NIMS NOW

National Institute for Materials Science

Vol.2 No.2 February, 2004 English Edition

SPECIAL FEATURES

Progress in Nanostructure Analysis Techniques

Nanostructure of SmCo Permanent Magnets

Tadakatsu Ohkubo
Metallic Nanostructure Group
Materials Engineering Laboratory (MEL)

SmCo-based permanent magnets were first developed in the 1970s. It has recently attracted renewed interest, particularly as materials for application in sensors, motors, and other devices used in the high temperature region, because of the high Curie temperature, low temperature dependence of the remanance, and good corrosion resistance in comparison with NdFeB magnets. Although considerable research has already been done on the effects of chemical composition and heat treatment on magnetic properties, the mechanism of the coercivity increase during slow cooling in the final stage of heat treatment has not been clarified.

Therefore, we studied the nanostructure of sintered $Sm(Co_{0.72}Fe_{0.20}Cu_{0.055}Zr_{0.025})_{7.5}$ permanent magnets obtained by different cooling processes using the 3-dimensional atomic probe technique, which enables direct observation of the atomic distribution, and the transmission electron microscope, which is capable of structural observation and analysis on the nano scale.

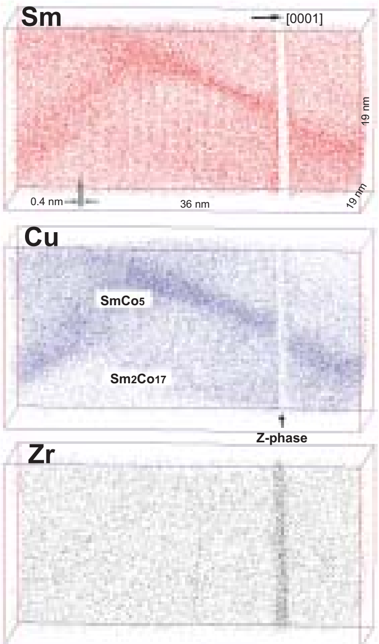

Fig. 1 Three-dimensional elemental map of Sm, Cu, and Zr obtained by atom probe technique (points indicate the positions of individual atoms detected).

As shown in **Fig. 1**, the Cu concentration increases during slow cooling in the cell boundary phase ($SmCo_5$ phase) which contains a large amount of Sm and Cu, and the Cu concentration profile is wider than that of Sm. This result is also supported by calculations by Koyama et al. of the Computational Materials Science Center. It is thought that this change in concentration distribution is the underlying cause of improvement in magnetic properties in the slow cooling process.

Several structures models have been proposed for the plate-like precipitates (Z phase) as observed in **Fig. 1**. However, based on the atom probe composition analysis and high resolution electron microscope observation, as shown in **Fig. 2**, it was confirmed that the $Zr(Co,Fe)_3$ precipitate has the Be_3Nb structure with a≈0.5 nm, c≈2.4 nm, in which Sm is replaced by Zr during slow cooling.

Information obtained by this type of nanostructure analysis is being fed back to material development, and is expected to contribute to more compact and thinner devices.

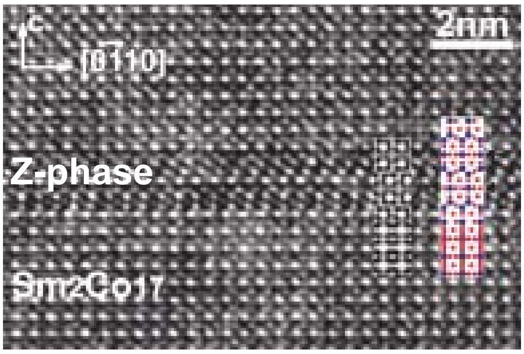

Fig. 2 High resolution electron microscope image from Sm_2Co_{17} (matrix) and Z-phase.

