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Development of Superior Resistant Materials by HIP Process and Their Applications

Masatoshi Ayagaki*1 Singo Izumi*1
Tadami Ohishi*1 Taku Tanaka*1

Abstract:

In many cases, technological innovation is based on the progress of material technology. High-performance materials continue to be in demand in many industrial fields. In the iron and steel industry, improving the quality of construction materials for iron and steelmaking facilities is important in enhancing cost and quality competitiveness. Nippon Steel's Plant & Machinery Division has used the hot isostatic pressing (HIP) process to impart properties not obtainable from conventional ingot metallurgy and has developed super alloys based on chromium, nickel, and cobalt, and high speed tool steel alloys, as well as cermets as advanced materials with superior heat, corrosion, and wear resistance. The development of such superior resistance materials and their applications as materials for constructing iron and steelmaking equipment are introduced.

1. Introduction

HIP is a material processing technology in which high isostatic pressure is applied to a powder part or compact at elevated temperatures to produce diffusion bonding. The HIP process was invented by Saller et al. at the Battelle Memorial Institute of the United States in 1955, and was initially used for diffusion bonding of clad nuclear fuel elements[1]. Consolidation of beryllium metal powder into a shape was first carried out in 1964. HIP was then applied to high-speed tool steel, superalloy and titanium alloy powders, mainly in the United States and Europe, and these applications were later expanded to include cermets and ceramics. In Japan, installation of HIP units mainly for research on various new materials significantly increased during the "new materials boom" of the 1980s. The Plant & Machinery Division installed a superhigh-temperature, superhigh-pressure and large-sized HIP unit in 1987 and used it to develop various materials extremely resistant to heat, corrosion and wear and related products. These materials and products were successfully used in iron and steelmaking equipment components. This report describes the functions and characteristics of the HIP process and introduces the development and application of superior resistant materials created with the HIP process for iron and steelmaking equipment components.

*1 Plant & Machinery Division

2. Functions of HIP Process and Characteristics of HIP Facilities

2.1 Functions of HIP process

The functions of the HIP process include: (1) pressure sintering of powder materials; (2) removal of internal defects in sintered parts and castings; (3) production of composite structures by diffusion bonding; and (4) repair of fatigue creep-damaged parts, as shown in **Fig. 1**. HIP has gained prominence as an important process for improving the quality, reliability, and durability of metals and ceramics.

If the material has a density of over 95%, such as a casting or

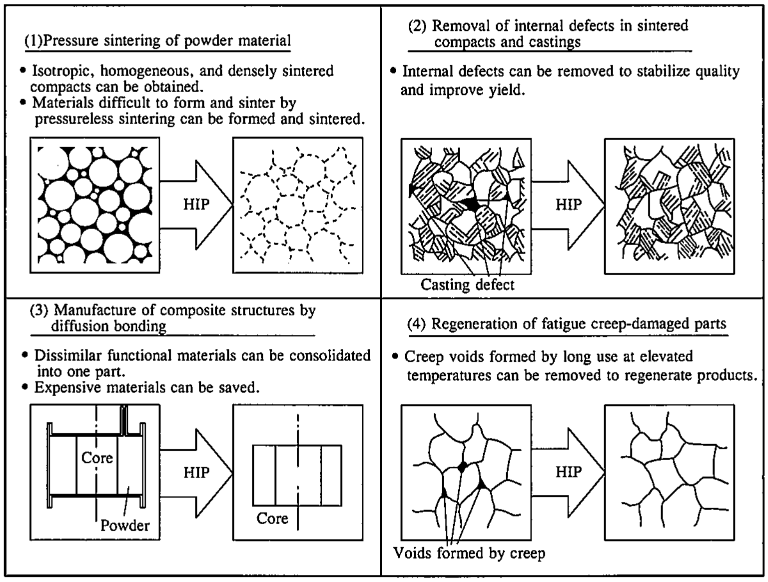


Fig. 1 Functions of HIP process

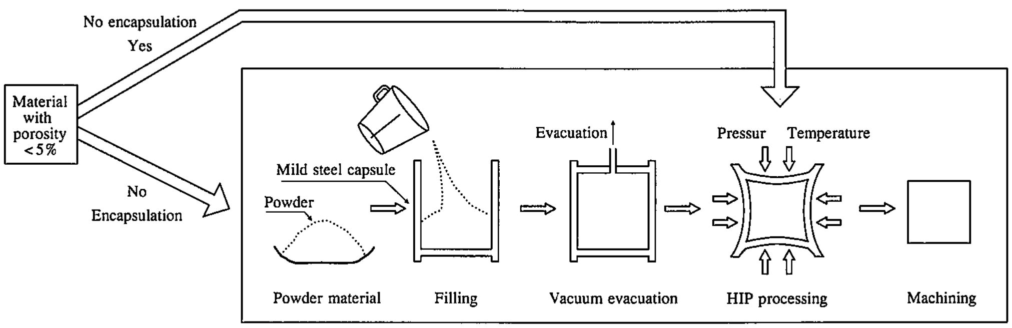


Fig. 2 HIP process

sintered compact, it is directly processed in the furnace of the HIP unit, and if the material is lower in density like a powder, it is encapsulated before the HIP operation as shown in **Fig. 2**. Based on Ashby's theory techniques were developed for setting the HIP temperature, pressure, time and other parameters and for predicting the deformation of materials exposed to the HIP process[2,3]. The optimum HIP conditions can be thus selected by considering material properties, shape, and size.

