

Fabrication of Carbon Nanowires without External Carbon Source

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- Self-regenerating material with electrical conduction and oxidation resistance -

Carbon nanowires are synthesized by various conventional methods, including mainly arc vaporization, laser vaporization, and chemical vapor deposition. However, all of these synthesis techniques require an extrinsic carbon source to supply carbon atoms to the substrate surface. As drawbacks, it is difficult to achieve uniform coating on materials with a complex surface configuration using growth methods that depend on an external carbon source, and if exfoliation occurs, no simple repair method is available.

In this research, we developed a new synthesis method and succeeded in fabricating the world's first carbon nanowires in the class of diameter: 1nm~100nm and length: 100nm to several μm , which are capable of self-regeneration and possess electrical conduction and oxidation resistance. In contrast to the conventional methods, the new method uses high-temperature bulk-to-surface precipitation of carbon atoms dissolved in the material itself, and thus does not require an external carbon source. This means that the growth of the carbon nanowires does not depend on the macro surface configuration, and if exfoliation from the surface occurs, it is possible to re-precipitate and grow the nanowires any number of times by performing heat treatment in a vacuum.

Observation with a scanning tunneling microscope (STM) showed that it is possible to fabricate carbon nanowires coexistent with the bottom surface of a single crystal graphite radical by preparing the (111) plane of a single crystal of nickel containing carbon atoms in solid solution, and precipitating the solute carbon to the surface by controlled heat treatment in an ultra-high vacuum (see figure). The surface shown in the figure is composed entirely of carbon atoms.

These carbon nanowires have electrical conductivity and are extremely stable, resisting oxidation when exposed to the atmosphere. In addition to single nanowires, a bundle structure of carbon nanowires was also observed. Similar nanowires were also found when carbon atoms were doped in polycrystalline nickel. At present, we are studying application to a variety of practical materials and hope to expand the uses of these nanomaterials to STM probes with oxidation resistance and a self-regenerating function, oxidation-resistant battery electrode materials, and ultra-high vacuum materials with a self-regenerating surface which resists gas adsorption.

(Previously reported in Jpn. J. Appl. Phys. Part 1 and the Japanese-language press including Nikkan Kogyo Shimbun, Japan Industrial Journal, Nikkei Sangyo Shimbun, and Kogyo Zairyo)

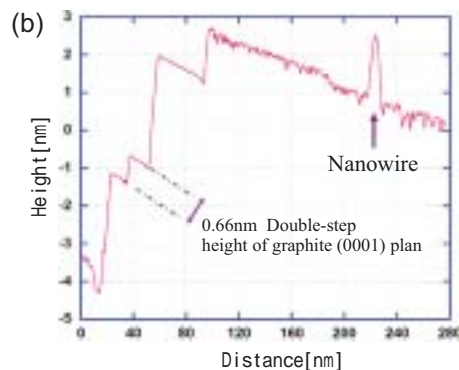
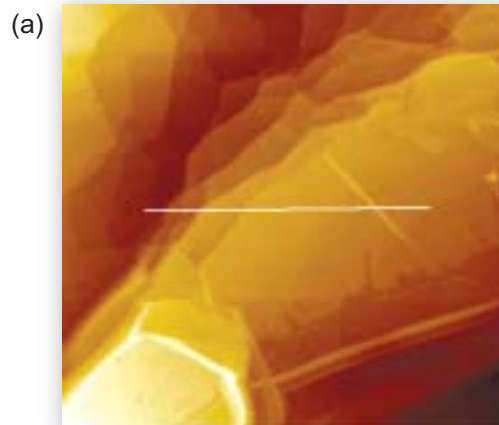


Fig.(a) STM image of bottom surface of graphite radical and carbon nanowires precipitated and grown on (111) plane surface of Ni doped with approximately 0.3at.% solid solution carbon by heat treatment under ultra-high vacuum, and (b) cross-sectional profile of area marked by white line in the preceding STM image.

