P], [O], [N], and [C]. The important points of refining are the desulfurizing capability in K-BOP for austenitic and duplex structure stainless steels, and the decarburizing and denitrizing capabilities in SS-VOD for high Cr ferritic steels. Figure 4 shows the difference of chemical compositions of low sulfur and normal austenitic stainless steels. As stated above, desulfurization is effective in improving hot ductility. The [S] concentrations of 10 ppm or under have been attained in the low sulfur steels. As described in another

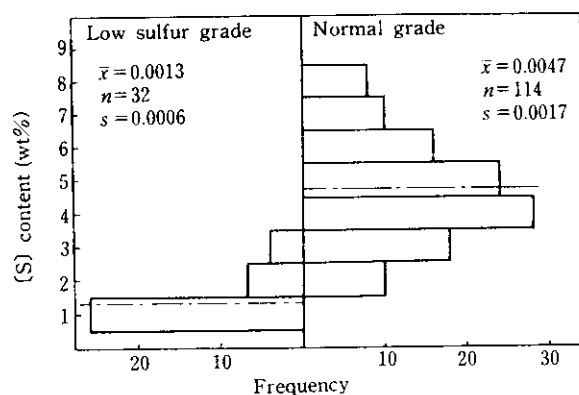


Fig. 4 Comparison of S content between low sulfur steel and normal grade steel

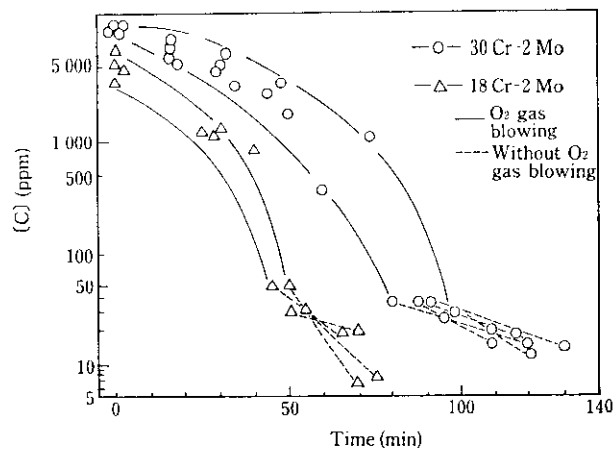


Fig. 5 Decarburization by SS-VOD

report⁶⁾, an excellent point of KSC process is that stable desulfurization is attainable by the single slag method.

On the other hand, high Cr ferritic stainless steels such as 30 Cr-2 Mo and 18 Cr-2 Mo have high corrosion resistance, with notable freedom from stress corrosion cracking, and their use is markedly increasing. To attain the characteristics of the high Cr ferritic stainless steels, however, the concentrations of interstitial impurities, [C] and [N], must be reduced to extremely low range. There are many reports^{4,7,8)} on decarburization and denitrization of high Cr steels. At Kawasaki Steel, the attainment of high Cr steels is made by using the SS-VOD where a strong stirring under vacuum is possible. Figure 5 shows an example of decarburizing behavior under the VOD treatment. In addition to the strong stirring mentioned above, the following four points are important for stable refining:

- (1) Control of molten steel temperature
- (2) Slag property control by taking into consideration the composition change during refining
- (3) Reduction of air leak in the vessel
- (4) Adoption of refractories for high-temperature

3.2.2 Continuous casting technique

Subjects for solution in the continuous casting of high grade stainless steels such as SUS 310 and SUS 631 are the prevention of slab defects such as surface and internal cracks.

The surface cracks of slabs can be classified into longitudinal crack generated in the mold, and transverse crack and corner crack generated in the secondary cooling zone or straightening area. It is known that the cracks generated in the mold largely depend on the cooling conditions in the mold and properties of the mold flux. On the other hand, the cracks generated in the secondary cooling zone or straightening area occur when the cooling of a slab has relatively advanced, and it is thought that these cracks are caused by the slab

embrittlement in specific temperature range. Therefore, it is important to optimize mold cooling conditions, mold flux properties, and mold oscillation conditions, and to control slab temperature around the straightener.