2.2 Characteristics of HIP facility

A large-scale HIP facility that was built in-house and installed for the Plant & Machinery Division is schematically depicted in **Fig. 3**. The HIP facility consists of a pressure vessel, a high-pressure gas compressor, furnace structural parts including a heater, a heating power supply, controls, a cooler, and safety devices, among other things. The HIP unit proper has a pressure vessel to seal in the high-pressure gas and an electric furnace to heat the workpieces. The maximum HIP vessel size is 480 mm in diameter and 1,500 mm long. The maximum HIP temperature and pressure are 2,000°C and 200 MPa, respectively. This is one of the largest superhigh-temperature and superhigh-pressure HIP units in Japan. HIP equipment is used to develop superior resistance materials and related products and for consignment HIP processing of chiefly ceramic parts from outside the company.

3. Development and Application of Superior Resistance Materials

The ability of the HIP process to create superior resistance materials that cannot be produced by ingot metallurgy is mainly due to the utilization of powders. The reasons involved are:

(1) Materials with a high melting point that cannot be manufactured by ingot metallurgy can be produced.

(2) High-alloy materials whose potential performance cannot be put to full use due to segregation and grain coarsening in ingot metallurgy can be improved in performance by homogenization and grain refinement.

(3) Various advanced properties can be obtained from the combination of metallic materials with different materials such as ceramic particles.

The Plant & Machinery Division has developed heat-resistant, corrosion-resistant and wear-resistant materials by utilizing the basic principles listed above. It has also applied them to the construction of iron and steelmaking equipment, and verified their cost effectiveness. Typical examples are introduced below.

3.1 Development and application of heat-resistant materials

Heat-resistant materials are required to have: (1) elevated-temperature creep resistance; (2) oxidation resistance; and (3) thermal stability, among other properties. Conventional ingot metallurgy adjusts material properties by alloy design as well as by solution and precipitation control and by grain size control in the manufacturing process. High-melting point materials are difficult to melt, and conventional ingot metallurgy is limited for manufacturing heat-resistant materials due to such factors as thermal instability resulting from microstructural change at elevated temperatures. A chromium-based heat-resistant alloy with dramatically improved properties was developed by utilizing the HIP process.

3.1.1 Chromium-based heat-resistant alloy

(1) Development

Although chromium has potential as a heat-resistant material, it is difficult to form with ingot metallurgy because of its high melting point of more than 1,800°C. Furthermore, owing to its low level of toughness at room temperatures, it has few applications as a machine structural material[4]. The Plant & Machinery Division developed chromium-based alloy manufacturing technology by using chromium powder and HIP sintering technology, enabling the application of chromium-based alloys. Chromium-based sintered alloys use chromium, a metal with a high melting point and basic heat-resistant properties such as oxidation resistance as the base material. They have excellent creep resistance and mechanical properties because of a grain size of more than 300 μm achieved through recrystallization structure control and by possessing a transgranular dispersion of fine oxide particles as shown in **Fig. 4**. A new chromium-based alloy was developed and designated PR. As shown in **Table 1**, compared with cobalt-based ingot metallurgy heat-resitant alloy, the alloy has more than three times the compressive creep resistance and over twice the oxidation resistance.

