Inclusions (in metal) control technology

Creation of High-Reliability Products Using Technology for Controlling Inclusions in Metals

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Abstract

The term "inclusions" refers to substances that are generated or mixed into metals during metal manufacturing processes, and their control is an essential factor in determining the material's properties. Inclusion control technology can be broadly categorized into three types: technology for thoroughly removing inclusions to enhance metal purity, technology for controlling inclusions to render their properties harmless, and technology for controlling the morphology and dispersion of inclusions for utilization. These technologies contribute to ensuring material stability and productivity in manufacturing processes and promote the utilization of by- products by applying them to mineral phase control of the by-products in metal manufacturing processes, thereby contributing to the advancement of by-product resource utilization and the establishment of a green society. This paper provides an overview of the history of the development and future prospects of these technologies, focusing on product lines representative of Kobe Steel.

Introduction

Kobe Steel got its start in the materials business, beginning with the production of large steel ingots for vessels in 1905. Production operations for steel wire rod and bar were launched in 1920. Today, the company continues to lead the charge in fields requiring high reliability, such as with solid type and built-up type crankshafts as well as valve spring steels for automobile engines. Technology to control inclusions in steel supports the quality of these products.

Inclusions are non-metallic compounds such as oxides, sulfides, and nitrides in steel. Inclusions in steel can cause problems such as impact fracture in low-temperature environments, fatigue failure from cyclic stress, and wire breakage in wire rod drawing and stranding processes.

Inclusions have a wide range of origins, including reoxidation of molten steel, entrainment of refractory materials, slag entrainment during refining, and deoxidation products (oxides formed in low-carbon steel when deoxidizing elements are added after decarburization blowing). The generation and entrainment of deoxidation products are inevitable. As such, our primary objective is not to eliminate them, but rather to reduce their size and render them harmless. However, inclusions do not always have a negative effect on the properties of materials. In fact, inclusions can be used purposefully to improve properties, such as by using them to control the structure of the steel or improve machinability.

Therefore, control of inclusions is a key factor governing a material's specifications. Inclusion control has two main requirements. The first is to remove harmful inclusions as much as possible to achieve high cleanliness; the second is to control the composition and size of inclusions that serve a purpose or that are harmless to the desired parameters and retain them in the material. Inclusion control technology is indispensable for safeguarding material quality as well as productivity in manufacturing and contributes to Kobe Steel's materiality of ensuring safety and security in community development and manufacturing. This paper outlines the history and future prospects of inclusion control technology in terms of its development and application to Kobe Steel's leading product lines.

1. Technology for high cleanliness levels in steel materials: Cast and forged steel, bearing steel

Kobe Steel's cast and forged steel products have a longer history than any other product category within the company's materials business. In 1914, the company manufactured a large crankshaft using a 1200-ton press, the largest in Japan at the time, and aggressively pursued the industrialization of a field that had long been a necessity. Today, the company produces large products indispensable for ships, such as solid type and built-up type crankshafts, by drawing on its extensive experience and technological expertise.

The manufacturing process for steel casting and forging involves melting raw materials such as pig iron and scrap, casting them as part of molten steel processing, and then forming the product using a high-temperature press. The formation of coarse inclusions, which substantially reduce the fatigue limit of the product, must be inhibited during refining. Creating steel ingots with a high cleanliness level requires the elimination of sulfur and oxygen as inclusion sources.

This is why Kobe Steel's Takasago Works began using an out-of-furnace refining method in 1993. This method enabled the production of super-clean steel via stirring conditions that accelerate reactions with slag and promote the surfacing and detachment of oxide inclusions.[1)]

A method to inspect inclusions in products is also a necessity for quality assurance. Kobe Steel has developed a unique automated ultrasonic inspection system for solid type crankshafts that guarantees quality and reduces labor requirements. "Advanced Measurement Technology Supporting KOBELCO's Manufacturing" on pages 66-69 of this issue contains pertinent details.

