Materials

■ Materials

Nickel-base Superalloy Materials for Increasing Power Generation Efficiency of A-USC Steam Turbines

To help minimize global warming, coal-fired power plants need to be made more efficient to reduce their CO_2 emissions. In a coal-fired power plant, coal is burned in a boiler to generate heat energy. This is converted to rotational energy by the steam turbine, from which the generator generates the power. To increase the power generation efficiency, the steam temperature and pressure must be raised as much as possible. Hitachi is aiming to produce highly efficient coal-fired power plants by developing new nickel-base superalloys that can withstand high temperatures and high pressures.

Shinya Imano (left), Senior Researcher, PMI Unit, Department of Materials Research for Power Plants, Materials Research Laboratory, Hitachi Research Laboratory; Eiji Saito (right), Senior Engineer, Thermal Power Business Department, Thermal Power System Division, Thermal Power Systems Division, Power Systems Company, Hitachi, Ltd.

From Steel to Nickel-base Superalloys

With the aim of producing a highly efficient A-USC (advanced ultra super critical) coal-fired power plant, we have been developing a steam turbine plant that uses a nickel-base superalloy. The material used for conventional turbines is steel, and the maximum steam temperature is 600℃. However, if the steam temperature is raised to 700℃, the power generation efficiency can be improved from the previous 40% to about 46% to 48%. Currently, coal-fired power plants make up about 40% of total world power generation, so if these A-USC coal-fired power plants were used, CO_2 (carbon dioxide) emissions could be reduced by up to 20%.

Nickel-base superalloys have excellent durability against high temperatures, so they have been frequently used for small parts that must be used at high temperatures, such as engine parts in airplanes and gas turbines. However, in order to make a large turbine rotor that weighs more than 10 t out of a nickel-base superalloy, something that has never been done before, issues that must be researched include improving the processability of large steel ingots, achieving strength for withstanding high temperatures above 700℃ for a long time and metallic structure stability, and also reducing costs.

Development of High-performance Hitachi Original NiFe-base Superalloy at Low Cost

The material that was studied as the basis for this development was a nickel-base superalloy called Alloy 706, which is used in large gas turbines. This material has excellent manufacturability for a large material, has a lot of iron content, and has a relatively low cost because it does not contain substances such as cobalt, molybdenum, and carbide. However, the limit of its temperature resistance was about 650℃. We used a simulation tool to evaluate the stability of the metallic structure. As a result of this study, we developed the Hitachi original NiFe-base superalloy, which has increased resistance to long-term deterioration by reducing the niobium content and adding aluminum, and also has excellent manufacturability. We succeeded in increasing the temperature resistance to 700℃. It is forecast that we will achieve our target for 700℃-class rotor materials of a creep rupture strength of 100 MPa in 100,000 hours.

Also, the results from a segregation simulation test and a cross section study of the large steel ingot prototype material demonstrated that the segregation characteristics of Hitachi original NiFe-base superalloy are superior to those of Alloy 706. Currently, we are pushing the limits of manufacturability in trying to achieve our weight and size development targets that correspond to steam rotors that are actually used, namely a large forged part that is over 10 t and has an outer diameter of about 1,000 mm.

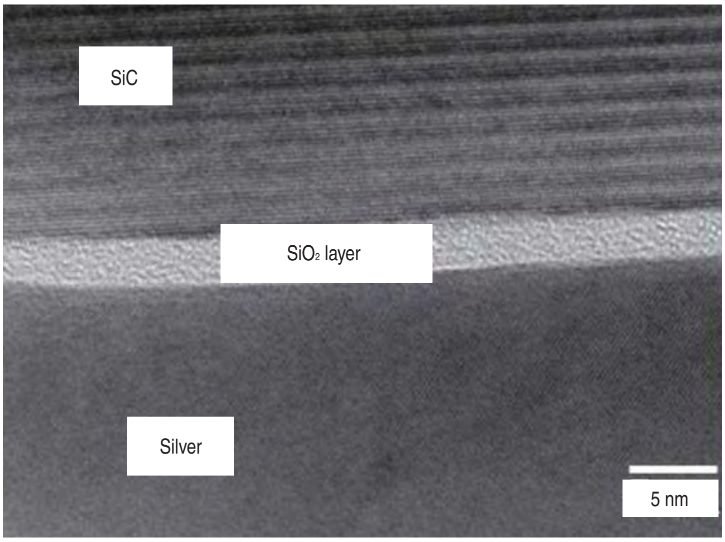
Hitachi Original Low Thermal Expansion Ni-base Superalloy for More Compact Steam Turbines

