Featured Articles

Innovative Functional Materials for Green Innovation

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OVERVIEW: As exploiting unutilized sources of heat energy, improving the efficiency of electrical power equipment, and energy efficiency are urgent issues for the creation of a sustainable society, Hitachi is developing innovative functional materials for achieving green innovation. Specifically, the materials under development include thermoelectric materials that take advantage of the ability of non-toxic and cheap silicon to convert waste heat into electric power, new magnetic materials that improve the electrical efficiency of electric motors using smaller quantities of rare earth metals, and a high-entropy alloy with high strength and corrosion resistance fabricated on 3D printers that provide energy-efficient processes for materials processing.

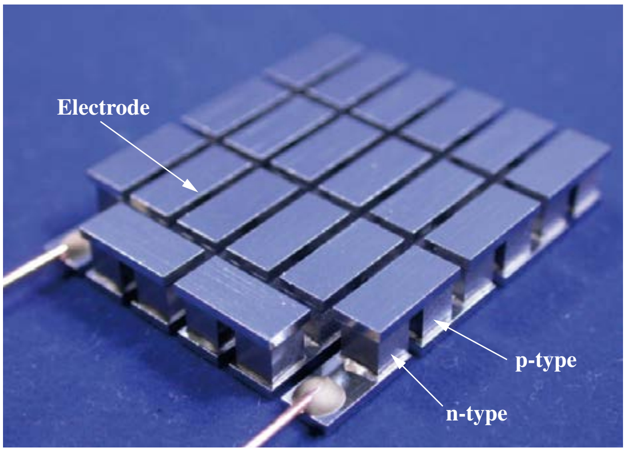
INTRODUCTION

TO improve energy efficiency and conserve the Earth's resources and environment picking up pace around the world, there is a need not only to use energy more efficiently and exploit unutilized sources of thermal energy, but also to help prevent global warming by developing energy technologies with low carbon dioxide (CO_2) emissions. Hitachi is developing innovative functional materials that facilitate work on such green innovations.

This article describes thermoelectric materials that convert unutilized thermal energy into electric power, new magnets that help improve electric motor efficiency using smaller amounts of rare earth metals, and a high-entropy alloy with high strength and corrosion resistance that can be fabricated using a three-dimensional (3D) printer process that forms materials with lower energy consumption than past techniques.

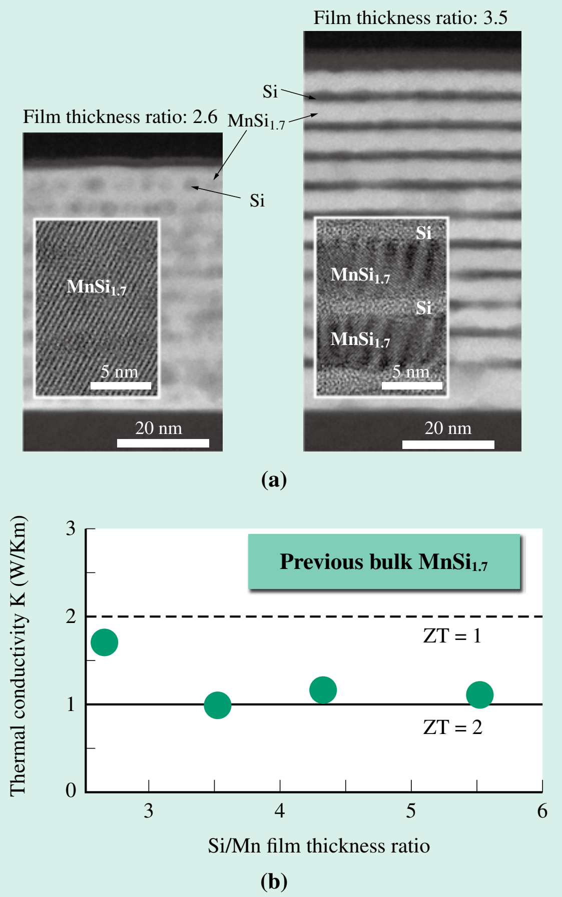
THERMOELECTRIC MATERIALS

Thermoelectric conversion is a method of generating electric power by the direct conversion of thermal energy to electrical energy using the Seebeck effect, which generates power from the temperature difference across a thermoelectric semiconductor. Prompted by the problems associated with rising energy consumption, including the scarcity of fossil fuels and global warming caused by CO_2, there has been interest in recent years in thermoelectric conversion modules that can recover high-temperature industrial or automotive waste heat (at temperatures around 500°C) that has gone unused up until now. Fig. 1 shows a high-temperature thermoelectric conversion module being developed by Hitachi Chemical Co., Ltd. that uses a silicon-germanium (SiGe) material. Made of p-type and n-type SiGe connected in series via an electrode, the thermoelectric conversion module has a function that generates electric power in response to the temperature difference between its upper and lower sides. The conversion efficiency of the module is determined by the dimensionless figure of merit ZT ($Z = S^2/\rho\kappa$, where S = Seebeck