(2) Application

(i) Hot strip mill reheating furnace skid riders

As shown in **Photo 1**, when used in hot strip mill reheating

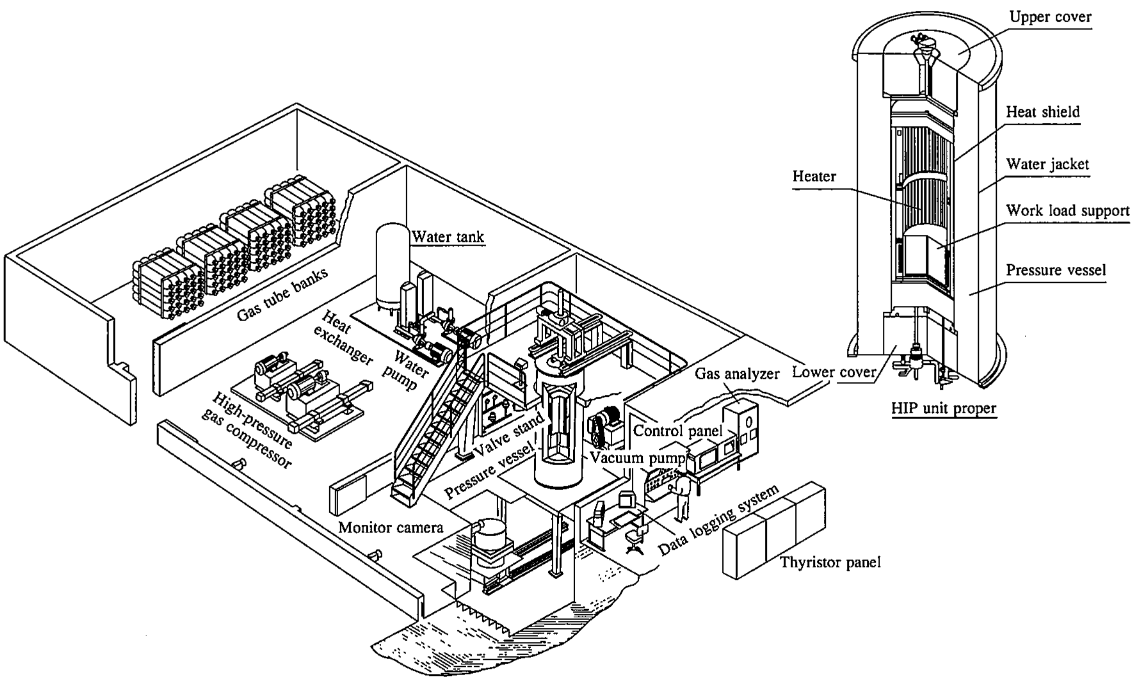


Fig. 3 HIP facility

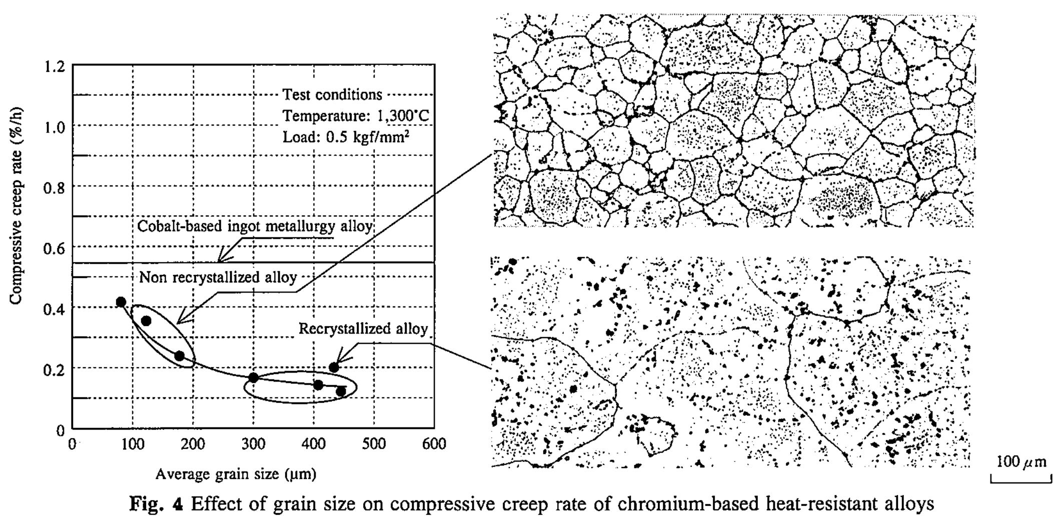
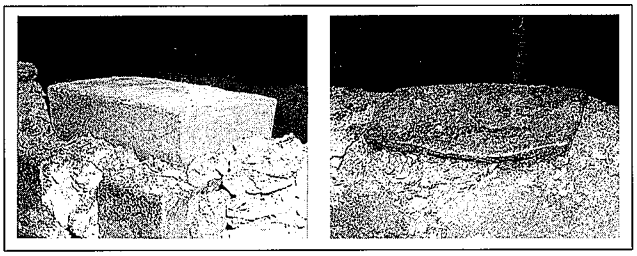


Fig. 4 Effect of grain size on compressive creep rate of chromium-based heat-resistant alloys

Table 1 Properties of new chromium-based heat-resistant alloy PR

Evaluation item			Creep resistance 1300℃ 0.5kgf/mm²	Oxidation resistance 1300℃ ×100h	Melting point
Material	Process	Basic composition	%/h	g/m²h	℃
PR	HIP	Cr-trace elements	0.37	0.15	>1700
Cobalt-based	Ingot metallurgy	40Co-Cr-Ni-Fe	1.11	0.33	1380



Chromium-based HIP alloy PR Cobalt-based ingot metallurgy alloy

Photo 1 Hot strip mill reheating furnace skid riders after six months of use

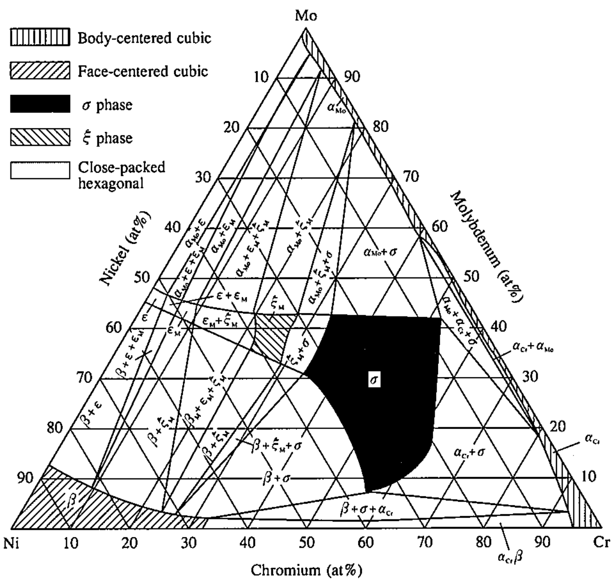


Fig. 5 Phase diagram of ternary Ni-Cr-Mo system at 600°C

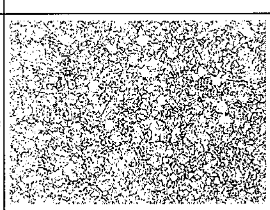
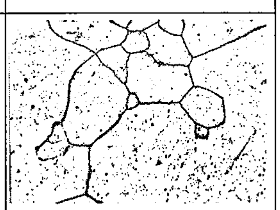
Material	PN-625	Ingot metallurgy alloy
Hardness Hv	240	174
Corrosion resistance (relative ratio)	2.0	1
Wear resistance (relative ratio)	2.4	1
Microstructure	 100μm	 100μm

Photo 2 Microstructure of non precipitation-type nickel-based alloy PN-625

furnace skid riders, the chromium-based HIP heat-resistant alloy PR gained over three times the permanent set resistance than the conventional cobalt-based ingot metallurgy alloy. Riders made from the conventional cobalt-based ingot metallurgy alloy rapidly deform and wear, so that they are likely to develop skid marks. The new chromium-based HIP heat-resistant alloy is being applied increasingly to improve the condition of the hot strip mill reheating furnace skid riders.