Bearing steel constitutes another example of a material for which inclusion control supports a high level of cleanliness. Bearing steel is an essential material for industrial machinery. It requires a high level of cleanliness to ensure rolling-contact fatigue life. Al_2O_3-based inclusions constitute a primary example of non-metallic inclusions that reduce rolling-contact fatigue life, although CaO-containing inclusions are also problematic. Kobe Steel conducted tracer testing and kinetic analysis on operating machines to determine at what point in the process these inclusions form or become entrained. These studies revealed that slag entrainment is the origin of the formation of CaO-containing inclusions. A further finding was that the number of inclusions could be reduced to about one fourth by applying countermeasures to prevent entrainment and promote the surfacing of inclusions.[2)]

The oxygen concentration in super-clean steel is as low as a few ppm, necessitating an evaluation method capable of accurately determining the amount and size of trace inclusions. Chemical extraction and separation of a large sample via acid decomposition is suitable for this. However, it is problematic that CaO-containing inclusions are chemically unstable in acid. The KOBELCO Group focused its research on the slime method, in which steel is dissolved in ferrous chloride to extract inclusions. We subsequently developed a method for extracting and analyzing CaO-containing inclusions from several kilograms of steel by optimizing the treatment solution temperature and pH.[3)]

Additionally, we used computational fluid dynamics to study behavior related to surfacing and separating inclusions in molten steel. Inclusions that flow into the mold of continuous casting machines for steel production must be removed so they don't become trapped in the steel ingot during solidification. For this purpose, we researched submerged entry nozzle shape theory and the conditions necessary to use electromagnetic stirring equipment. Molten steel flow simulation visualizes the effects of these conditions to predict the motion and behavior of inclusions in a continuous casting machine.[4)]

Furthermore, inclusions can be isolated by exploiting the changes in buoyancy caused by agglomeration and coalescence. To reproduce this behavior, we developed a turbulent agglomeration model for inclusions, accounting for their surface properties (wettability), as well as a technique to couple this model with molten steel flow models. This technique is being used to study agglomeration and separation behavior in continuous casting machine tundishes (**Fig. 1**).[5)] As shown in the

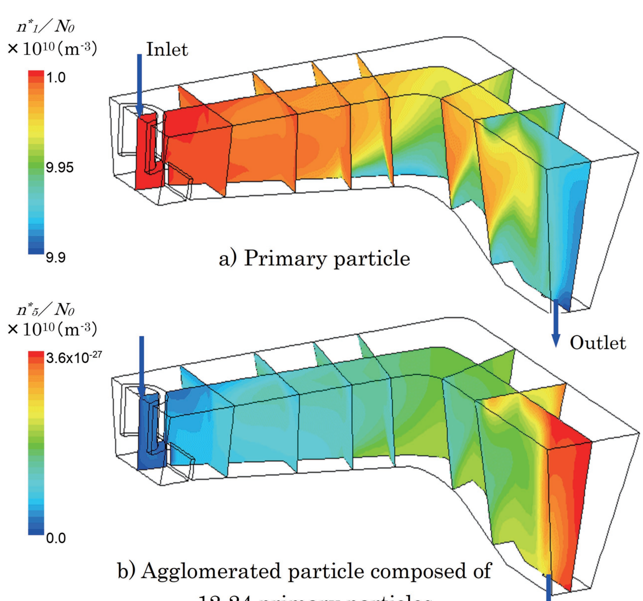

Fig. 1 Distribution of number of inclusions in 3CC tundish (normalized by initial concentration)

figure, the number of individual particles decreases (Fig. 1(a)) and the number of agglomerated particles increases (Fig. 1(b)) as agglomeration progresses throughout downstream flow.

Technology to ensure a high level of cleanliness by controlling inclusions, as described in this section, is indispensable in bringing out the original properties of steel. The shipbuilding and energy sectors are industries with such a need. In response to intensifying resource-related challenges, such as carbon neutrality, there is a growing need to improve transportation efficiency by increasing the size of ships. The cast and forged steel products widely used throughout these sectors must therefore meet specific requirements. It is evident that there is increasing demand for evaluation and inspection techniques that can optimize the characteristics of steel through inclusion control. These characteristics must be present alongside lightweight solutions and a guaranteed fatigue limit and crashworthiness. Through continuous improvement of the related technologies, we are contributing to the safety and security of society.