With the objective of producing steam turbines in the 600℃ class that are more compact, we have also developed a high strength, low thermal expansion nickel-base superalloy together with Hitachi Metals, Ltd. This is an alloy that is being considered for application in products that are built into steel materials, which have lower thermal expansion than nickel-base superalloys. Based on M252, which has low thermal expansion, it has improved hot working and strength characteristics. In Hitachi original low thermal expansion Ni-base superalloy, we added molybdenum to reduce the thermal expansion. This means that although it costs more than Hitachi original NiFe-base superalloy, the creep rupture strength at 700℃ in 100,000 hours is forecast to be 160 MPa, and the equivalent value at 740℃ is an extremely high 100 MPa. If the bolts for the casing that covers the steam turbine rotor is manufactured from a high-strength material, the casing can be made smaller by making the bolts thinner and the flange smaller. As such, it is anticipated that this material will contribute to making A-USC steam turbines more compact. We are also studying the use of Hitachi original low thermal expansion Ni-base superalloy in small materials such as the turbine moving blades and stator blades.

When evaluating the development and reliability of new materials, simulation technology and verification tests for evaluating the fusion, casting, forging, thermal processing, and stability of the metallic structure during use are indispensable. Taking advantage of our strength in being among the first to include these simulation technologies in our product development, we would like to continue to focus on developing new materials for achieving highly efficient coal-fired power plants.

* Some of this research was performed as part of "Strategic Development for Energy Use Rationalization Technology/Research and Development of New Materials for Steam Turbines for 700℃-class Ultra Super Critical Power Generation," a project sponsored by New Energy and Industrial Technology Development Organization (NEDO), and "Development of Material Technology for Commercialization of Advanced Ultra Super Critical Power Generation," a project subsidized by the Agency for Natural Resources and Energy of Japan.

Lead-free Junction Technology for High-temperature Environments Using Silver Oxide Microparticles