In this issue

NIMS NEWS

1st International Symposium on Nano-Characterization and Technology

< Continued on p.3

Characterization of Nano-scale Precipitates in Magnesium Alloys

D. H. Ping
Metallic Nanostructure Group
Materials Engineering Laboratory (MEL)

Magnesium (Mg) alloys have shown potential applications in the automotive, communications and aerospace industries due to it's light weight, which is about two third of aluminum and one quarter of iron. In order to improve the creep resistance and yield strength for real applications of existing Magnesium alloys and to develop new alloys, it is necessary to have a better understanding of the microstructural evolution and strengthening mechanism.

Recently, we have successfully applied three-dimensional atom probe (3DAP) technique, which enables the observation of individual atoms, to both conventional Mg alloy and nanocrystalline Mg alloy, and characterized the structure and chemical composition of nano-scale precipitates combined with transmission electron microscopy.

Fig. 1a is a high-resolution electron microscopy (HREM) image of a nano-scale Mg-Y-Zn precipitate with a 6-layer periodic stacking-fault-like structure, which formed in 2H-Mg matrix grains of a high-strength nanocrystalline $Mg_{0.97}Y_{0.02}Zn_{0.01}$ alloy. **Fig. 1b** is the 3DAP analysis results obtained from the nano-scale precipitates. The elemental mapping (the upper part of **Fig. 1b**) shows the Y and Zn atoms are periodically enriched in very narrow layers (one or two atomic layers). The concentration depth profile shown in **Fig. 1b** (lower part) gives a quantitative result of the enrichment.

The evident strengthening effect and creep resistance improvement of rear earth (RE) addition on Mg alloys was achieved due to fine precipitates. Aging hardening behavior occurred in some RE-added Mg alloys. In Mg-RE-Zn-Zr alloys, a high number density of uniformly dispersed disc-like fine precipitates formed after annealing. **Fig. 2a** shows a HREM micrograph of one of the precipitates, which was identified as an ordered G.P.-zone (fine precipitate with a regular arrangement of atoms). The distinguishable contrast is caused by the segregation of RE and Zn elements to a single layer of the basal plane of the α-Mg matrix phase. **Fig. 2b** gives the elemental mappings around the ordered G.P.-zone, in which the basal plane of the α-Mg matrix phase is clearly resolved. It is clear that the RE and Zn atoms are segregated at one atomic plane (the basal plane), and the quantitative concentration of the enrichment is also given in **Fig. 2b**.

Since the physical and mechanical properties of alloys are closely related to the nano-scale structure, the 3DAP technique is expected to make an important contribution in the development of new alloys.

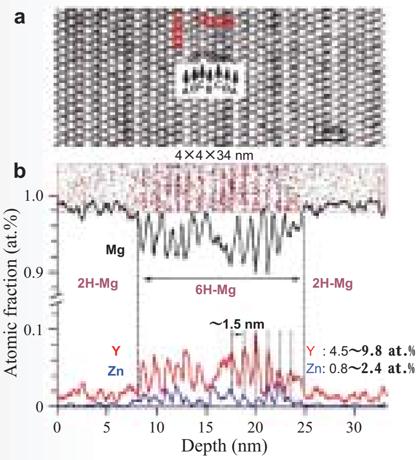

Fig. 1 (a) HREM image of the nano-scale precipitate with 6-layer periodic structure, (b) 3DAP analysis results (atomic map, compositional profiles).

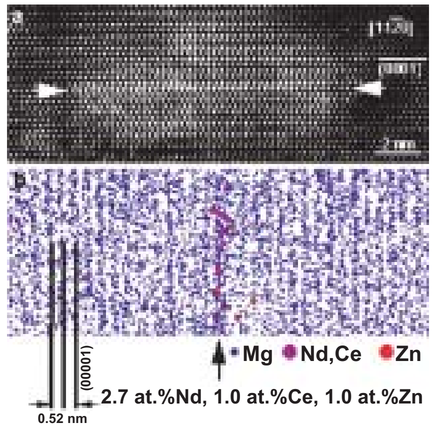

Fig. 2 (a) HREM image and (b) atomic map of an ordered G.P. zone.