3.2 Development and application of corrosion-resistant materials

Many superalloys, primarily based on nickel, are developed for production by ingot metallurgy as corrosion-resistant materials for various service environments. Cobalt-based ingot metallurgy alloys are also developed for use under some service conditions. There are many iron and steelmaking equipment parts that require both corrosion and wear resistance at the same time, such as electrogalvanizing line conductor rolls. This combination of corrosion and wear resistance was difficult to achieve with nickel-based ingot metallurgy alloys. Nickel-based alloys and a chromium carbide-cobalt-based alloy composite, each with dramatically improved corrosion and wear performance, were developed by utilizing the powder HIP process.

3.2.1 Nickel-based corrosion-resistant alloys

(1) Development

(i) Non precipitation-type nickel-based corrosion- and wear-resistant alloy

Most nickel-based corrosion-resistant alloys are compostionally designed to fall in the single-phase austenite region (face-centered cubic, β) in the phase diagram of the ternary Ni-Cr-Mo system[5] shown in **Fig. 5**. Ingot metallurgy nickel-based alloys are low in wear resistance because their hardness is Hv 200 or less. A non precipitation-type nickel-based corrosion- and wear-resistant alloy, designated PN-625, was developed with improved corrosion and wear resistance by using a rapidly solidified and atomized powder to produce the fine-grained microstructure as shown in **Photo 2**.

(ii) Precipitation-type nickel-based corrosion- and wear-resistant alloy

A new precipitation-type nickel-based corrosion- and wear-resistant alloy, designated PN-52X, was designed with the composition (β + ξ_M) to precipitate intermetallic compounds in the ternary phase diagram of **Fig. 5**. It also has greater hardness compared with the non precipitation type. As shown in **Photo 3**, this material also has many particles of fine intermetallic compounds precipitated by hot isostatically pressing and by sintering a rapidly solidified and atomized powder. Accordingly,

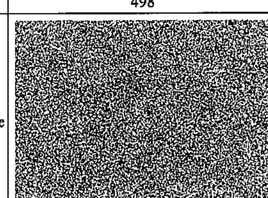
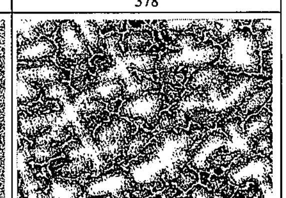
Material	PN-52X	Ingot metallurgy alloy
Hardness Hv	498	378
Microstructure	 100μm	 100μm

Photo 3 Microstructure of precipitation-type nickel-based alloy PN-52X

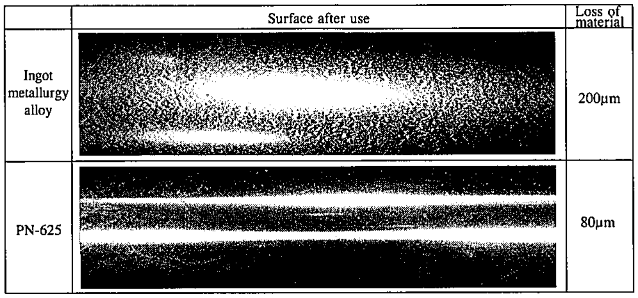


Photo 4 Conductor roll surface material loss after use

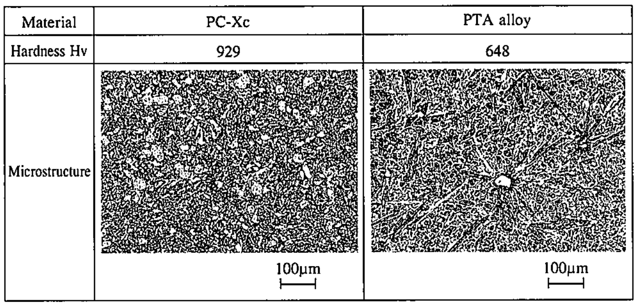


Photo 5 Microstructure of dispersed ceramic-cobalt-based alloy composite PC-Xc

a hardness much higher than that of ingot metallurgy alloys is achieved. The surface material loss of parts due to corrosion and wear are effectively prevented by applying the precipitation-type nickel-based alloy to parts whose surface material loss is governed by wear and the non precipitation-type nickel-based alloy to parts whose surface material loss is governed by corrosion.

(2) Application

(i) Continuous electrogalvanizing line conductor rolls

When electrogalvanizing line conductor rolls that must resist corrosion were made from the non precipitation-type nickel-based corrosion and wear-resistant alloy PN-625, they exhibited dramatically reduced electrolytic corrosion and wear-induced surface roughening compared with ingot metallurgy alloy conductor rolls as shown in **Photo 4**. The characteristics that enhance productivity and produce other benefits are shown in **Photo 4**.

3.2.2 Corrosion- and wear-resistant chromium carbide-cobalt-based alloy composite

(1) Development

As a material featuring higher wear resistance than that of a precipitation-type alloy, a chromium carbide-cobalt-based alloy composite, designated PC-Xc and having chromium carbide (Cr_3C_2) dispersed in the Co-Cr-W alloy matrix with excellent heat, corrosion, and wear resistance was developed. Compared with the conventionally transferred plasma arc (PTA) welded powder coating, PC-Xc is extremely hard as a result of finely dispersed hard carbide particles as shown in **Photo 5**. This is possibly due to the solid-phase sintering characteristic of the HIP process compared with the PTA process, which melts the powder material. **Fig. 6** shows the effect of the Cr_3C_2 content on hardness and strength of PC-Xc. The hardness of PC-Xc remarkably improves with increasing levels of Cr_3C_2. **Fig. 7** shows the elevated-temperature hardness of PC-Xc. It is evident that PC-Xc is a material with excellent wear resistance at elevated