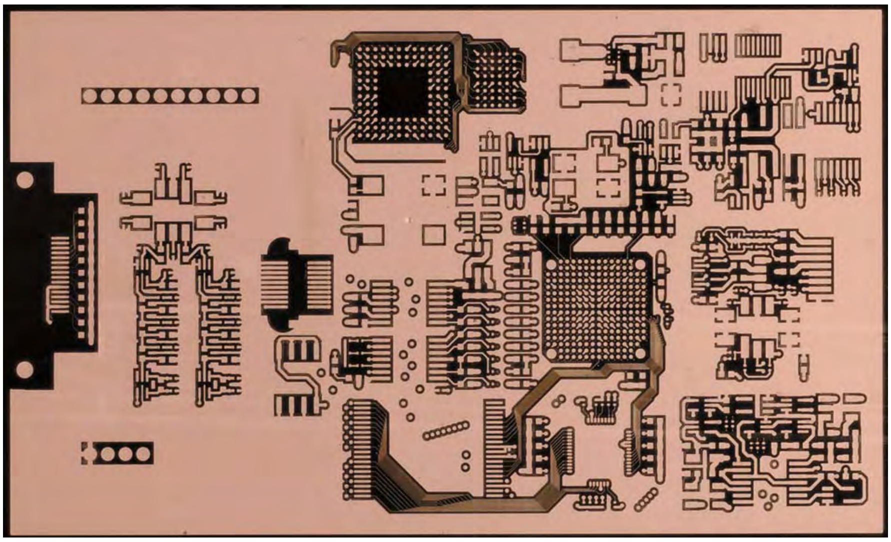


Interface of junction with SiC

In electronic components used in vehicles and industrial equipment, the operating temperature of semiconductor devices is rising to higher levels as current densities rise. For this reason, high reliability is required in high-temperature environments. Also, for new devices such as those made from SiC (silicon carbide), there was demand for a junction material that has both high dissipation performance and high heat resistance. Previously, many materials that contained lead were used in junction materials for high-temperature environments, but from the perspective of environmental protection, in recent years demand has grown for junction materials that do not contain harmful lead. This is the background to Hitachi's development of a new, low-cost and lead-free junction technology that uses silver oxide microparticles*. A feature of this technology is that it enables direct joining with electrodes made from aluminum, titanium, and other substances that are often used in electronic components. Because the surfaces of these electrode materials are formed with a hard and stable oxide layer, with previous junction materials whose main raw material was lead or tin, it was necessary to remove this oxide layer. In this development, it was discovered that the exothermic reaction that is generated when reducing silver oxide microparticles is effective for joining to these oxide layers. It was also confirmed that joining was possible in the same way for silicon and SiC that have surface oxide layers.

* Silver oxide microparticles: Silver oxide particles that are a few micrometers in size.

Copper-clad Laminate Using Epoxy Resin Made from Biomass

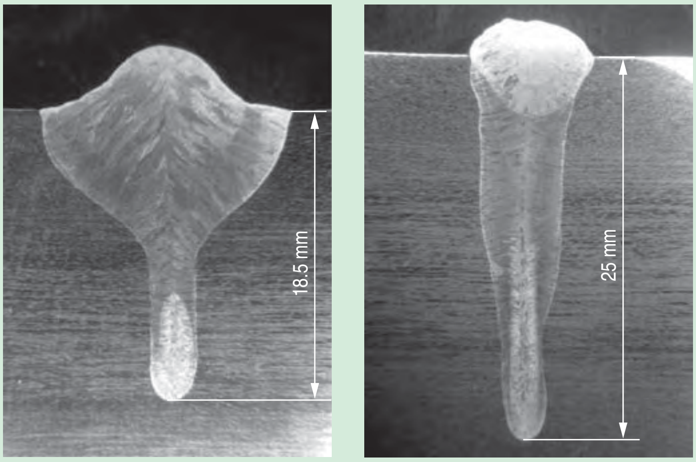

Prototype printed circuit board made from epoxy resin using lignin as the main raw material [90×55 (mm)]

Biomass is CO_2 from the atmosphere that has been solidified by plants and animals, and unused wood biomass originating from wooden raw materials reached about 5 million tons in 2007. Using the carbon source contained in this material instead of oil to produce plastic has been a recent focus of public attention.

In this development, Hitachi used the lignin found in wood biomass as the main raw material, and by keeping the molecular weight of the epoxy resin to a low level by adjusting the catalyst during synthesis, succeeded in synthesizing an organic solvent-soluble epoxy resin. The glass-transition temperature of the hardened materials of the epoxy resin that was produced was a high level of 200℃ or higher, and testing of the printed circuit board confirmed that characteristics such as the insulation performance were equivalent to printed circuit boards that originated from oil. This will open the way for the commercial use of epoxy resin created from the lignin found in wood biomass. Because it uses renewable resources that originate in living organisms, this technology helps build a society that recycles its resources.

Note that this is the result of a joint development with The University of Tokushima and the Yokohama National University.

Thick Plate Laser Welding Technology



Previous technology
Developed technology

Shape of welding penetration of stainless steel (SUS316L) using laser welding with an output of 10 kW

Laser welding is welding that uses the energy of a laser beam. Because the density of the energy is high, it enables joining with deep-penetration welding and shortens the welding time. As such, it has received attention as a junction technology that delivers both high quality and productivity.

In a joint development with Joining and Welding Research Institute of Osaka University, Hitachi developed a gas jet laser welding technology that sprays a shield gas at high speed to protect the welding area. This enabled the welding penetration to be increased by about 40% without increasing the laser output. As a result, the same welding penetration as with the current output can be obtained with a lower output, enabling the laser output to be lowered by up to 50% and the power consumed during welding to be reduced.

Further, plume restriction technology was developed that greatly reduced the metal vapor (plume) that is generated during welding, which stabilizes the welding and reduces the burden on the environment.