Development of High Strength Heat Resistant Steel by Nanoprecipitate Design

Masaki Taneike
Fujio Abe
Heat Resistant Design Group
Steel Research Center

Further improvement in the generating efficiency of thermal power plants has been strongly required worldwide in recent years, both for resource saving and for CO_2 emission reduction as a measure to prevent global warming. Because high temperature/high pressure steam is an essential requirement for increasing generating efficiency, the development of ferritic-type heat resistant steels which can withstand these high temperature conditions has become an important problem.

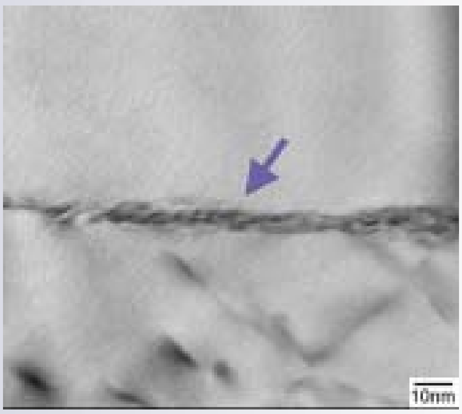

Fig. 1 Arrangement of nano-size vanadium nitride precipitates.

Since its inception in 1997, the STX-21 Project (Ultra-Steels) has vigorously promoted research in this area, and has proposed a large number of innovative alloy design guidelines. In practical applications, these high temperature steels must display adequate high temperature strength over a period of 100,000 hours (approx. 11 years, 5 months), which corresponds to the use period in actual steam turbines. In the present research, we succeeded in developing a new heat resistant steel which displays excellent high temperature strength at 650 ℃ up to the equivalent of 100,000 hours based on the alloy design guidelines obtained to date combined with alloy microstructure control, ensuring long-term high temperature strength.

The strength of this ferritic high temperature steel is increased by dispersion of fine particles in the steel structure. Conventional steels are strengthening mainly by dispersion of carbides with a size on the order of 300 nm. In contrast, in the developed steel, carbides were eliminated by absolutely minimizing the carbon content, and strengthening was obtained by dispersion of extremely fine vanadium nitrides (grain size: several nm; see **Fig. 1**), which possess excellent high temperature stability. Thus, nano-level microstructure control makes it possible to maintain high temperature strength over an extended period of time (**Fig. 2**).

Structure and Magnetic Properties of FePt Nano-granular Thin Film

Yukiko Takahashi
Metallic Nanostructure Group
Materials Engineering Laboratory (MEL)

With popularization of the personal computer, internet communications involving large volumes of data have become extremely common. Various storage technologies are used to accumulate such large quantities of data, including semiconductor, optical, and magnetic devices. Among these, magnetic recording has become the principal method, as it offers a combination of large capacity, high speed, and low cost.

To store large volumes of data on a limited area, it is necessary to refine the grain size of the ferromagnetic phase where data are stored to the nano-scale size. However, ferromagnetic phase particles have already been refined to a size where they are influenced by thermal disturbances, as expressed by k_BT. The FePt phase, which is an ordered structure ($L1_0$ structure) with large magnetocrystalline anisotropy energy, has attracted attention as the key to a next-generation magnetic recording medium, but in spite of this interest, some method of achieving a fine-grained dispersed structure and orientation suitable for the recording method is still required for practical applications.

Fig. 1 and **Fig. 2** show electron microscope images of thin film of FePt with a thickness of 10 nm, which were fabricated on an MgO single crystal substrate. The film contains dispersed FePt grains with a facet structure and size on the order of 50 nm. These FePt grains have formed by epitaxial growth at the c plane, which is a prerequisite for perpendicular magnetic recording. As shown in **Fig. 3**, with this thin film, a strong magnetic field of more than 50 kOe is required for magnetization saturation, but it would be absolutely impossible to write data with a magnetic field of this strength using existing technology. We overcame this difficulty and succeeded in magnetizing these FePt particles with no large reduction in anisotropy by capping amorphous Al_2O_3 on the FePt grains.