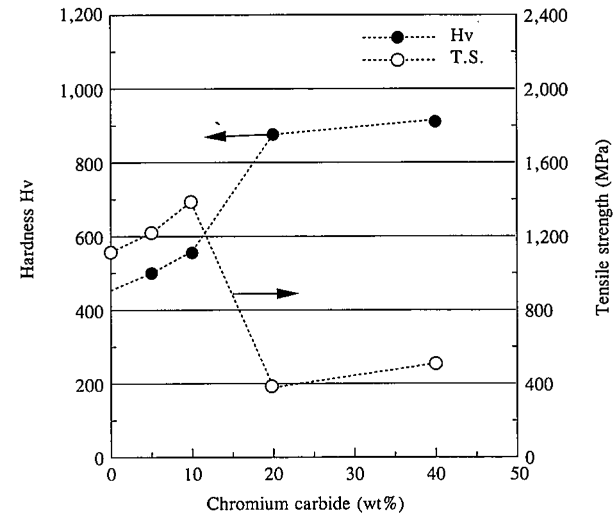


Fig. 6 Effect of chromium carbide content on hardness and strength

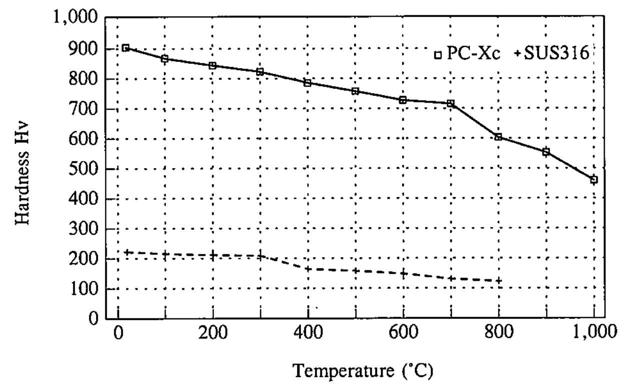


Fig. 7 Elevated-temperature hardness of dispersed ceramic-cobalt-based alloy composite PC-Xc

temperatures.

(2) Application

The chromium carbide-cobalt-based alloy composite PC-Xc considerably extended the service life of slide bearings and other parts used at elevated temperatures.

3.3 Development and application of wear-resistant materials

Wear-resistant parts require both wear resistance and strength reliability. The two contradicting properties must be satisfied at the same time. This requirement is met by microstructural control of hard carbides and matrix, mainly as quality, quantity, and grain refinement, by high alloying and rapid solidification or by combination with a higher-strength material through double-pour casting, buildup welding, or other suitable methods. Ingot metallurgy is limited in high alloying and microstructural grain refinement due to material defects, such as segregation, and delayed the drastic improvement of wear-resistant parts.

Cobalt-based and high-speed tool steel-based wear-resistant materials were developed by using a powder HIP process that can freely control material properties over a wide range. The production of a segregation-free microstructure with a high alloy content and combined with ceramics is one example.

The high-speed tool steel-based wear-resistant materials suddenly diminish in hardness at about 600°C because they have a martensite microstructure. The cobalt-based wear-resistant

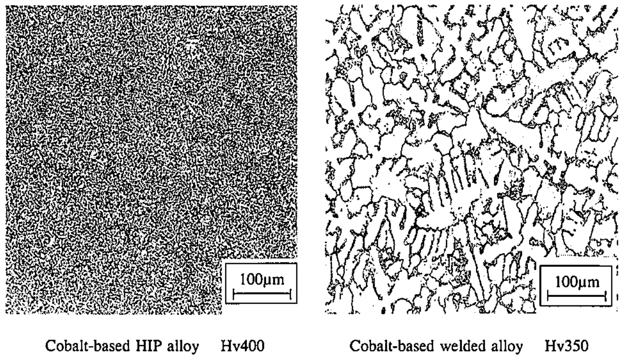


Photo 6 Microstructure of cobalt-based HIP alloy

Table 2 Cobalt-based wear-resistant alloys

Type	Composition	Hardness
PC-A	Low-C,Cr,W,Co	Hs 60
PC-T	Mid-C,Cr,W,Co	Hs 70
PC-F	High-C,Cr,W,Co	Hs 80

materials do not decrease in hardness as much and can be used at higher temperatures. The development and application of the two families of wear-resistant materials are introduced below.

3.3.1 Cobalt-based wear-resistant materials

(1) Development

Cobalt-based HIP materials with wear resistance imparted by dispersing chromium and tungsten carbides in a cobalt-based austenite matrix were developed. Stellite is available as a cobalt-based wear-resistant alloy. The powder HIP materials of the same composition are provided with a microstructure of higher hardness and finer grain size than those of welded Stellite as shown in **Photo 6** and can thus be increased in alloy content and section thickness. The new cobalt-based HIP wear-resistant materials are available in three types: PC-A, PC-T, and PC-F. By considering wear resistance and thermal shock resistance, each has different carbide contents as shown in **Table 2**. As shown in **Fig. 8**, they retain their hardness relatively well at elevated temperatures, and have been selected to meet specific thermal conditions. **Fig. 9** illustrates how these austenitic materials excel in powder wear resistance. In particular, PC-F has wear resistance comparable to that of ceramics and is ideal for wear-resistant parts that cannot be made from ceramics.

(2) Application

(i) Compound pipes for pneumatic transport of pulverized coal

Steel pipes lined with PC-F by the HIP process, or compound pipes, as shown in **Photo 7**, were used in a pneumatic pipeline transporting pulverized coal. The HIP process can line small-diameter pipes that are difficult to line by weld overlaying or thermal spraying. The HIP compound pipes stabilized pneumatic pipeline operations and reduced pneumatic pipeline maintenance costs.