SiGe: silicon germanium

Fig. 1—SiGe Skeleton Thermoelectric Conversion Module (Produced by Hitachi Chemical Co., Ltd.).
The module has an output of 8.4 W for a temperature difference of 630°C (high-side temperature: 650°C, low-side temperature: 20°C).



TEM: transmission electron microscope

Fig. 2—Cross-sectional TEM Image of $MnSi_{1.7}$/Si Laminate Film and the Dependence of Thermal Conductivity on the Ratio of Si to Mn.
(a) shows a cross-sectional TEM image of $MnSi_{1.7}$/Si laminate film, and (b) shows the dependence of thermal conductivity on the ratio of Si to Mn. A $MnSi_{1.7}$/Si laminate film with a Si to Mn thickness ratio of 3.5 has sharp boundaries between the $MnSi_{1.7}$ and Si layers and provides thermal conductivity of 1.0 W/Km, the value needed to achieve ZT = 2.

coefficient, ρ = resistivity, κ = thermal conductivity, and T = temperature) of the elements that are used. For example, being able to achieve a value of ZT = 2 can improve engine fuel efficiency by 5%, so there is a need to develop materials with high ZT.

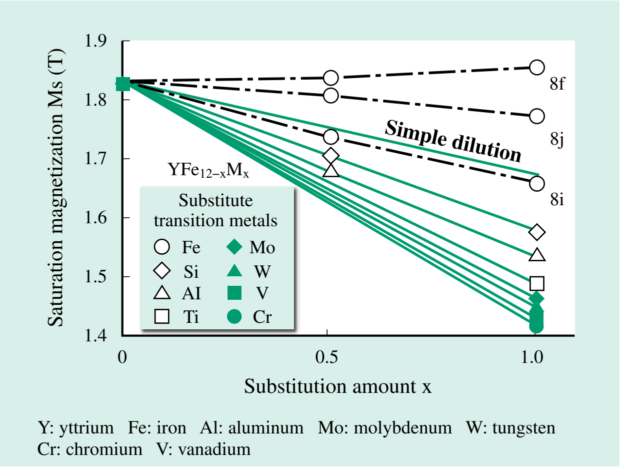
This section looks at manganese-silicon ($MnSi_{1.7}$), which is made up of Si, a high-temperature thermoelectric material that is cheap and places a low load on the environment, and describes what is being done to improve ZT by reducing its thermal conductivity.

While $MnSi_{1.7}$ has a large Seebeck coefficient(1), reducing its thermal conductivity is generally difficult due to its hard lattice. In response, Hitachi studied the use of a $MnSi_{1.7}$/Si thin-film composite material with a nanoscale organization and structure, and Si applied to the interface with the primary $MnSi_{1.7}$ phase to increase the dispersal of phonons that carry thermal energy. The $MnSi_{1.7}$/Si thin-film composite was produced by heat-treating a Mn/Si laminate film built up using a sputtering method with alternate layers of Mn and Si that caused the Mn and Si to react. Fig. 2 (a) shows high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) cross-section images of $MnSi_{1.7}$/Si thin-film composites with different Si and Mn thickness ratios. When the thickness ratio of Si to Mn is low (2.6), a granular composite structure is formed that is made up of $MnSi_{1.7}$ and Si microcrystals with grain diameters of several nanometers. In contrast, when the thickness ratio of Si to Mn is high (3.5), a $MnSi_{1.7}$/Si laminate film is formed with a sharp interface between the $MnSi_{1.7}$ and Si layers, which are each several nanometers thick. As shown in the cross-sectional TEM images shown in the insert, heat treatment caused the $MnSi_{1.7}$ primary phase to crystalize in both thin films.