We have also developed a nano-composite thin film magnet which possesses magnetic properties superior to those of rare earth magnets by exchange bonding of Fe, which has a high saturation magnetization, and FePt, which displays large anisotropy.

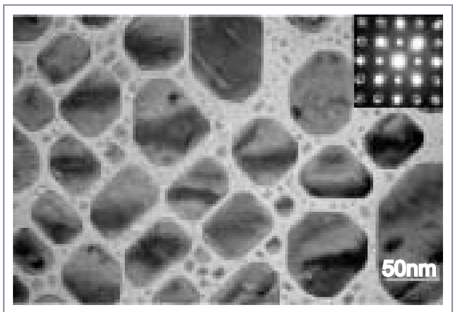

Fig. 1 Electron microscope image of thin film with island-shaped FePt.

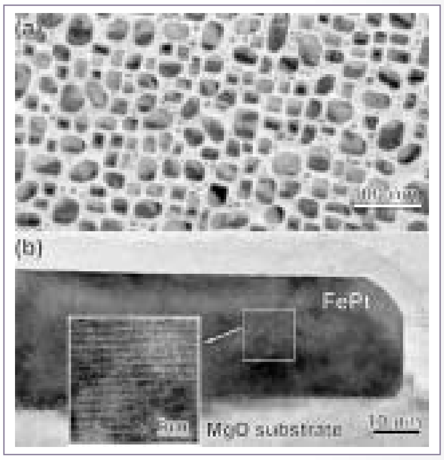

Fig. 2 Electron microscope images of self-assembled FePt particulate film, (a) in-plane and (b) cross section.

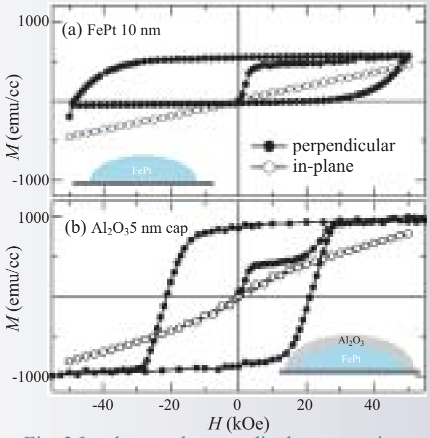

Fig. 3 In-plane and perpendicular magnetization curves of island-shaped FePt thin film (a) without Al_2O_3 capping, and (b) with Al_2O_3 capping.

The developed steel also offers advantages for practical applications because expensive alloying elements and special manufacturing processes are not required.

In the future, we plan to investigate material properties such as weldability and oxidation resistance, which are required for application to large-scale structures, in various steel grades in cooperation with industry with the aim of early practical application. (These research results have been published in *Nature*, 2003, *424*, No. 6946, July 17, and in Japanese-language newspapers including the *Asahi Shimbun*, *Sankei Shimbun*, *Nikkan Kogyo Shimbun*, *Japan Industrial Journal*, *Nikkei Sangyo Shimbun*, *Chemical Daily*, *Japan Metal Daily*, *Science News*, *Ibaraki Shimbun*, and *Denki Shimbun*.)

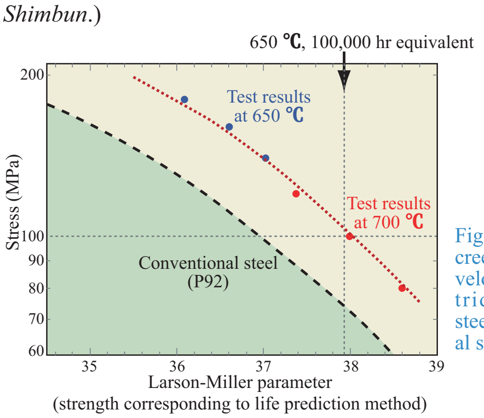

Fig. 2 Comparison of creep strength of developed steel (nanonitride-strengthened steel) and conventional steel (P92).