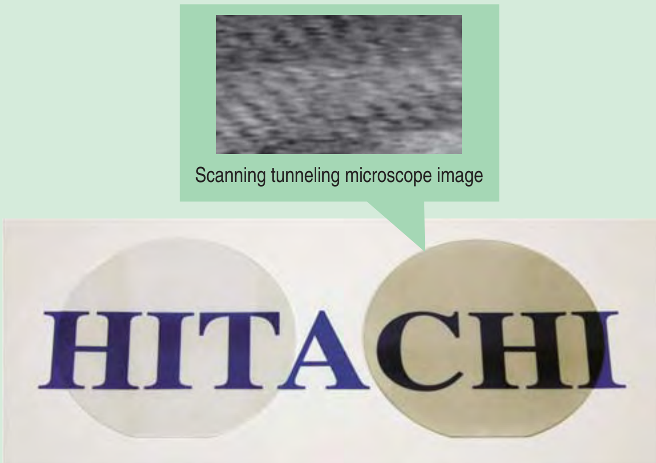
These technologies enable welding that consumes less power and is more considerate of the environment than previous methods, and Hitachi aims to make commercial use of them by about 2011 as technologies for welding equipment in nuclear and thermal power stations, among other users.

Technology for Graphene Growth Using the Vapor Phase Epitaxial Method

Graphene is a one-atom-thick planar sheet of carbon atoms that are packed into a honeycomb pattern with a thickness of 0.34 nm. Hitachi was the first in the world to succeed in producing graphene on a sapphire substrate that is suitable for electronic devices while controlling the number of layers using the hot vapor phase epitaxial method that is suitable for mass production. Graphene is a material that has an electron mobility that is several dozen times that of silicon, and there are high expectations for its use in high-speed electronic devices for the ultra high-speed networks of the future.

In this development it was discovered that sapphire has a catalytic property for graphene growth. A technology was developed for directly producing from one to several layers of graphene on a sapphire substrate without using a metallic catalyst. Also, by utilizing the transparent sapphire substrate and the fact that the light transmittance of one graphene layer is 97.7%, a technology was developed for deciding the number of graphene layers using the simple method of light transmittance measurement.

These technologies were jointly developed with Tohoku University, and further development of the core technology is planned for the commercialization and mass production of high-speed electronic devices, transparent electrodes, catalysts, sensors, and functional coating materials that use graphene.

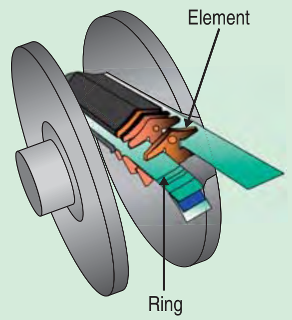


Before graphene production
After graphene production

Scanning tunneling microscope image of the sapphire substrate and the produced graphene before and after graphene production

Maraging Steel Strip for Continuously Variable Transmission Belts

In recent years, among the several types of transmissions for automobiles, belt-type CVT (continuous variable transmissions) have been used increasingly, because they have smoother shifting and better fuel efficiency than AT (automatic transmissions).
In CVT systems, belts composed of stacked belt rings and elements transmit engine power. For these belt rings, a well-known ultra-high strength steel called maraging steel has been used. It was selected because of its formability, in order to form rings, and also for its weldability, high strength, and high toughness to enable it to endure loads during operation.
Fatigue strength in the high cycle region is especially important for long-time reliability. In this region, refinement of non-metallic inclusions is important, because internal non-metallic inclusions initiate fatigue cracks and greatly affect fatigue strength. Non-metallic inclusions need to be made finer to improve fatigue strength. Maraging steel obtains its high strength and toughness from the Ti (titanium), Mo (molybdenum), and Co (cobalt) that it contains. Ti easily forms TiN (titanium nitride) non-metallic inclusions under the presence of nitrogen in the steel. Therefore, it is very difficult to control the size of TiN.
Hitachi Metals, Ltd. has made it possible to make TiN non-metallic inclusions finer by using its own special melting methods and refining techniques. The size of TiN can be made much less than in the conventional process. Therefore, Hitachi's techniques of controlling TiN non-metallic inclusion brought higher fatigue strength and higher reliability to CVT belts. Hitachi's maraging steel improves fatigue strength in the high cycle region using the process that it developed. Hitachi is contributing to reducing CO_2 through its maraging steel strip for CVT belts.
(Hitachi Metals, Ltd.)