Fig. 2 (b) shows how thermal conductivity depends on the thickness ratio of Si to Mn. The dotted and solid lines in the figure represent the thermal conductivities required to achieve ZT = 1 and ZT = 2 respectively, assuming a power factor (S^2/ρ)(2) obtained from bulk material. The thermal conductivity was lower than the bulk thermal conductivity for a Si to Mn thickness ratio of 2.6. This is believed to be due to increased dispersion of phonons at the $MnSi_{1.7}$/Si interface. Furthermore, a value of κ = 1.0 W/Km was obtained for $MnSi_{1.7}$/Si laminate films with a Si to Mn thickness ratio of 3.5 or higher, which is the level required to achieve the ZT = 2 material figure of merit required for a 5% or more improvement in engine fuel consumption. Hitachi intends to continue developing bulk composite materials with the aim of using them in thermoelectric conversion modules.

NEW MAGNETS THAT USE SMALLER QUANTITIES OF RARE EARTH METALS

Magnets are used in a wide variety of fields, including electronics, telecommunications, medicine, machine tools, and automotive electric motors. In terms of reducing the load on the environment and creating a sustainable society, a particularly urgent issue is to improve the efficiency of the electric motors used in hybrid electric vehicles (HEVs) and electric vehicles (EVs), the market for which is growing rapidly. This



Y: yttrium Fe: iron Al: aluminum Mo: molybdenum W: tungsten
Cr: chromium V: vanadium

Fig. 3—Dependence (at Absolute Zero) of Saturation Magnetization on Substitution Amount (x) Obtained by First-principles Calculation.
The Ms of $YFe_{12-x}M_x$*, in which the Fe has been partially replaced with a transition metal remains below the Ms for simple dilution (indicated by the solid line) in which the magnetic moment of transition metal M is taken to be zero. In contrast, the Ms for* YFe_{12-x}*, in which no transition metal is used and only the amount of Fe is reduced (indicated by the dotted line), exceeds Ms for simple dilution.*

requires achieving even higher performance for the magnetic materials that provide the magnetic flux in these motors. Neodymium-iron-boron ($Nd_2Fe_{14}B$) is the main phase in the highest-performing neodymium magnets, which were reported in 1983. While $Nd_2Fe_{14}B$ has a high saturation magnetization of 1.61 tesla (T) at room temperature, it contains 11.8 atomic percent (at%) of the rare earth metal Nd (82.4 at% of Fe)(3). The ability to manufacture new magnetic materials that provide high magnetic properties using smaller quantities of rare earth metals than neodymium magnets will achieve green innovation after 30 years or so.

Hitachi has chosen R $(Fe, M)_{12}$ (where R indicates a rare earth metal and M a transition metal) as a candidate for such new magnetic materials, because this configuration is recognized as the magnetic primary phase that uses the smallest amount of rare earth elements. R $(Fe, M)_{12}$ exists as an equilibrium phase in which some of the element Fe has been replaced with a suitable amount x of a transition metal such as titanium (Ti) [transition metals include aluminum (Al), Si, Ti, Vanadium (V), chromium (Cr), Mn, molybdenum (Mo), and tungsten (W)](4). However, samarium-iron-titanium ($SmFe_{11}Ti$), for example, which has a Curie temperature similar to $Nd_2Fe_{14}B$, is capable of magnetization only to 1.13 T at room temperature, despite having a high proportion of Fe atoms (approximately 84.6 at%)(4). In contrast, $SmFe_{12}$, which does not contain any transition metal, has been reported(5) to have high magnetization of 1.43 T, with a maximum thin-film thickness of about 500 nm, because it is difficult to produce in bulk form. In other words, the problem with replacing some of the Fe atoms with a transition metal is that it tends to significantly reduce magnetization. In response, Hitachi focused on the Fe network in RFe_{12} with the aim of acquiring new knowledge to enable the production of new magnetic materials that could be used to make bulk magnets by determining on the basis of electron theory how saturation magnetization Ms is influenced by the transition metal required for structural stability. It chose yttrium (Y), a nonmagnetic element, as the rare earth metal, R.

The first step was a first-principles calculation of $Y(Fe, M)_{12}$ in order to use electron theory to elucidate why adding a transition metal reduces magnetization (see Fig. 3). From the results, Hitachi found that the reduction in magnetic flux was due to the transition metal atoms adopting an antiferromagnetic configuration in which their magnetization moments were opposite that of the Fe atoms. This means that keeping the amount of transition metal to a minimum will significantly improve magnetization. Accordingly, the rapid quenching method* can be used for the manufacture of bulk magnets was adopted for the production of nonequilibrium-phase RFe_{12}. This led to the world's first successful production of YFe_{12} on a bulk scale (see Fig. 4).