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1st International Symposium on Nano-Characterization and Technology

From "Seeing is Believing" to "Seeing is Creating"

The 1st International Symposium on Nano-Characterization and Technology (ANCT 2003) was held from November 11 to 14 at the NIMS Sengen Site. The symposium, which was devoted to "active nano-characterization technology" as a new method of nano-characterization representing a fusion of nanomaterial creation and functional evaluation, included a number of distinguished invited researchers who are active in the front lines of frontier fields of nano-characterization such as transmission electron microscopy (TEM), scanning tunneling microscopy (STM), non-contact atomic force microscopy (NC-AFM), near-field scanning optical microscopy (NSOM), and nanometer x-ray analysis using synchrotron radiation. In addition to the keynote address, invitational lectures, and a poster session, the symposium also featured displays by a number of private companies. Discussion and exchanges of ideas among researchers from universities, independent administrative institutes, and the private sector were particularly spirited.

Nanocrystallization in Amorphous Alloys

—High Spatial Resolution Element Mapping by STEM—

Eiji Abe
A. P. Tsai
Aperiodic Materials Group
Materials Engineering Laboratory

Because the transmission electron microscope (TEM) enables direct observation of the atomic configuration in solids, it is the most effective technique for understanding the atomic configuration in the aperiodic structure region where materials do not display periodicity, for example, in local defect structures. In recent years, the annular dark field scanning transmission electron microscope (ADF-STEM; refer to NIMS NOW English Edition, Vol.1 No.1 April 2003, p. 4), which uses a finely-focused electron beam of atomic level order (diameters as small as 0.1 nm) as the scanning probe, has drawn attention as a novel method of obtaining information on local structures which had been difficult with the conventional high resolution electron microscope. This paper demonstrates a representative application of ADF-STEM.

It has been reported that the strength of amorphous (random atomic configuration) $Al_{87}Ni_{10}Ce_3$ alloys produced by the rapid-solidification process can be improved dramatically by applying short-time heat treatment to promote high density precipitation of Al crystal grains. However, a detailed understanding of the distribution of nanoparticles and added elements is indispensable for elucidating the strengthening mechanism. The figure at the left is a conventional type of high resolution TEM image called a phase contrast image, which was obtained from a specimen of this nanocrystal. In comparison with the amorphous matrix, nanocrystal grains can be identified as regions which show the characteristic contrast of a periodic crystal lattice, as can be seen in the area in the yellow circle in the figure. However, these areas are difficult to distinguish at a glance.

Using an ADF-STEM, the authors mapped the intensity of electrons with high scattering angles from various probe positions (within a certain fixed angular range), as shown in the image in the center. Because the intensity of high-angle scattered electrons is basically proportional to the square of the atomic number (Z), the image contrast is brighter at the positions of heavy atoms, i.e., with higher Z. This type of mapping is called a Z contrast image. As this alloy is composed of Al (Z = 13), Ni (Z = 28), and Ce (Z = 58), nanograins of Al, which is the lightest element, are immediately recognizable as dark regions in the image. In particular, we would like to draw the reader's attention to the small, extremely bright points (e.g., positions indicated by arrows) observed in the amorphous structure. Because Ce has a markedly larger atomic number than Al and Ni, these points are considered to be individual Ce atoms. The image at the right was obtained by preliminary statistical processing of the intensity distribution of the Z contrast image. Weak intensity areas are shown in green and strong areas in red, providing a good approximate representation of the distribution of Al nanograins and Ce atoms.

As an additional advantage of the ADF-STEM method, spectral analysis can be performed simultaneously with imaging, making it possible to obtain a more detailed understanding of element distribution and chemical bonding states. Thus, this method has high potential for future development as a comprehensive method for characterizing local structures in nanomaterials.