(ii) Rolling mill guides

Rolling mill guides were made from PC-A, PC-F, or PC-T to

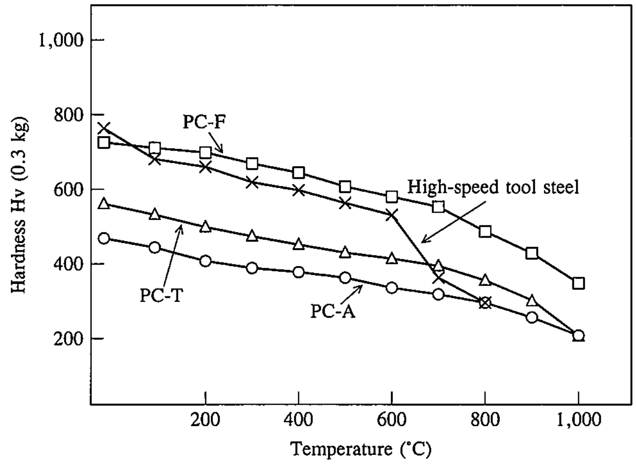


Fig. 8 Elevated-temperature hardness of wear-resistant materials

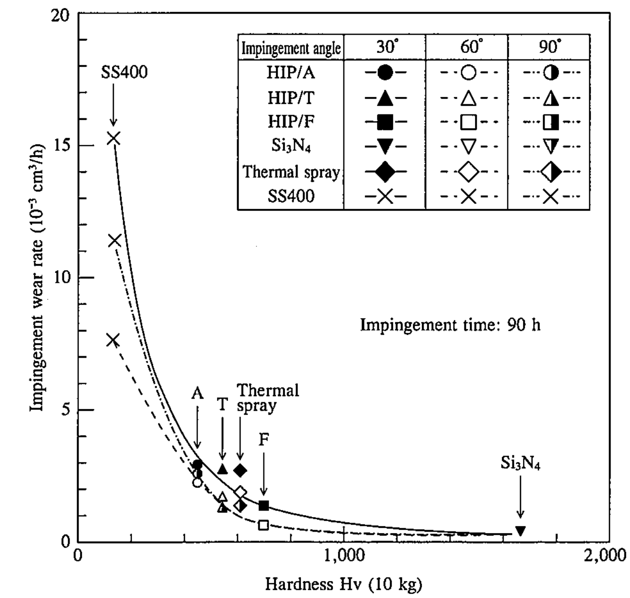


Fig. 9 Powder wear characteristics

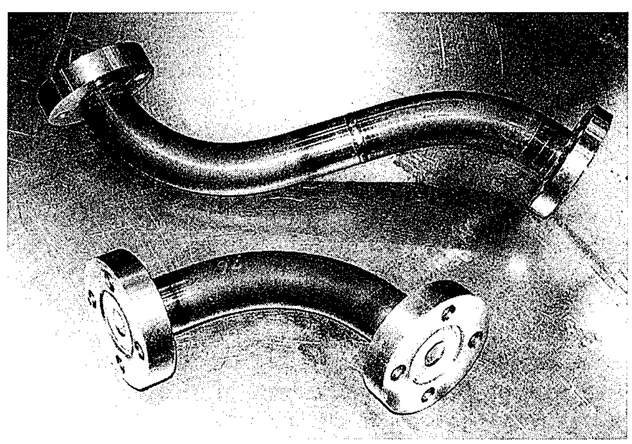


Photo 7 Compound pipes for pneumatic pipeline

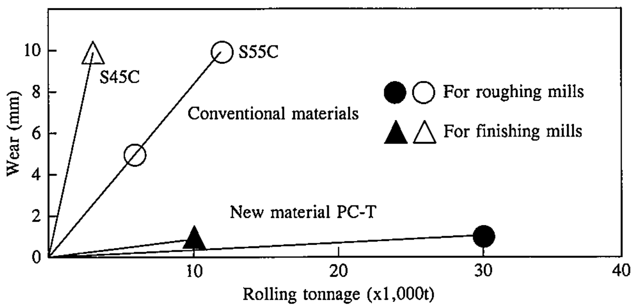


Fig. 10 Wear performance of rolling mill guides

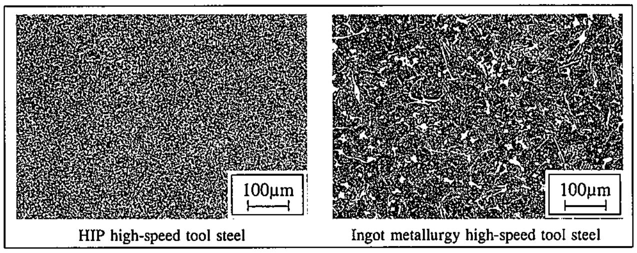


Photo 8 Microstructures of high-speed tool steel

Material	Tensile strength (MPa)	Charpy impact value (J/cm²)
Ni-Hard cast iron GH Hs 78	392	2.5
High-chrome cast iron Hs 80	784	2.5
Ingot metallurgy high-speed tool steel Hs 88	930	3.1
HIP high-speed tool steel PH-10 Hs 88	1,430	8.9
HIP high-speed tool steel PH-Xc Hs 92	840	3.9

Fig. 11 Mechanical properties of rolling mill roll materials

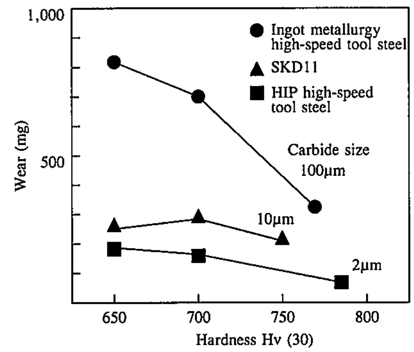


Fig. 12 Results of cold wear test

meet specific thermal conditions in order to capitalize on these material's excellent elevated-temperature wear resistance. The improvement in wear resistance dramatically prolonged service life of the rolling mill guides as indicated in **Fig. 10**. The guides are seizure free and can be used with minimum maintenance.