It is thought that the internal cracks of slab occur from the solid-liquid coexisting layer, and that these cracks expand in the specific embrittlement temperature range below the solidus line. The cause of the generation of these cracks is that the thermal stress during slab cooling process or external stress introduced by the bulging between rolls is larger than the shell strength. It is possible to prevent these cracks by optimizing the secondary cooling conditions. Thus, for wider application of continuous casting, it is necessary to determine casting conditions on the basis of the fundamental high temperature properties.

Figure 6 shows concepts of determining the second cooling pattern to prevent slab from cracking. At first, the slab surface temperature transition is estimated by changing the cooling water density of each secondary cooling zone. Then, using the hot workability measured

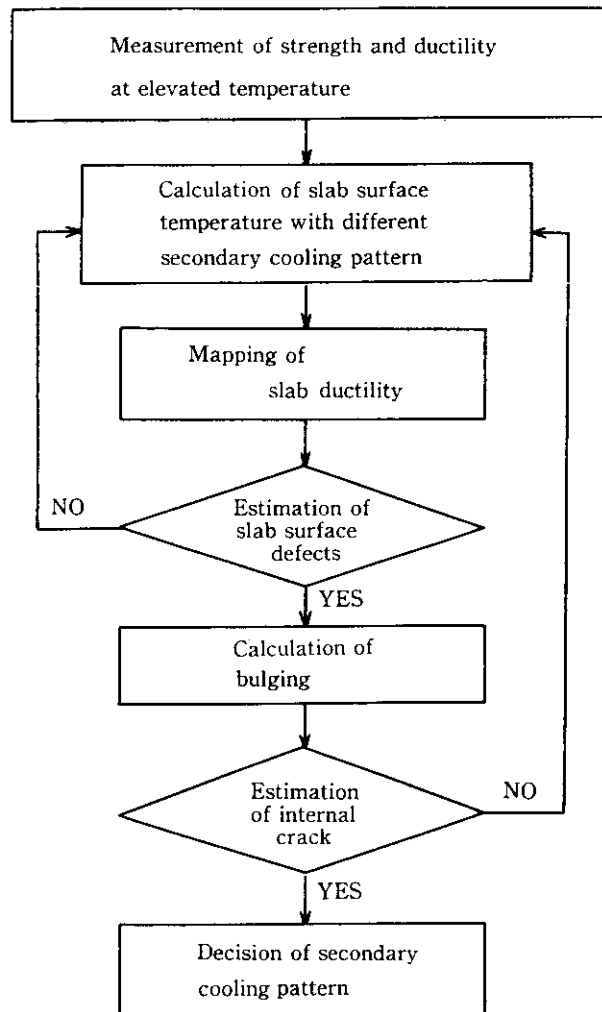


Fig. 6 Flow chart for the determination of slab secondary cooling pattern

at various temperatures by laboratory experiments, the transition of embrittlement state in the continuous casting machine is deduced. Cracking is considered to occur at the straightening performed when the slab surface temperature is in a specific embrittlement temperature range. Therefore, iterative calculation should be carried out by changing the cooling water density of each secondary cooling zone to obtain optimized solution so that the straightening of the strands can be done out of the specific range. On the contrary, when the slab surface temperature is corrected in the range above the embrittlement temperature, the internal cracking due to bulging between rolls is apt to occur. Therefore, the secondary cooling pattern should be modified so as to prevent the internal cracking and, at the same time, to perform straightening at a place outside of the embrittlement temperature area.