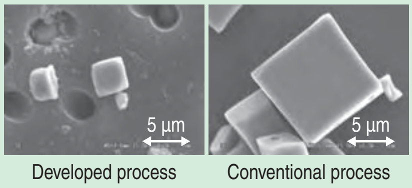


(a)

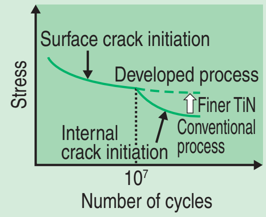
(mass %)

Ni	Co	Mo	Ti	Fe
18	9	5	0.45	Bal.

(b)



(c)

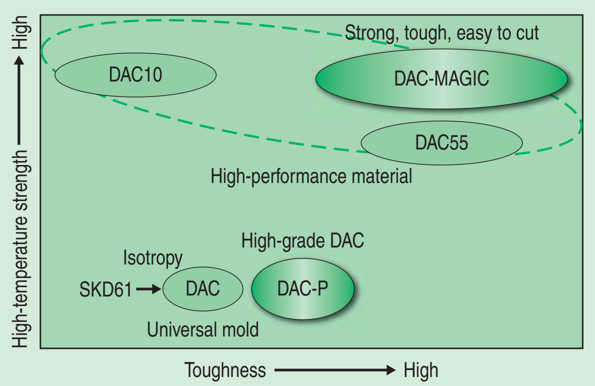


(d)

Schematic view of CVT belt (a), chemical compositions of maraging steel used for CVT belts (b), refined TiN particles (c), and schematic S-N curves of fatigue strength (d)

High Performance Hot Work Die Steel "DAC-MAGIC"

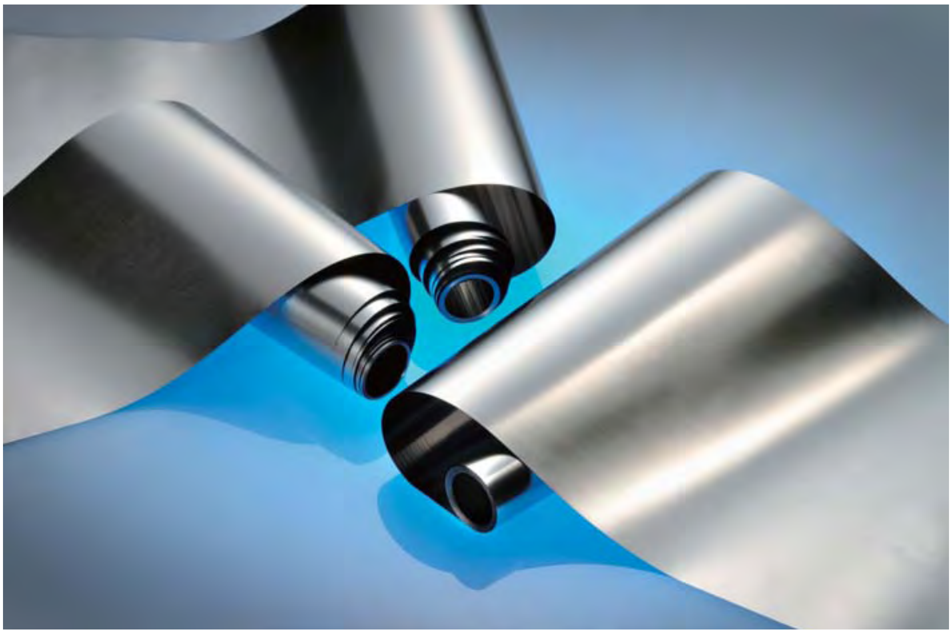
The die cast method is a production method that forms parts by shooting out a melted alloy such as aluminum at high speed and high pressure. The demand for such parts has grown as automobile parts become more lightweight and electronic devices become more widespread. Because of demands for these die casts, such as increased productivity, increased product size and reduced mold production costs, diverse properties are now required for the steel used to make the die cast molds. The biggest problem is heat cracks caused by repeated heating and cooling as melted alloys are cast in the mold, which means that high-temperature strength and toughness are required characteristics for a mold material. Toughness is also a required property to prevent large cracks in the mold. A material that is easy to cut is also in demand for mold production. Previously, the most popular materials in Hitachi Metals product for die cast molds were DAC and DAC-P, while the high-performance grades were DAC10 with a high-temperature strength and DAC55 with high toughness. In contrast, the DAC-MAGIC from the latest development is a material that combines the strengths of the previous high-performance materials, while also being easy to cut.
(Hitachi Metals, Ltd.)