3.3.2 High-speed tool steel-based wear-resistant materials

(1) Development

High-speed tool steel is a typical wear-resistant material. When high-speed tool steel parts are made by ingot metallurgy, they have coarsened carbides and are likely to develop segregation. These conditions are not favorable for wear resistance and surface roughening resistance. The powder HIP process can not only improve these conditions, but also impart higher performance. As applications, a fine carbide-dispersed high-speed tool steel (PH-10) and a ceramic-high-speed tool steel (PH-Xc) were developed.

The properties of PH-10 and PH-Xc are described below.

(i) Mechanical properties

The microstructure of a new HIP high-speed tool steel part is compared with that of an ingot metallurgy high-speed tool steel part in **Photo 8**. The former part has fine carbides uniformly dispersed in the high-speed tool steel matrix. This fine-grained microstructure imparts excellent mechanical properties as shown in **Fig. 11**.

(ii) Cold wear resistance

The microstructural grain refinement by HIP has a great impact on wear resistance[6]. **Fig. 12** shows the cold wear test results of ingot metallurgy high-speed tool steel, forged high-speed tool steel SKD11, and the fine carbide-dispersed HIP high-speed tool steel PH-10 with the carbide size controlled to less than two μm. Wear resistance generally depends on hardness, but is more affected by microstructure than hardness. **Photo 9** shows the cross-sectional microstructures of wear test specimens. Large plastic flow is noted in the surface of the ingot metallurgy high-speed tool steel specimen and the forged SKD11 specimen. Coarse carbides unable to keep up with the plastic deformation shattered. These carbides initiate surface fissuring and spalling. The repetition of fissuring and spalling is presumed to accelerate the wear of the cast and forged high-speed tool steel parts. The fine carbide-dispersed HIP high-speed tool steel PH-10 has finely and spherically controlled carbides. Since these fine, spherical carbides keep up with the plastic deformation and are less susceptible to breakage, PH-10 is considered to exhibit excellent wear resistance.

(iii) Hot wear resistance

The hot wear test results of hot rolling mill roll materials are shown in **Fig. 13**. The fine carbide-dispersed HIP high-speed tool steel PH-10 does not differ from the ingot metallurgy high-speed tool steel in hot wear resistance unlike cold wear resistance, but the ceramic-dispersed HIP high-speed tool steel PH-Xc has sharply improved hot wear resistance.

(2) Application

(i) Steel pipe straightening machine rollers

When steel pipe straightening machine rollers that are used cold were made from the fine carbide-dispersed HIP high-speed tool steel PH-10, they lasted four times longer than conventional rollers of SKD11. They also contributed to the roller change interval being increased from one to four months. The performance of the straightening machine was also improved, leading to higher operability and lower running costs.

(ii) Hot rolling mill rolls

When wire rod mill intermediate stand rolls were made from the fine carbide-dispersed HIP high-speed tool steel PH-10, they far exceeded conventional chilled iron rolls in wear resistance and surface roughening resistance as shown in **Fig. 14** and **Photo 10**, but did not appreciably differ from high-speed tool steel rolls made by the CPC process. As a result, the development of new hot rolling mill roll materials with improved hot wear resistance