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Creating Nanofibers from Fullerenes

- Fullerene nanowhiskers and nanofibers -

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Fullerene is name given to a type of hollow molecule with a closed cage shape, comprising 60 carbon (C) atoms in a spherical soccer ball-shaped C_{60} molecule, or so-called "bucky ball," with a diameter of approximately 0.7nm (nm = 10^{-9} m). (See Fig. 1.) Larger cage-shaped carbon molecules such as C_{70} , which consists of 70 carbon atoms, are called higher fullerenes. Since the discovery of C_{60} in 1985, a wide range of research has been carried out on C_{60} as new dream material. Studies have focused on the extremely hard property of the C_{60} molecule, which may surpass that of diamonds, the discovery of superconductivity and a high lubricating capacity, and

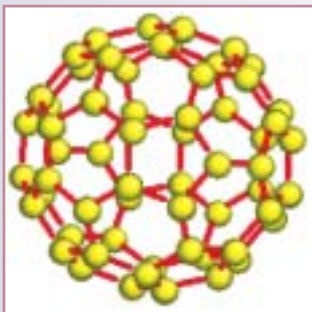


Fig.1 Schematic diagram of C_{60} molecule.

the formation of hydrogen compounds, and have included research on applications such as surface modification techniques and pharmaceuticals utilizing organic molecules, new semiconductors, etc.

In recent years, our group discovered a type of crystalline fiber (diameter of several 100nm or less; face-centered cubic structure and body-centered tetragonal structure) which is formed by C_{60} in a mixed solution of C_{60} and a colloidal solution of the ferroelectric ceramic lead zirconium titanate (PZT). We named this new material, which was detected by transmission electron microscope observation, the C_{60} nanowhisker. We also found that C_{60} nanowhiskers can be produced by the simple method of adding alcohol to an organic solution of C_{60} .

To produce nanowhiskers by this method, a basically equal amount of isopropyl alcohol was added gently to C_{60} -saturated toluene, and the resulting solution was allowed to stand in a cool environment of approximately 21 °C for several days or longer. An example is presented in Fig. 2(a), which shows the condition immediately after isopropyl alcohol was added to the C_{60} -saturated toluene solution. Short C_{60} nanowhiskers have formed near the interface between the toluene and the isopropyl alcohol. In Fig. 2(b), which shows the same solution after approximately 1 week, the C_{60} nanowhiskers have precipitated to the bottom of the glass bottle in a filamentous form. In Fig. 3, the C_{60} nanowhiskers have

grown to a fibrous shape, which can be called C_{60} nanofiber. Fig. 4 is a photograph of a sheet produced from C_{60} nanofibers. It was also possible to obtain C_{70} nanofibers in the same manner.

It is thought that similar fibers can be produced from fullerenes with metal atoms enclosed inside the fullerene structure (endohedral fullerenes) and fullerenes bonded with organic molecules. Using extremely fine fullerene fibers of nanometer-order diameter, a variety of novel resins, semiconductors, pharmaceuticals, and other materials with unprecedented performance are considered possible. Ultimately, the development of a number of new products is expected, including environmentally benign batteries and high sensitivity sensors and electronic devices.

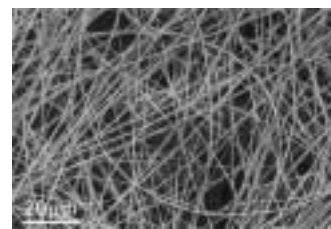


Fig.3 Scanning electron microscope (SEM) photograph of C_{60} nanofibers.

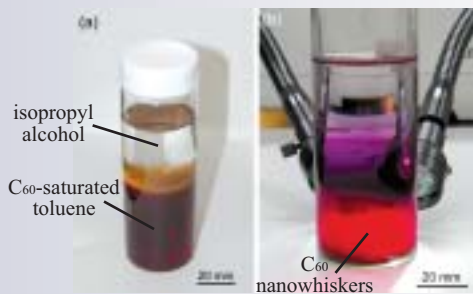


Fig.2 C_{60} nanowhiskers growth process.

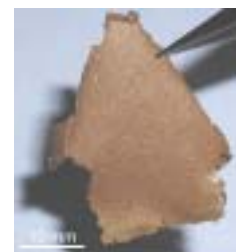


Fig.4 Sheet made from C_{60} nanofibers.