Positioning of steel for die cast mold

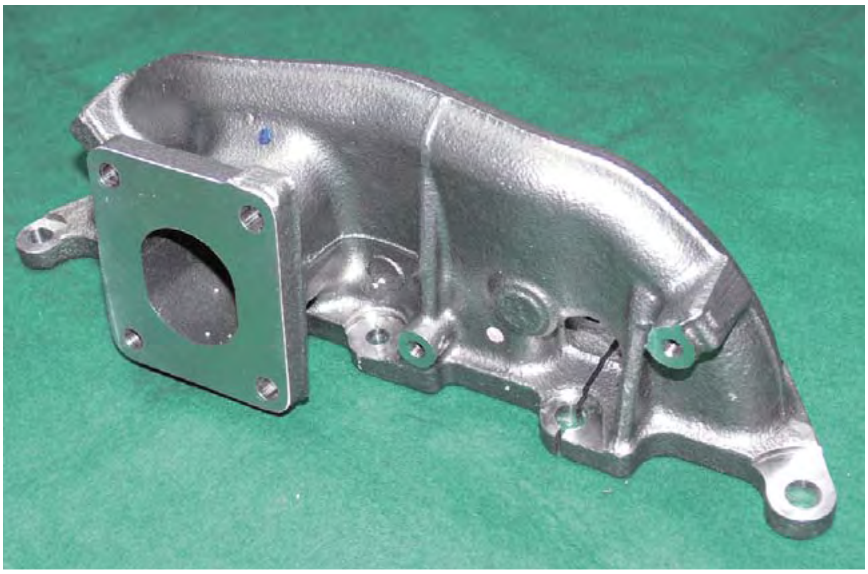
High Performance Amorphous Alloy for Distribution Transformers

The demand for AMDTs (amorphous distribution transformers) is growing around the world, because they have the advantage of saving energy and reducing the environmental burden, which results from their lower no-load loss compared with CRGO-DTs (cold rolled grain oriented electrical steel distribution transformers).
Moreover, new amorphous alloys are expected to overcome the weak points of current AMDTs, namely their larger size and louder noise as compared with CRGO-DTs.
In order to satisfy these requirements, Hitachi Metals, Ltd. has developed a new amorphous alloy that has higher saturation induction (1.64 T) and a B-H (flux density-magnetizing force) loop that has greater squareness ratio than a conventional amorphous alloy with 1.56 T of saturation induction. AMDTs using the newly developed high performance amorphous alloy can achieve both smaller size and lower noise, while maintaining a no-load loss that is comparable with AMDTs using the conventional amorphous alloy.
(Hitachi Metals, Ltd.)

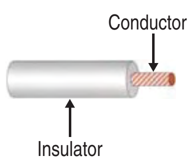
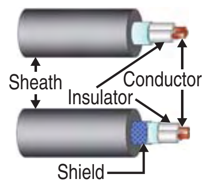
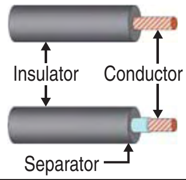

High performance amorphous alloy for distribution transformers

HERCUNITE-A3K: Heat-resistant Cast Steel for Turbo Gasoline Engine Exhaust Parts

"Low fuel consumption" has become the most important target for car manufacturers since CO_2 reduction has become a key environmental target of the worldwide community. One efficient technique to achieve lower fuel consumption is to reduce the size of gasoline engines using a turbocharger. Such engines require a high exhaust gas temperature of up to 1,000℃ because the air-fuel ratio is close to the stoichiometric value. Therefore, heat-resistant cast iron needs to be replaced by heat-resistant cast steel for exhaust components such as the manifold. Normally, 25Cr (chromium)-20Ni (nickel) or 18Cr-37Ni cast steel is used for parts whose surface is heated up to 1,000℃. However, because of a sudden increase in the price of rare metals such as Cr and Ni, there is strong demand from customers for new materials that contain less of such alloys. Due to this technical requirement, 20Cr-10Ni-based cast steel called HERCUNITE A3K has been developed. This material contains a low amount of these costly alloys in comparison to alternative materials, and can still be used at high metal surface temperatures of 1,000℃. This gives cost benefits, while maintaining high performance. A3K is frequently used now as a material solution on reduced-sized, highly efficient engines (less than 2,000 cc) that utilize turbo charging.
(Hitachi Metals, Ltd.)