A feature of light rare earths is that they cannot be used to produce RFe_{12}, and it was found that production was possible only if at least the elements Y and gadolinium (Gd) were used. This can be understood to be a phenomenon specific to rare earths classified as belonging to the medium weight range. As the structure of the metastable-phase YFe_{12} produced was stable up to 900°C, it is often chosen for use in applicable magnet processes. This discovery was a breakthrough toward creating RFe_{12} bulk magnets, which had not been produced until now. The magnetic characteristics of YFe_{12} were determined at room temperature. The saturation magnetization measured by Mössbauer spectroscopy was 1.40 (5) T, the magnetic anisotropy field measured by the singular point detection method was 1.7 (2) T, and the Curie temperature obtained by

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* A cooling speed of 10^4 to 10^6 K/s is achieved by laying a thin film (10 to 40 µm) of molten metal on a rapidly rotating copper roll to dissipate heat. The process can be used to produce metastable and amorphous phase materials and obtain samples in ribbon form.

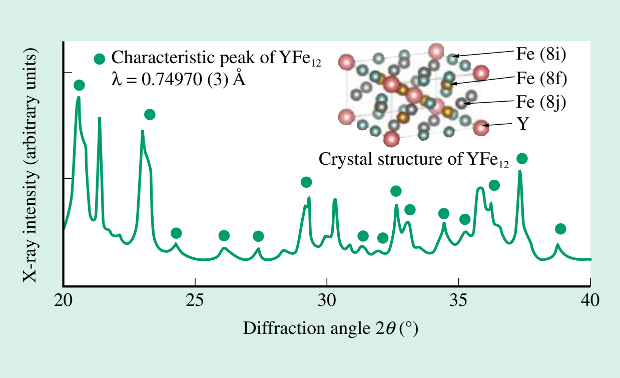


Fig. 4—Constituent Phase Analysis by High-resolution Powder X-ray Diffraction.
X-ray diffraction shows that the intended YFe$_{12}$ is present in a rapidly quenched ribbon specimen that was heat-treated at 900°C. For a specimen heat-treated at 1000°C, only the Y$_2$Fe$_{17}$ and Fe equilibrium phases are present.

determining the point of inflection in the magnetization-temperature curve was 212°C. Because these magnetic characteristics are low compared to Nd$_2$Fe$_{14}$B, there is a need to add appropriate elements to increase the magnetic performance. For example, calculations indicate that magnetization can be increased by removing Fe atoms at specific sites (see Fig. 3).

In addition to using theory and experiment to make further improvements in these magnetic properties, technical development is also needed to obtain a single phase.

HIGH-STRENGTH, CORROSION-RESISTANT ALLOY FOR 3D PRINTING OF METALS

In business fields, such as resources and energy, that require tolerance of harsh environments, for example, parts for chemical plants or oil and gas drilling equipment that are used under conditions where they are exposed to highly corrosive gases require high strength and corrosion resistance to improve the availability and longevity of equipment. This has led to interest in high-entropy alloys that have been reported to offer excellent tensile strength, wear resistance, and resistance to high-temperature oxidation or corrosion in the presence of acids or alkalis(6), (7). Being composed of a large number of different elements, high-entropy alloys are prone to composition variability during casting and are difficult to work due to their high degree of hardness. One option for overcoming these problems is the use of electron beam additive manufacturing whereby an electron beam is used to fabricate parts with complex shapes.