Figure 7 shows the slab surface temperature transition estimated by the procedure mentioned above, and Fig. 8 indicates the changes of reduction of area, used as index of embrittlement at various positions in a strand machine. Case I pattern is used when 9% Ni steel is made by continuous casting. Case II is the transition of

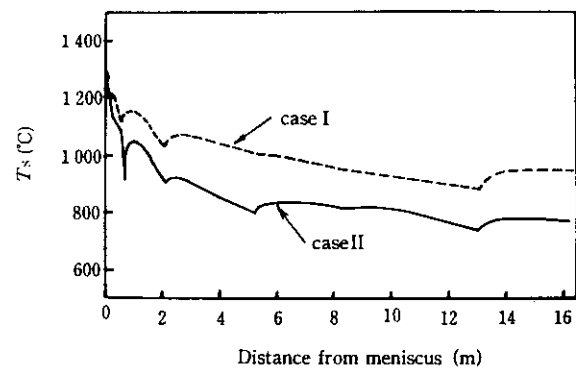


Fig. 7 Variation of surface temperature T_s of the slab during strand casting⁹⁾

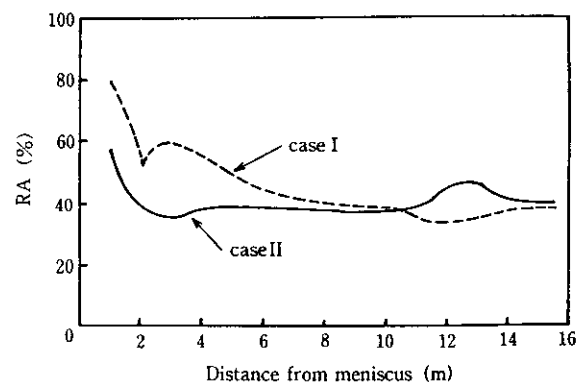


Fig. 8 Variation of reduction of area at the slab surface during strand casting⁹⁾

the surface temperature calculated using the SUS 304 pattern. In the case I, the reduction of area in the upper secondary cooling zone is higher than in the case II, so that the case I is effective in cracking prevention. However, the bulging is estimated to be three times that in the case II, so that the case I is disadvantageous in internal cracking prevention. In the case II, the reduction of area around the straightener is higher than in the case I, so that the case II will be advantageous in surface cracking prevention. On the basis of the above results, making of sound slabs without cracks was attained by using various cooling patterns, according to the characteristics of each steel.

In the continuous casting of high grade stainless steels, it is important to select mold powder suitable for respective steels. Particularly, in the casting of the steels including active elements such as Al and Ti, it is essential to consider the mold flux composition change during the casting. In the case of the continuous casting of SUS 631 which is a precipitation hardening steel including Al over 1%, the flux solidifies with the casting time elapsing. The main causes of this phenomenon is assumed to be an increase of Al_2O_3 in the mold flux because of the reduction of SiO_2 in the flux by Al, and an increase of basicity of the flux on account of the reduction of SiO_2 .

The flux solidification not only reduces the lubrication between mold and slab but also seriously affects the solidification process in the mold and may cause the longitudinal cracking of surface or breakout. The flux solidification can be prevented by selecting appropriate properties, for examples, low melting point (with flux composition change during casting taken into consideration) and low basicity. **Figure 9** shows the indexes of slab surface defect of the conventional and newly-developed powders. The newly-developed powder is lower than the conventional one in basicity, viscosity, and solidifying temperature; therefore, the index of slab surface defect has markedly decreased and slab quality and yield have been improved.

As described above, the continuous casting of high grade stainless steels has been standardized as operational procedure by optimization of secondary cooling pattern and molten powder property.

3.2.3 Hot rolling techniques

The hot rolling of high grade stainless steels has the following problems to be solved:

- (1) Deformation resistance is large and hot workability is poor.
 - (2) Edge and surface cracking occur during hot rolling.
- Cracking occurs because of the strong stresses gen-