New Advances in High Strength Steel with Delayed Fracture Resistance

- Control of Ti carbides improves hydrogen trapping performance -

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One important task for realizing higher levels of strength in high strength steel is prevention of hydrogen-induced delayed fracture, which occurs when hydrogen in the service environment penetrates and accumulates in steel products such as bolts and mechanical parts.

Although various methods of suppressing delayed fracture have been proposed to the date with successful results, these conventional methods alone are insufficient to realize further increases in current strength levels. Therefore, a method of skillfully capturing and controlling the movement of intruding hydrogen by dispersing hydrogen trapping sites in steel material was recently considered.

The present research demonstrated that carbide particles in steel materials can be used as hydrogen trapping sites when an innovative heat treatment technique is applied to steel containing a small amount of added titanium, and further

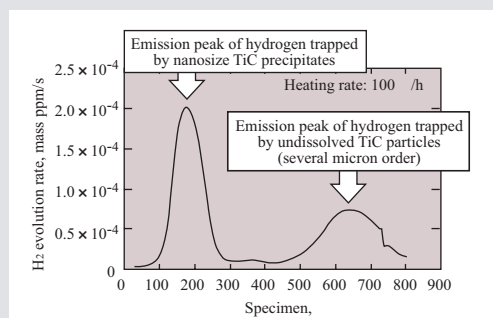


Fig. 1 Results of analysis of hydrogen elimination in heating of 0.42%C-0.30%Ti steel after tempering at 550 °C.

Elucidation of High-Temperature Ferromagnetism in Boron Compound

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In recent years, spintronics has attracted intense interest as a semiconductor technology which enables control not only of an ordinary charge, but also spin (magnetization). Considerable attention has been given to reports in Nature and elsewhere that CaB_6 boron semiconductors display high temperature ferromagnetism when doped with trivalent La (charge), even though all of the component elements are non-magnetic. The authors had doubts about the theoretical coherence of the explanation of this phenomenon, and therefore attempted a hypothetical verification.

The investigation was carried out by growing good quality $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ crystals and investigating their magnetization, as shown in Fig. 1. We obtained the magnetization curve shown by the green line in Fig. 2, and observed ferromagnetism in the La-doped CaB_6 is similar to that in previous reports. However, we also discovered that this ferromagnetism disappears completely when the crystals are washed lightly in hydrochloric acid, even though the La-doping is unaffected. An analysis of impurities showed that the La-doped specimen contained 0.010wt% Fe prior to washing in HCl, but after acid washing, this had decreased to less than 0.001wt%, and simultaneously, the material had lost its ferromagnetic property.

This clearly implies that the ferromagnetism described in previous reports was in fact caused by magnetic impurities. The 0.010wt% content of Fe prior to acid washing is at first glance a minute amount, but nevertheless is sufficient to account for ferromagnetism. In other words, the reported phenomenon can be explained convincingly by a mechanism in which Fe impurities aggregate and are electrochemically "plated" on to the crystal surface by the electrolytic reaction which occurs during the flux removal after crystal growth. This discovery also explains why ferromagnetism tends to be observed only in doped specimens. Because doping reduces electrical resistance, the plating reaction involving magnetic impurities proceeds more strongly in doped specimens, and as a result, ferromagnetism which is not intrinsic to the substance can be observed.

Based on similarities with the band structure of CaB_6 , CaB_2C_2 , which has a mixed layer of boron and carbon, was also expected to exhibit ferromagnetism, and experimental results

showing ferromagnetism have been reported in Science. To investigate this phenomenon, we developed a new synthesis technique using a tantalum-sealed container and successfully synthesized a specimen of pure CaB_2C_2 containing no detectable Fe. Contrary to previous reports, the magnetism of this pure CaB_2C_2 was found to be diamagnetic.

This research has solved the apparent mystery of high temperature ferromagnetism in boron oxides, and at the same time, demonstrates the importance of careful evaluation of impurities in specimens.



Fig.1 $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ crystals.