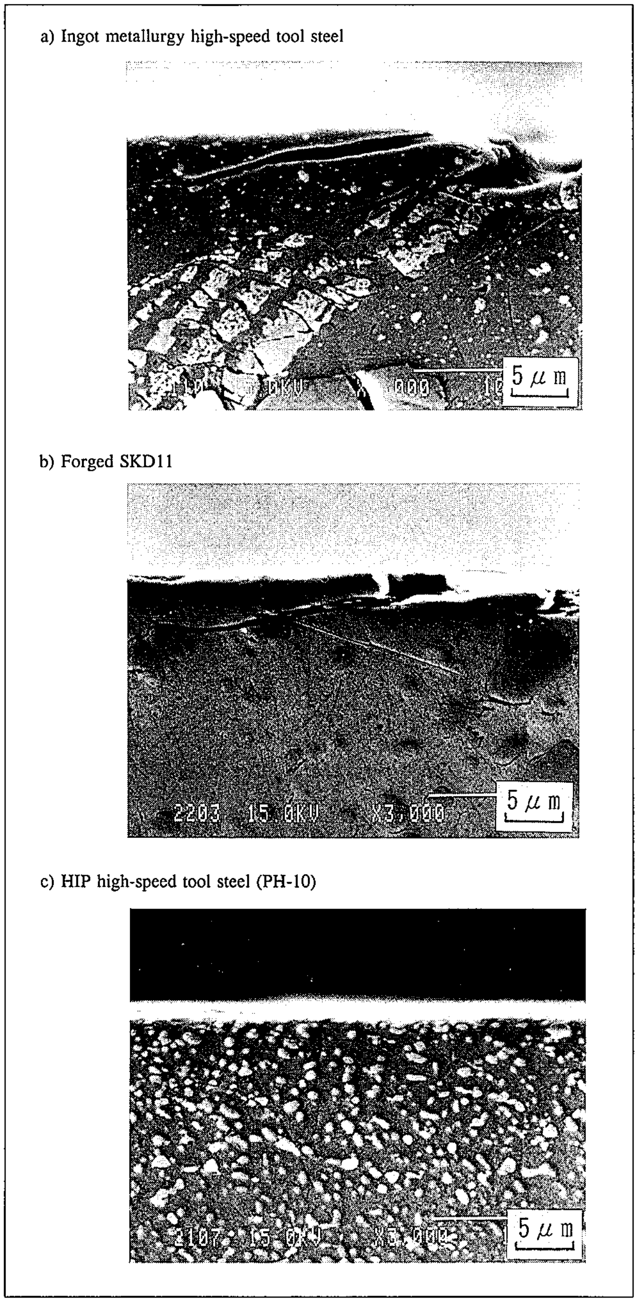


Photo 9 Cross-sectional microstructures of cold wear test specimens

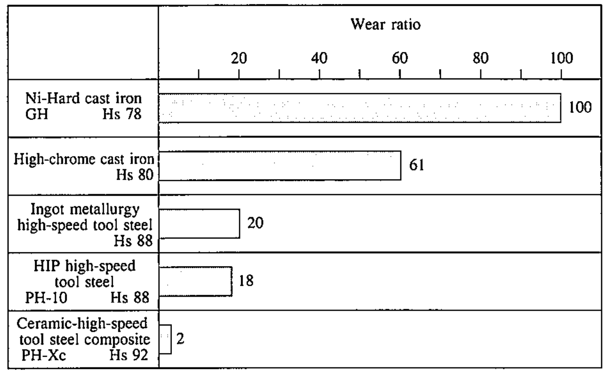


Fig. 13 Hot wear test results of hot rolling mill roll materials

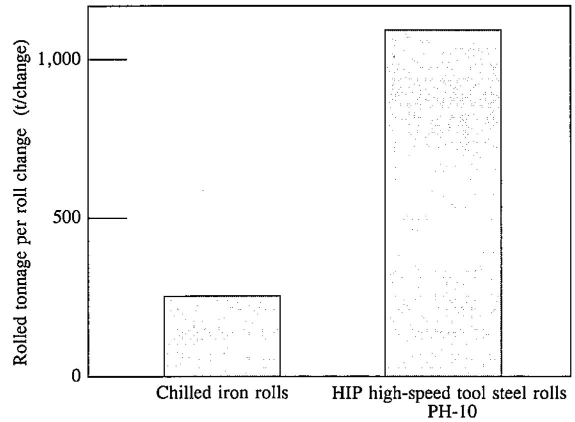
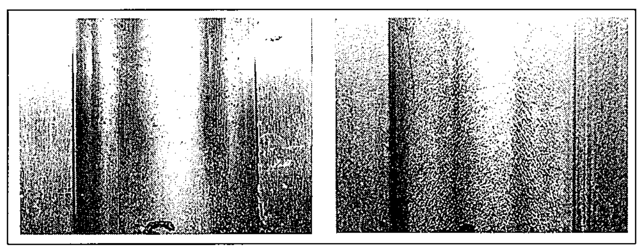


Fig. 14 Performance of hot rolling mill rolls



HIP high-speed tool steel roll Chilled iron roll

Photo 10 Surface of intermediate stand rolls after use

is imperative.

(iii) Bar and wire rod mill guide rollers

Bar and wire rod mill guide rollers made from the ceramic dispersed-high-speed tool steel PH-Xc were confirmed to have four times higher wear resistance than chilled iron rollers as shown in **Fig. 15**, and exceeded cemented carbide rollers in seizure resistance.

4. Conclusion

As discussed earlier, the HIP process provides materials with degrees of heat, wear, and corrosion resistance that cannot be imparted by conventional ingot metallurgy, and parts made from such HIP processed materials are used in iron and steelmaking facilities to good effect. Since the installation of a HIP facility eight years ago, the Plant & Machinery Division has forged ahead with the development and application of HIP materials in cooperation with the company's steelworks and research laboratories. HIP materials are being applied as construction materials for parts to be used in iron and steelmaking facilities.

Technology for creating new materials by utilizing the HIP process is still new. Given the basic principles of material property control, the HIP process with its large freedom concerning crystal control and composition design, among other things, has the potential of achieving the higher performance and increasing the functionality of materials. New high-performance materials developed and implemented through the application of the HIP process are expected to find increasing usage not only in the iron and steel industry but also in other industrial fields.

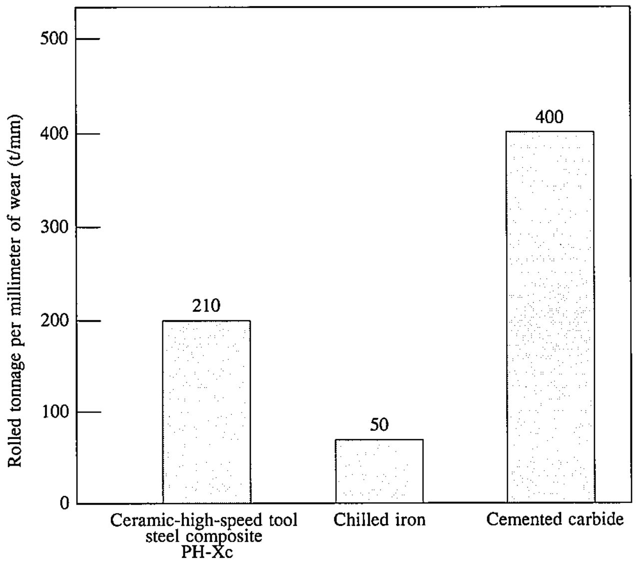


Fig. 15 Service performance of guide rollers

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