Phase contrast image   Z contrast image

2 nm   2 nm   2 nm

Fig. High-resolution TEM image obtained from specimen of amorphous $Al_{87}Ni_{10}Ce_3$ alloy heat treated at 230 ℃ for 5 min. A fine structure has formed, which contains Al crystal grains with diameters on the several nanometer order dispersed with high density in the amorphous matrix.

NIMS Forum 2003

NIMS Forum 2003 was held on Friday, November 21 at the Tokyo Big Sight International Exhibition Center, following a similar meeting last year. The forum is sponsored jointly by NIMS and the Nikkan Kogyo Shimbun to publicly announce advanced research at NIMS, encourage technology transfer, and promote cooperation and exchanges with industry.

The first session of the forum featured announcements by NIMS' Director-General of each unit on representative research topics such as the development of ultra-high temperature materials and application of strong magnetic field technology to biotech and environmental problems. The second session focused on technology transfer-related topics, and included an explanation of technology development at NIMS and presentations on research topics with a high potential for technology transfer. A total of 14 oral presentations were given. Other activities included a 50-topic poster display section, demonstrations of NIMS material databases, and a technology transfer consulting area.

The conference concluded successfully with total attendance of 460 persons, mainly from private-sector companies, and 600 consultations, including joint poster displays. In particular, the high level of communication among participants showed strong interest in transfer of NIMS research results.

NIMS will continue to put great effort into technology transfer through this forum in order to encourage commercialization of useful products based on the results of advanced research.

Biomimetic Design of Materials with Tunable Wavelength Reflectance

—Application for Chemical Sensor Using Change of Structural Color in Novel Materials—

Hiroshi Fudouzi
Intelligent/Smart Materials Group
Materials Engineering Laboratory (MEL)

Younan Xia
Associate Professor, Dept. of Chemistry
University of Washington

Structural colors and their color phenomena are known to exist in nature. The structural colors do not depend on pigments or luminescence. One typical example is Bragg diffraction, which occurs due to the periodic structure of the refractive index in the light wavelength range and can be observed in the shell of the jewel beetle (*Chrysochroa fulgidissima*), wings of the Morpho butterfly, peacock feathers, and opals. The tropical blue damselfish, which is known for the beauty of its cobalt-blue coloration, is another example. The coloration of this tropical fish changes depending on the surrounding environment. As shown in **Fig. 1A**, the cytoplasm, which has a low refractive index, contains a regular arrangement of nanosize reflectance plates with a high refractive index. The structural color changes instantaneously when the spacing between these plates expands or contracts.

Based on this behavior, the authors created a novel material which shows biomimetic changes in structural color (**Fig. 1B**). This new material is a composite with a high periodic structure, in which colloid particles are closely packed and silicon gel is filled with the gaps between particles. The material displays structural color due to Bragg diffraction of light in visible wavelength. This structural color can be designated wavelength and also be controlled by varying the spacing in the lattice plane (**Fig. 2**). Silicon gel swells in the presence of a solvent, and its volume increases. As a result, the spacing of the lattice plane increases, and the wavelength of the structural color shifts to the longer wavelength side. Conversely, the silicon gel shrinks when the solvent evaporates, and the structural color then returns to its original state.

The specimen in **Fig. 3A** is a composite consisting of polystyrene particles with a diameter of 202 nm, and was formed as a thin film (thickness: approx. 50 μm) on a silicon wafer. In air, the structural color of the thin film is green. However, when the film is immersed in volatile silicon oil in a beaker, its structural color changes to red. When the film is lifted from the beaker and the solvent evaporates, the structural color returns to the original green. These changes in structural color were measured from their reflected spectra, with the results shown in **Fig. 3B**. The wavelength of light attributable to Bragg diffraction was 550 nm before swelling and 658 nm after swelling. **Fig. 3C** shows a thin film composed of polystyrene particles with a diameter of 175 nm, which displays a purple structural color. Droplets of two kinds of silicon oil were used to induce swelling of the thin film, causing the structural color to change to sky blue and green, respectively. Because swelling ability of the material differs from solvents, one can observe changing structural color depending on the type of solvent. This material can be expected to application as a simple chemical sensor which enables visual judgment in a manner similar to litmus paper.