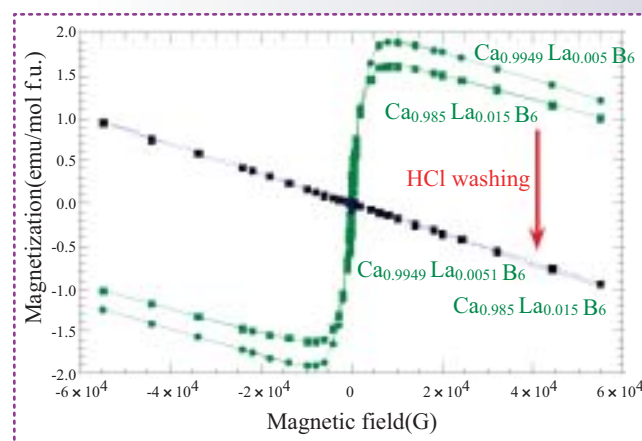


Fig.2 Magnetization curve of $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ crystals.

revealed the possibility that the hydrogen trapping capability of these particles can be controlled as required for specific applications.

Fig. 1 is a graph showing the hydrogen evolution rate during heating of a specimen containing artificially-introduced hydrogen. With conventional TiC particles, which are several microns in size, hydrogen evolution occurs only at temperatures of 500 °C and higher. However, with the heat treatment mentioned above, a hydrogen emission peak was observed not only at this temperature, but also in a comparatively low temperature range of 200 °C and under. This demonstrates that hydrogen trapping sites with different binding energy with respect to hydrogen exist simultaneously in the same material.

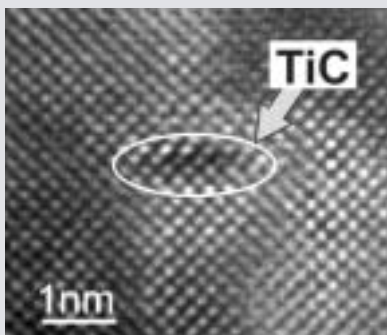


Fig. 2 High resolution electron microscope photograph of nanoscale Ti carbides.

Close observation with an electron microscope revealed high density dispersion of nanometer-scale TiC (approximately 2nm) in the heat-treated steel. This type of TiC is not found in the conventional steel, clearly suggesting that nano-scale TiC precipitates function as hydrogen trapping sites, corresponding to the low-temperature hydrogen emission peak in Fig. 1.

This research also showed that the binding energy of hydrogen with the hydrogen trapping sites can be controlled over a wide range by varying heat treatment conditions. This means that it should be possible to create steels with the optimum hydrogen trapping performance for specific service conditions by using various combinations of hydrogen trapping sites with different trapping capacities, providing a new technique for developing high strength steels with resistance to hydrogen-induced delayed fracture and further improving the strength of steel materials.

(Previously reported in the Japanese language press, including Nikkan Kogyo Shimbun, Japan Industrial Journal, Nikkei Sangyo Shimbun, Chemical Daily, and Science News.)

First Successful Synthesis of Co Oxide Superconductor

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Superconductivity is a phenomenon in which substances show zero electrical resistance when cooled to very low temperatures. Since first discovered in mercury in the 20th century, this phenomenon has been observed virtually in all metals. With the discovery of superconductivity in copper oxides in 1986, it became clear that superconductivity occurs not only in metals, but also in oxides, and furthermore, that oxides exhibit superconductivity at relatively high temperatures compared to metals. These findings attracted worldwide interests, generating intense activity which could be called "superconductivity fever." In the search for materials which show superconductivity at even higher temperatures, oxides of nickel and cobalt also drew attention, as these elements are close to copper in the periodic table and also have properties similar to those of copper. To date, numerous research projects have been carried out in the expectation that superconductivity phenomena similar to those observed in copper will also be found in nickel and cobalt oxides.

Using a sodium cobalt type oxide with a layered structure as a precursor, we applied a combined soft chemical process of partially extracting interlayer sodium ions and inserting water molecules into the interlayer spacing, resulting in the successful synthesis of a cobalt oxide with a CoO₂ interlayer distance twice as large as in the original material (Fig.1). Measurements of the

magnetic susceptibility (Fig.2) and resistivity of this cobalt oxide showed a clear evidence of superconductivity with a transition temperature of about 5K (-268 °C), making this the world's first cobalt oxide superconductor.



Fig.1 Crystallographic structure of precursor (Na_{0.7}CoO₂ (left) and newly-discovered Na_{0.35}CoO₂·1.3H₂O with superconductivity.