2. Technology to reduce the size of inclusions and render them harmless: Wire rods

Wire rod products are widely used in components that must be highly reliable in terms of fatigue limit and sag resistance. Example products include steel cord for tire reinforcement as well as valve springs that support the intake and exhaust actions of engines. Valve spring steel (**Fig. 2**), a market segment in which Kobe Steel boasts a large share, must maintain favorable fatigue properties under cyclical loads of several thousand cycles/minute. The inherent strength of a material has conventionally governed the properties of the end product. However, the problem of fracture caused by inclusions surfaced upon development of 1900-MPa-class Si-Cr oil-tempered steel wire, which became a JIS standard in 1970.[6)]

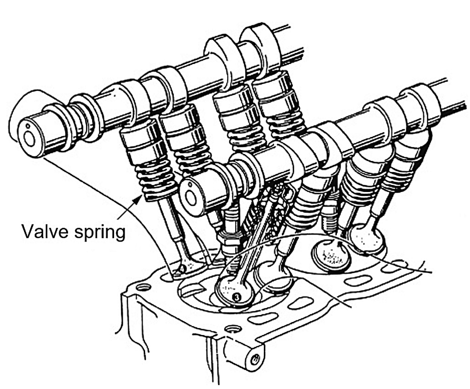

Fig. 2 Valve springs built into automobile engine

High-carbon steel wire rods containing about 0.5% to 0.8% carbon are used for valve spring steel and steel cord to ensure strength. When manufacturing these wire rods, deoxidizing elements such as Ca, Al, Mn, and Si are added to reduce the amount of dissolved oxygen in the steel. However, the oxide-based inclusions resulting from this process can become coarse inclusions that are potential fracture initiation points if allowed to remain in the product. Since Oxide inclusions, an inevitable result of deoxidizing treatment, are difficult to remove, countermeasures are taken to elongate and minimize the size of the inclusions during manufacturing so they do not become fracture initiation points, thus rendering their effects on wire rod products harmless.

The ease of minimizing size by elongation depends on the type of inclusion. Hard inclusions such as Al_2O_3 are particularly difficult to reduce the size of. This is why silicon is added as a deoxidizing element in valve springs, which require high strength. Furthermore, a technique is applied in which the inclusions are transitioned to a low-melting-point (Ca, Mn, Mg) O-SiO_2-Al_2O_3 system via reaction with slag of the CaO-SiO_2-Al_2O_3 system. This results in inclusions with physical properties that support a reduction in size.

Al_2O_3 formation caused by the reaction between the slag and the dissolved Al in the molten steel must be prevented because it is difficult to reduce the size of inclusions with Al_2O_3. An analysis technique to determine the Al concentration in molten steel is necessary to study this reaction thermodynamically. However, the problem with the analysis method of using acid dissolution followed by ICP optical emission spectroscopy is that some Al_2O_3 in the inclusions is also dissolved and contributes to the Al concentration measured.

Hence, Kobe Steel uses secondary ion mass spectrometry (SIMS)[7)] to analyze the mass of secondary ions emitted in response to ion irradiation of the sample surface. This reveals the concentration of dissolved Al in trace amounts, on the order of ppm, making it possible to investigate the conditions that support Al_2O_3 inclusion formation in detail for steel composition design.[8)]

We have also used SIMS with other elements for kinetic analysis of reactions between dissolved Ca and inclusions. These studies revealed that the inclusions in steel cord have a high CaO content primarily because of their coalescence with entrained slag, rather than because of the reaction between dissolved Ca and inclusions. Based on this, molten steel stirring was optimized to foster slag