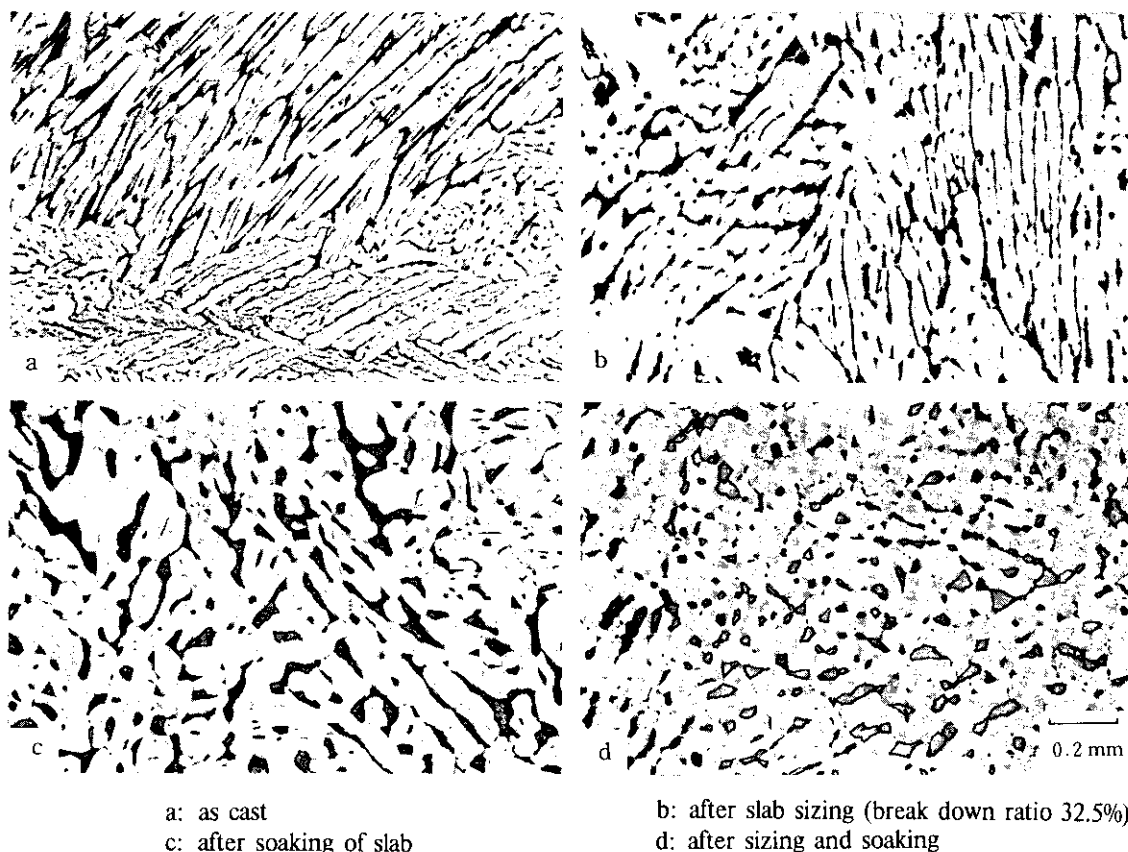


Photo 1 Microstructure of stainless steel containing δ -ferrite phase

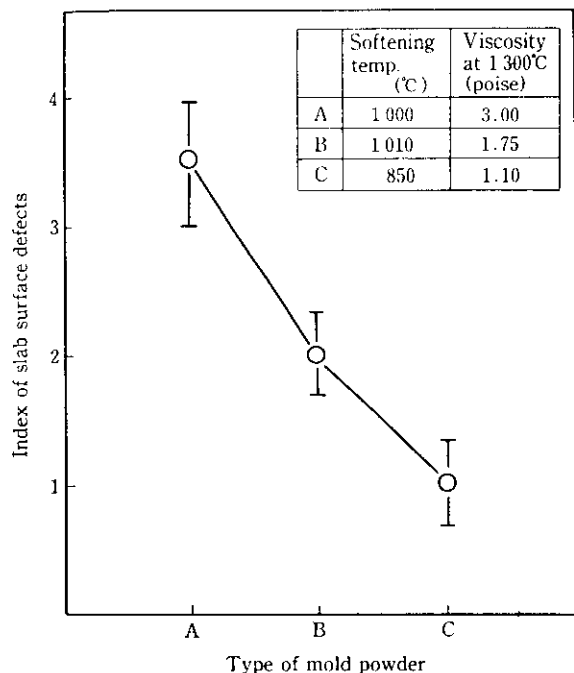


Fig. 9 Effect of mold powder on the occurrence of slab surface defects

erated in the interfaces between austenite and δ -ferrite phases of which deformation resistances are different. When a grain boundary cannot bear the stress acting on it, micro-cracks occur in the boundary and coalesce into large cracks.