Exhaust manifold for turbo gasoline engine

Railway Rolling Stock Cables Conforming to European Standards

	For control		For power
	EN50306-2	EN50306-4	EN50264-3-1
Structure			
Rated temperature	105°C	90°C	90°C
Rated voltage	300 V	300 V	600 V, 1,800 V

Lineup of products conforming to European standards (scheduled for market entry from September 2010)

In recent years, railway transport has become more popular because its energy consumption and CO_2 (carbon dioxide) emissions are low relative to the transported volume, which lessens the burden on the global environment. The development of railway networks is accelerating in global markets, especially in Europe and Asia, which is increasing demand for railcars and materials. Compatibility with European standards is becoming a necessity for the railcars and materials used in global markets, including the European Union (EU). These European standards are becoming the global standard. This is the background to the development by Hitachi Cable, Ltd. of railway rolling stock cables that conform to the European standards. This will strengthen Hitachi's business in global markets, which are expected to see future growth.

The European standards require materials to have many different properties at the same time, such as flame resistance and durability. In particular, they emphasize fire safety with high flame resistance, and low smoke generation and low toxicity when the cables burn, in order to minimize the effects on humans. The various requirements were satisfied by using a covering material that uses as its main agents engineering plastic that blends flexible elastomers, and cross-linked polyolefin to which excellent oil and fuel oil resistance has been added.

(Hitachi Cable, Ltd.)

Transparent Conductive Film with Ultra Low Electric Resistance

A novel conductive transparent film has been developed by Hitachi. The film has several unique characteristics, as follows. (1) 0.1 Ω/sq surface resistance, which is one one-hundredths of that of conventional ITO (indium tin oxide) film, and light transmittance that is more than 80%.

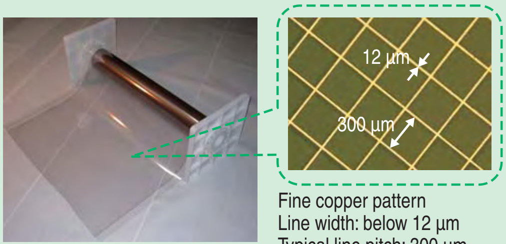
(2) A conductive layer with a surface flatness of less than 0.5 μm is exposed to the surface.

(3) A wide variety of conductive layer designs can be used. The minimum line width is 10 μm.

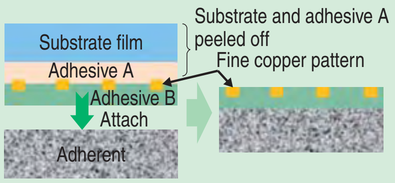
(4) Various plastic films, such as PET (polyethylene terephthalate) and PP (polypropylene), and heat durable films, such as PEN (polyethylene naphthalate) and PI (polyimide), can be used as the substrate. If necessary, the film can be peeled off.

(5) As the adhesive layer, pressure sensitive adhesive, UV (ultraviolet) curable resin, and thermosetting resin can be used. It is expected that touch tone LC (liquid crystal) and OLED (organic light emitting diode) will be able to be used as the transparent conductive film, and also film with a higher yield antenna and electrodes with higher efficiency PV (photovoltaic batteries) are anticipated.

(Hitachi Chemical Co., Ltd.)



(a) Fine copper pattern
Line width: below 12 μm
Typical line pitch: 300 μm
Surface resistance: 0.1 Ω/sq



(b)

Specifications	Appearance		Scroll
	Width		800 mm
	Thickness		Direct attachment: 120 μm, filmless: 20 μm
	Conductive layer	Line width	Minimum 10 μm
		Line pitch	≤300 μm (variable)
Characteristics	Aperture		Maximum 92%
	Haze		<1.5%
	Surface resistance		<0.1 Ω/sq
	Roughness		<0.5 μm
	Adhesion test	Heat/humidity	Pass (65°C, 95%RH, 500 h)
		Water resistance	Pass (80°C, 3 h, in water)
	Weather resistance		Δy<0.001 (35 mW/cm², 500 h)

(c)

Film features (a), film usage (b), and film characteristics (c)