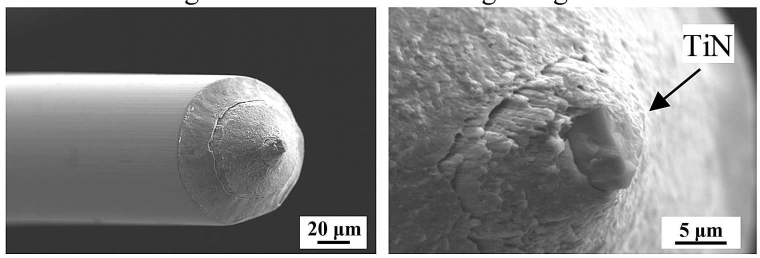

Fig. 3 Fracture surface of ultrafine wire originating from TiN

entrainment.[9), 10)]

Notably, high-carbon steel wire rods are decreasing in diameter as their applications expand. Wire for cutting silicon ingots, which requires ultrafine wires of 50-130 μm, is one such example. Fracture is conventionally caused by nonmetallic inclusions such as Al_2O_3 of about 30-50 μm. However, it has been validated that with the trend toward thinner wires, fine TiN inclusions of 5-20 μm can also cause fracture (**Fig. 3**).

TiN is used for microstructure refinement in the welding and plate sectors, as is described in the next section. Information regarding controlling TiN formation revealed by this development has also been used to suppress TiN formation in ultrafine high-carbon steel wire rods.[11)] Thermodynamics research that also accounts for solidification phenomena led to the hypothesis that the formation of TiN is caused by the concentration of Ti solute by macrosegregation. SIMS, as described above, is being used to analyze dissolved Ti concentrations on the order of ppm to ppb to support this hypothesis. Our unique extraction technology for TiN extraction and separation combines the acid dissolution method and atmospheric treatment. This technology is founded on expertise cultivated through the chemical extraction and separation technology we have developed over many years. Thus, our inclusion control and evaluation technologies refined through the development of various products have been passed along continuously, leading to new products.

3. Inclusion utilization technology: Steel plate, welding consumables, free-cutting steel

Kobe Steel began operating a steel plate mill at its Kakogawa Works in 1986, supplying a wide range of high-function steel plates to industries such as shipbuilding, architecture, bridge construction, energy, and industrial machinery. Steel plates are generally welded into structures on site. Steel plates that can handle welding with high heat input are necessary to reduce construction time and cost.

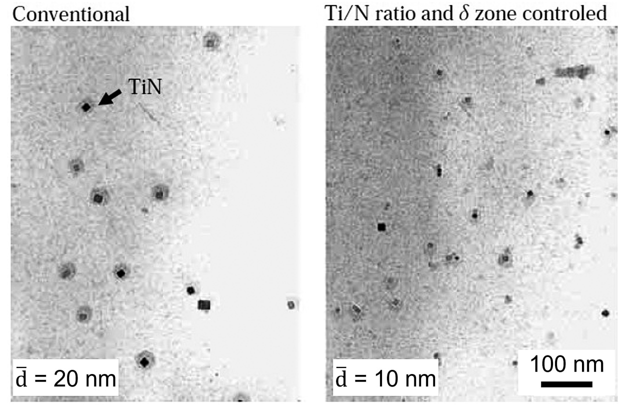

Fig. 4 Influences of Ti/N ratio and alloying elements on dispersion of TiN particles

Kobe Steel has developed a method to combat the reduced toughness caused by heat-input-induced microstructural changes in the heat-affected zone (HAZ) of welds. Specifically, we manufacture steel plates using the KST (Kobe Super Toughness) technique to improve toughness through the purposeful use of TiN, which is a precipitate (inclusion). Titanium and nitrogen ratios in the steel are optimized to enable fine dispersion of TiN in the steel and to suppress austenite grain coarsening, a primary cause of reduced toughness. In addition, by designing alloy compositions that narrow the δ ferrite temperature range, which inhibits the fine dispersion of TiN in high-heat-input welds exceeding 50 kJ/mm, Kobe Steel has developed a plate with a reduced average TiN grain diameter $\bar{d}$ and fine dispersion even when subjected to high-heat-input welding, as shown in **Fig. 4**.[12)]

Kobe Steel also develops and manufactures welding wire. FCW (flux-cored wire) with titania (TiO_2) is widely used in shipbuilding and bridge construction because of its favorable all-position welding workability. However, in general, titania-based FCW is more susceptible to high-temperature cracking than solid wire and is prone to cracking during solidification. A reported method to suppress this solidification cracking involves transitioning the solidification morphology from columnar crystals to equiaxed crystals by using TiN inclusions as nuclei for heterogeneous nucleation, as described for steel plates.