(These research results have been published in part in *Advanced Materials* and *Langmuir*, including use of photos on the cover of *Adv. Mater*. 2003, *15*, No.11.)

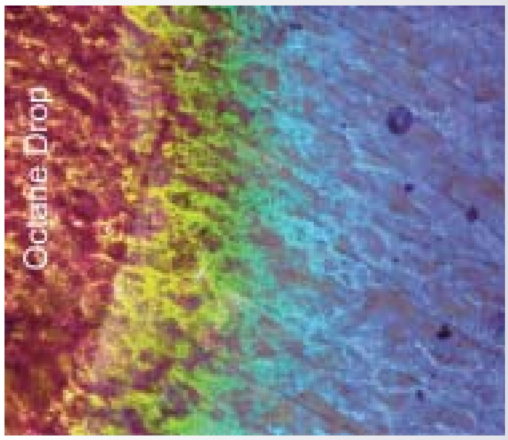

Fig. 2 Optical microscope image of novel material with tunable structural color. The material was swollen with octane liquid. Then the photo was taken with a CCD camera during evaporating the liquid.

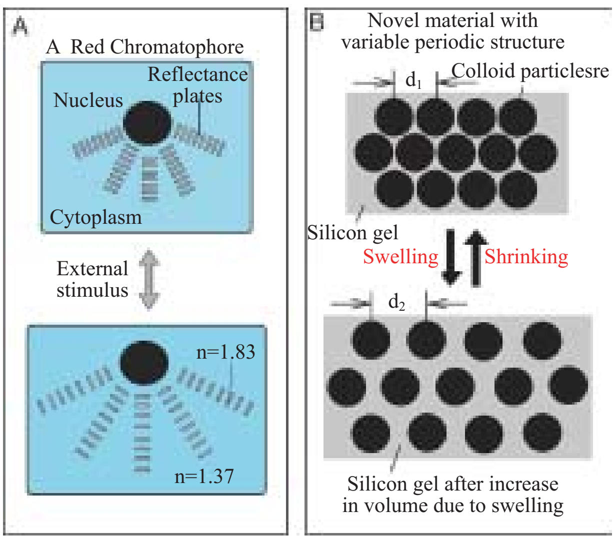

Fig. 1 A: Model of structural color change in blue damselfish (schematic illustration prepared based on commentary on motile red chromatophores by Dr. Ryozo Fujii, Toho University), B: Schematic diagram of material showing change the spacing in the lattice plane (particle spacing expands from d_1 to d_2 due to swelling).

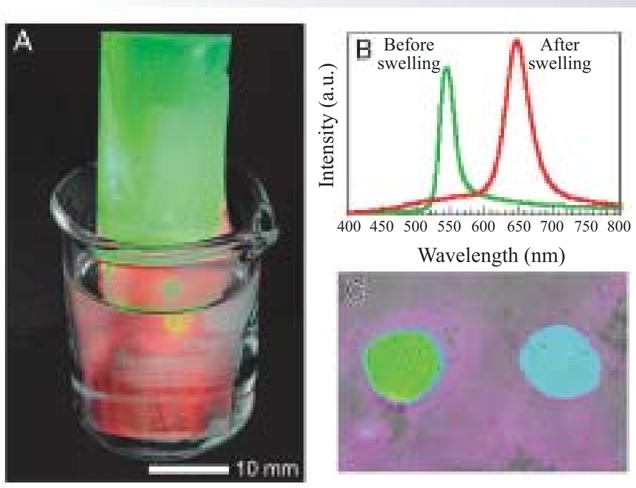

Fig. 3 A: Structural color of material is green in order to Bragg diffraction. The part immersed in solvent (silicon oil) changes to red. B: Comparison of reflected spectra in respective states. C: Material displays different structural colors when exposed to different silicon oil solvents. The original structural color is purplish, but changes to either green or sky blue.

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