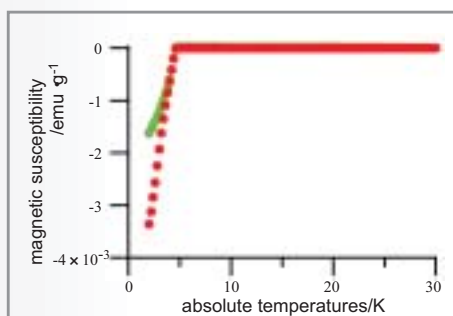


Fig.2 Magnetic susceptibility of Na_{0.35}CoO₂·1.3H₂O (Measured magnetic field, 20Oe. Red circles show the results of measurement of cooling in a zero magnetic field; green circles show cooling in magnetic field.)

At absolute temperatures of 5K and below, magnetic susceptibility shows a large minus value, indicating that this substance has achieved superconductivity.

One feature of the high-temperature copper oxide superconductors which first sparked "superconductivity fever" is their low dimensionality. In copper oxides, the CuO₂ plane plays an important role in superconductivity. Similarly, in the newly discovered cobalt oxide superconductor, the appearance of superconductivity can be attributed to the enhanced 2-dimensionality of the material, resulting from the expanded CoO₂ interlayer distance. On the other hand, one notable difference between copper oxide and cobalt oxide superconductors is the fact that copper atoms form a tetragonal lattice in the copper oxide superconductor, but in contrast, cobalt atoms form a triangular lattice. Thus, the comparative similarities and differences between these two superconductors are expected to provide useful suggestions for elucidating the superconducting structures of high temperature superconductors. Moreover, the discovery of superconductivity in a non-copper oxide material in the present work, together with the fact that soft chemical processes are a suitable method for synthesizing a diverse range of substances, is expected to contribute to the discovery of other new superconductors.

(Previously reported in the Japanese language press, including Asahi Shimbun, Mainichi Daily News, Sankei Shimbun, Japan Industrial Journal, Chemical Daily, Nikkei Sangyo Shimbun, and Nikkan Kogyo Shimbun.)

Joint Workshop with Max Plank Institute for Metals Research

On May 28-29, NIMS and Germany's Max Plank Institute for Metals Research (Max-Plank-Institut für Metallforschung: MPIMF) held the second in a series of workshops. The two institutes held the 1st Workshop in October of last year at MPIMF in Stuttgart, Germany based on a sister-institution agreement concluded earlier in 2002.

The 2nd Workshop was attended by the German Embassy's Councilor First Grade for Science, Technology, and the Environment, Dr. Mathis, as a guest, and featured presentations by six speakers from MPIMF and ten from NIMS. Spirited discussions covered a wide range of fields, from nanomaterials to biomaterials and computational material science. Following the conclusion of the workshop, NIMS conducted a tour of its facilities and equipment. Future workshops are to be held periodically, and are expected to lead to substantive joint research between the two institutes.



Publication of New Datasheets

NIMS is also contributing to the intellectual infrastructure by issuing a series of fatigue datasheets. The most recent are No. 91, on rolled steel for welded structures (SM490B), used in structures such as bridges and ships, which clarifies the fatigue properties of welded joints up to 10⁸ cycles, and No. 92, on titanium alloy (Ti-6Al-4V), which presents fatigue life properties in the ultra-high cycle region up to 10¹⁰ cycles (10 gigacycles).

Development of Novel Tissue Adhesive

- Realizes high bonding strength and low cytotoxicity -

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PRESS RELEASE

After surgical operations involving skin, organs, and blood vessels, the incision must be effectively closed. Although ordinary suturing thread is generally used to close affected parts, efforts have been made to develop a quick, simple closure method using tissue adhesives, and several types are already in clinical use.

As shown in Table 1, tissue adhesives can be broadly classified into three types. Of these, the cyanoacrylate type and gelatin-aldehyde type are artificial substances which are not naturally found in living organisms. Consequently, although these adhesives display high bonding strength, they have the drawback of high cytotoxicity. This is due to the fact that reaction products such as formaldehyde or glutaraldehyde delay the wound healing process. Conversely, the fibrin glue type has low toxicity, because the adhesive utilizes the blood coagulation process, but has the disadvantage of low bonding strength. Moreover, because blood is used as a material in manufacturing fibrin, the possibility of viral infection cannot be discounted.