However, increasing the nitrogen concentration to generate TiN increases susceptibility to pore defects caused by nitrogen gas. As such, we investigated techniques involving oxide inclusions outside of TiN. Results clearly indicated that TiO_2 could be used for solidification structure control to reduce solidification cracking susceptibility, which was reflected in product design.[13)]

Another example of the purposeful use of inclusions is seen with free-cutting steel. The steel used for hydraulic parts and similar applications, known as free-cutting steel, must exhibit good machinability in support of high-precision cutting. Although adding lead improves machinability, this element carries a high environmental burden. This led us to design a material based on the concept of promoting and dispersing large, spherical MnS particles in the steel. These particles become sites for generating microcracks that improve machinability, hence constituting a free-cutting steel that is lead free.[14)]

Much like the aforementioned steel properties achieved through the use of inclusions, it is quite possible that yet-unknown inclusions will support future needs for improvements in material properties. The inclusions control technology described can lead to new products by quickly revealing the utility of such inclusions and can support application-based morphological control.

4. Future prospects for inclusions control technology

The mid-to long-term challenge for the steel industry is to develop melting, refining, and casting processes that can use large amounts of directly reduced iron and steel scrap. Because these are low-CO_2 iron sources, they support resource recycling and a carbon-neutral society. Since the inclusions in steel are based on the raw materials and processes used, control technologies are needed to suppress the effects of inclusions in response to changes in conditions.

In terms of evaluation technology, for example, a wider range of raw materials could be used upon development of technology to quickly detect tramp elements such as Cu and Sn, which are present in scrap and are difficult to remove by refining.

Inclusion control technology is responsible for retaining compounds of the target composition and size in steel. Applying this technology to slag, a steelmaking byproduct, enables its extension to mineral phase control technology for slag recycling. One example application in the area of steelmaking slag lies in controlling expansion in roadbed materials. Identifying the mineral phase that causes expansion enables the design of slag that supports resource recycling.[15)] Kobe Steel is also working on developments in CCUS. This technology uses the Ca in the slag to fix CO_2 as $CaCO_3$, thereby reducing CO_2 and recycling the Ca.[16)] In the extraction step of this process, mineral phase control technology supports the production of slag from which Ca can easily be extracted. Hence, inclusion control technology promotes the recycling of by-products and can preserve steel quality under conditions that support carbon neutrality. This technology improves material reliability while addressing Kobe Steel's materiality of contributing to a green society.

While this paper has outlined inclusion control technology for steel products, this technology is significant within the KOBELCO Group in regard to the wide variety of other materials in which the company has expertise, including aluminum, copper, titanium, and magnesium. In summary, inclusion control technology serves as part of the foundation for promoting by-product recycling while safeguarding material quality and responding to resource and environmental issues. The KOBELCO Group leverages its synergies surrounding this technology to create diverse material products that live up to current needs and help build a green society.

Conclusions

The field of materials continually encounters problems with the increasing need for higher functionality, such as the TiN-induced fracture of wire rods described in Section 2. Kobe Steel's inclusion control technology has continuously evolved over many years of development. Identifying the origins of inclusions whenever new challenges have emerged and enabling the evaluation of new inclusions are cornerstones of this technological evolution. As a result, Kobe Steel has amassed an important group of technologies that support its one-of-a-kind products.

The future holds major change in the properties required of materials in line with societal change, such as carbon neutrality and issues related to resources. KOBELCO will continue contributing to societal development by introducing new and unique materials grounded in the inclusion control technology described in this paper.

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