In order to avoid cracking, microstructures have been improved by slab sizing or the combination of slab sizing and soaking. **Photo 1** shows microstructures of a stainless steel containing δ -ferrite phases. As-cast slab has elongated δ -ferrite phases still after reheating. However, the microstructures after slab sizing or soaking show partially broken down δ -ferrite phases, but still there are some in elongated form. The grainy δ -ferrite structure is uniformly dispersed, only by applying both slab soaking and sizing.

The improved hot workability becomes evident simply by microstructure investigation. In addition, Greable test has been performed in each hot working temperature range. The results are shown in **Fig. 10**. It is known empirically that cracking hardly occurs when reduction of diameter is larger than 23%. This condition is satisfied merely by the materials to which slab soaking is applied after slab sizing pretreatment at elevated temperatures.

Thus, by means of shape control of δ -ferrite phase, the crack generation and propagation can be reduced. Accordingly, hot workability is improved and the cracking during hot rolling can be avoided.

This procedure is more effective in the materials that contain δ -ferrite in higher ratios; however, it can be

◇	As cast	→ 1 250°C × 1.5 h
◆	Soaking	→ "
○	Slab sizing	→ "
●	Slab sizing and soaking	→ "

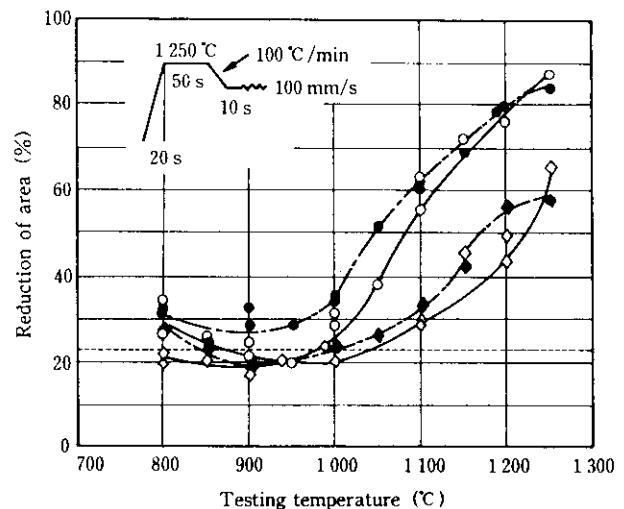


Fig. 10 Effect of slab sizing and slab soaking on the hot ductility of stainless steel containing δ -ferrite phase

applied to the hot rolling of various steels shown in Table 2, by selecting one or more of the following processes as necessary.

- (1) Hot rolling of as-cast slab
- (2) Hot rolling after pretreatment such as slab sizing
- (3) Hot rolling after slab soaking
- (4) Hot rolling after slab sizing and soaking

It has become possible to make sound hot coils, with increased product yield and quality. At the same time, the roll chance has been freed from restrictions caused by crack occurrences, contributing greatly to higher productivity.

4 Conclusions

Description has been made of some techniques developed in Kawasaki Steel to make high grade stainless steels such as high purity ferritic stainless steels and duplex structure stainless steels. To realize stable production of high grade stainless steels, investigation is made on fundamental high temperature properties, and the refining techniques have been developed for high purity steels. Also, the secondary cooling conditions have been improved for continuous casting, with new methods adopted in heat treatment and slab sizing. These techniques are applied to commercial grade stainless steels of Kawasaki Steel and greatly contribute to

their quality improvement. These techniques are believed to be effective in making other types of high alloy steels than stainless steels in the future.

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