Thus, the development of an adhesive which shows low toxicity toward living organisms while maintaining high bonding strength would solve a variety of clinical problems.

The Artificial Organ Materials Group therefore developed a new binary-type adhesive which consists of a hardening agent, or crosslinker (citric acid derivative: CAD) and a naturally-derived high polymer adhesive component (collagen or gelatin). The crosslinker is a low molecular weight compound in which the carboxyl groups in citric acid is modified with electron attracting groups. This material has the advantageous property of being metabolized by citric acid cycle in the body.

The bonding strength of the developed adhesive was investigated using porcine soft tissue. Fig. 1 shows the bonding strength when two tissue specimens were bonded with the adhesive. The bonded tissue showed substantially the same bonding strength (tearing) as the original tissue. Observation of the tissue in the vicinity of the adhesive interface revealed that the adhesive had penetrated

the tissue and also bonded by reaction with protein in the tissue (see cover, lower photograph).

Next, it was necessary to verify the safety of the adhesive. The results of toxicity tests using mouse fibroblast showed less than 1/10 the toxicity level of currently-used gelatin-aldehyde type adhesives.

Tissue adhesives offer several important advantages. If wounds from surgical operations can be closed with a tissue adhesive, the procedure itself is simplified, and post-operative removal of sutures is no longer necessary. Thus,

adhesives can shorten the total surgical time, alleviate the physical and economic burden on patients, and simplify post-operative management. Research on the newly developed material, aiming at clinical application, is now underway in cooperation with the Medical Department of Tsukuba University.

(Previously reported in the Japanese language press, including Nikkan Kogyo Shimbum, Japan Industrial Journal, Nikkei Sangyo Shimbum, Japan Economic Times (Nikkei Shimbum), Yomiuri Shimbum, Chemical Daily, and Science Times.)

Adhesive type	Bonding strength	Cytotoxicity
Cyanoacrylate type	Strong	High
Gelatin-aldehyde type	Strong	High
Fibrin glue type	Weak	Low
Developed adhesive	Strong	Low

Table.1 Features of current ly-used and newly developed tissue adhesives.

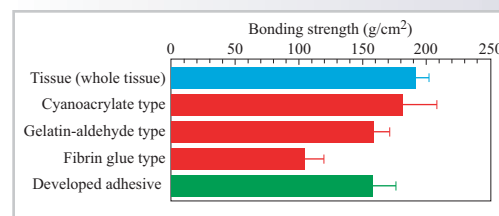


Fig.1 Bonding strength of new tissue adhesive in test with porcine soft tissue.

Launch of 1st NIMS Authorized Venture Business

In January 2003, NIMS created the "NIMS Venture Business Support System" to support venture businesses in developing and commercializing practical applications for research results achieved at NIMS, and in particular, to encourage the creation of venture businesses by NIMS researchers. Support includes access to research facilities and equipment on a fee-charged basis and preferential treatment in licensing of patent rights. On May 20, a group led by Director Kenji Kitamura of the Advanced Material Laboratory established a new business called Swing Co., Ltd., which was approved as the 1st NIMS venture business under this support system.

SWING plans to manufacture and market optical equipment and ceramic products for optical applications developed at NIMS, and is projecting sales of ¥6 million in its first year (FY 2003).

All New Look for the NIMS Homepage!

In July, the NIMS public homepage will undergo a complete revamping, including a review of Web contents and a makeover of the top page design for easier understanding and viewing. The English version will also be expanded, giving NIMS a more global reach and openness to researchers around the world. In the future, we will continue to develop new ideas that provide timely information in an easy-to-use homepage format. Please visit us at <http://www.nims.go.jp/>.

New Materials Databases Now Available from NIMS

As part of our commitment to improving the technical and intellectual infrastructure, NIMS now provides a variety of databases which are expected to be useful in new material development. Information includes 11 categories in three database fields, structural material DB, DB for various material properties, classified by material, and high function material DB. All can be accessed via the Internet, as the NIMS Material Database, at <http://www.nims.go.jp/>.

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