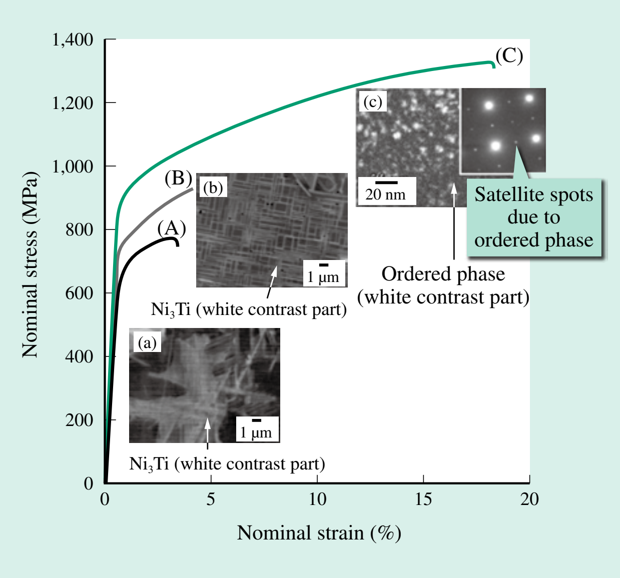
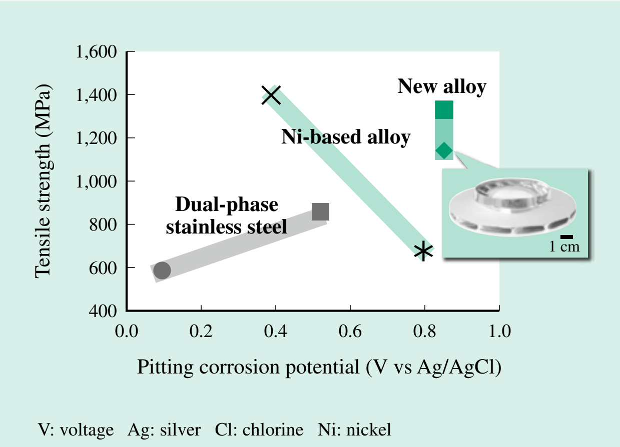


Fig. 5—Tensile Stress-strain Curve and Metallographic Structure for Materials Produced by Casting and by Additive Manufacturing.
In the graph and images, (A) and (a) indicate the material produced by casting, (B) and (b) indicate the material produced by additive manufacturing, and (C) and (c) indicate the material produced by additive manufacturing followed by heat treatment. The material produced by electron beam additive manufacturing shows superior tensile properties compared with those of the material produced by casting.

This additive manufacturing technique produces metal parts through a repeated process of localized melting and solidification during which an evenly-spread metal powder is selectively exposed to an electron beam based on 3D computer-aided design (CAD) data. As a result, in addition to minimizing the need for machining, this energy-efficient process does not require a mold or other tooling, and significantly reduces material loss and energy consumption. This section describes new alloys that have been produced using a combination of electron beam additive manufacturing and heat treatment that delivers better strength and corrosion resistance than past materials.

Fig. 5 shows the tensile stress-strain curves and metallographic structure for a material produced by the conventional casting method, a material produced by additive manufacturing, and a material produced by additive manufacturing after being heat-treated. The material produced by additive manufacturing has tensile properties superior to those of the conventional casting method. This is believed to be due to the uniform precipitation of an intermetallic compound (Ni$_3$Ti) that acts as a hardening phase as a result of the localized melting and rapid solidification that are



V: voltage Ag: silver Cl: chlorine Ni: nickel

Fig. 6—Comparison of Tensile Strength and Pitting Corrosion Potential in New Alloy and Conventional Alloys.
The new alloy has higher strength and corrosion resistance than the dual-phase stainless steel and the Ni-based alloy.

a characteristic of additive manufacturing. It was also found that malleability was significantly improved, without reducing tensile strength, by heat-treating the material produced by additive manufacturing, which causes the Ni_3Ti to dissolve into the matrix phase. As shown in Fig. 5 (c), this is believed to be due to the precipitation of a fine ordered phase that has a high concentration of Ni and Ti with a size on the order of several tens of nanometers. That is, the microscopic precipitates act as only a weak impediment to the movement of dislocations.

The anodic polarization curves of the material produced by additive manufacturing before and after heat treatment were measured to study the effect of the above heat treatment on pitting corrosion resistance in a 3.5% solution of sodium chloride (NaCl) at 80°C. The results showed that heat treatment increases the pitting corrosion potential by 1.8 times, which rapidly increases the corrosion current density. It is believed that this is due to the greater uniformity associated with precipitate breaking down into fine particles as shown in Fig. 5 (c).

Fig. 6 shows a comparison of the tensile strength and pitting corrosion potential between the new alloy and conventional materials. This shows that the superior strength and corrosion resistance of the new alloy are superior to those of common corrosion-resistant alloys like dual-phase stainless steel and the Ni-based alloy. In addition to further improving the properties of the new alloy, Hitachi also plans to trial it in actual environments with a view toward practical applications.

CONCLUSIONS

This article has presented innovative functional materials developed by Hitachi, describing thermoelectric materials that convert unutilized thermal energy into electric power, new magnets that achieve high-efficiency in electric motors while using smaller amounts of rare earth metals, and a high-entropy alloy with high strength and corrosion resistance that is manufactured using a low-energy 3D printing process.

In the future, Hitachi intends to achieve green innovation by pursuing even higher performance in these materials.

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