NIMS NOW

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RESEARCH FRONTLINE

New Cooling Technology

—Successful practical application of ceramic magnetic regenerator material—

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Typical examples of superconductors in familiar applications include MRI (magnetic resonance imaging) devices, which play an important role in medicine in clinical image diagnosis. Superconductor magnets capable of generating a powerful magnetic field are widely used in MRI. However, because cooling to a cryogenic temperature of 4K is required, expensive, hard-to-handle liquid helium must be used as a coolant.

To solve this problem, a 4K gas refrigerator was developed, enabling direct cooling of superconductor magnets without use of a coolant. The gas refrigerator utilizes a device called a regenerator, which temporarily stores cold, making it possible to generate cryogenic temperatures without a large compressor. The deciding factor in the performance of the regenerator is a substance called regenerator material, which is used to fill the regenerator and must possess a large volumetric specific heat.

Conventionally, lead (Pb) has been used in cyrocoolers. However, as shown in Fig. 1, the volumetric specific heat of Pb decreases to substantially zero at below 10K, making it impossible to reach temperatures as low as 4K with this type of gas refrigerator. Rare-earth intermetallic compounds such as $HoCu_2$ have been developed to compensate for this problem, but these substances also show a decrease in specific heat at sub-4K temperatures, and thus cannot meet the requirements of higher-performance refrigerators.

The Strong Magnetic Field Research Group began development of a new-generation regenerator material with the aim of achieving a broad improvement in 4K refrigerator performance and successfully developed a practical material. The developed regenerator material uses the oxide magnetic materials $GdAlO_3$ and Gd_2O_2S which, as shown in Fig. 1, have a high volumetric specific heat in the range of 4K-5K, at more than two times that of conventional regenerator materials in the same temperature range.

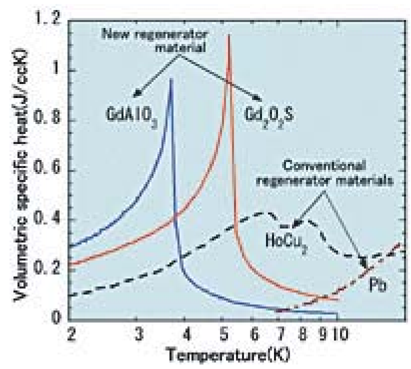

Fig.1 Comparison of volumetric specific heat of conventional regenerator materials and newly developed ceramic magnetic regenerator material.

If a large specific heat value were the only requirement, a number of substances could be used. However, very few substance can meet all the conditions required in a regenerator material, which include stable specific heat in a magnetic field, workability, strength, hardness, thermal conductivity, chemical stability, and economy. For this reason, intermetallic compounds have been used to date. Noting the properties of excellent oxide-type magnetic materials, we produced substances of this type in the form of polycrystalline ceramics. The resulting regenerator material shows excellent properties at 4K.

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NIMS NEWS

Science & Technology Week Events

As in past years, a nationwide, week-long series of science- and technology-related events was held under the name of Science & Technology Week, which includes Invention Day (April 18). NIMS participated in these events through a variety of activities, including the following.

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In this issue

Development of High Temperature Nickel-Base Superalloy with 1100℃ Heat Resistance

—Meets the goal of High Temperature Materials 21 Project—

Yutaka Koizumi
High Temperature Materials Group
Materials Engineering Laboratory

Gas turbines engines are an indispensable technology and are widely used in power plant, jet engines, and other applications. Recently, development of higher efficiency gas turbines has been desired as one means of achieving a substantial reduction in CO_2 emissions. Since fiscal year 1999, NIMS has been involved in the development of a variety of refrectory materials, including nickel (Ni)-base superalloys, ceramics, and high melting point superalloys, as part of the "High Temperature Materials 21 Project" in the NIMS 5 Year Plan. The practical aim of this project is to improve the thermal efficiency of turbines by enabling operation at higher turbine inlet gas temperatures.

As a result of joint research with Ishikawajima-Harima Heavy Industries, NIMS has succeeded in developing a nickel-base single crystal (SC) superalloy, TMS-162 alloy, which boasts the world's highest service temperature of 1100℃(creep life of 1000 hours at stress of 137MPa). Use of this alloy in combination with a thermal coating and air cooling is expected to lead to the development of an LNG (liquefied natural gas)-fired ultra-high efficiency combined cycle power generation technology, with a total thermal efficiency exceeding 60%, and the development of a jet engine for use in Japanese-manufactured aircraft.

The alloy design of this material was based on the generation 4 TMS-138 alloy, which has had the highest service temperature to date. The alloy was strengthened by increasing the amount of molybdenum (Mo) addition, resulting in refinement of the interfacial dislocation network which forms at the coherente interface between precipitates and the matrix in alloys (see Fig. 1), together with increased ruthenium (Ru) addition to stabilize the microstructure. Creep tests were conducted at test temperatures of 800〜1100℃ and stress of 137〜735MPa. As shown in Fig. 2, the time to 1% creep deformation at 1100℃ and 137MPa was more than 730 hours with the new superalloy, providing a creep life approximately 5 times longer than that of the generation 3 alloy CMSX-10, which is applied practically in new type jet engines, and 2.5 times longer than that of the generation 4 alloy TMS-138.

The newly developed Ni-base single crystal superalloy TMS-162 can be considered a generation 5 superalloy, and has the world's highest temperature capability, achieving the development objective for Ni-base superalloys in this project.

(These research results have also been presented in various newspapers, including the Nikkan Kogyo Shimbun, Japan Industrial Journal, Nikkei Sangyo Shimbun, Science News, and Japan Metal Daily.)

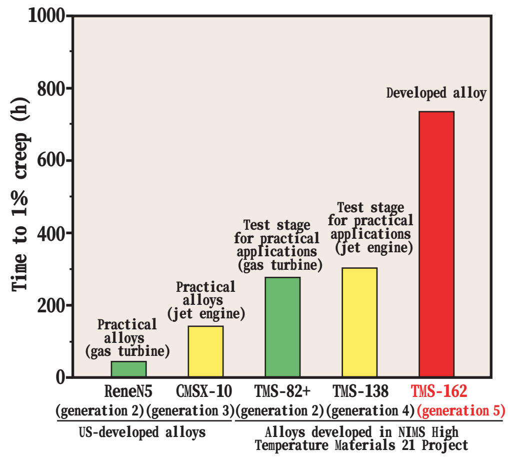

Fig.2 Time to 1% creep with developed alloy TMS-162 . (At 1100℃, 137MPa, the time to 1% creep deformation is excellent, at approximately 5 times that of the practical alloy CMSX-10.).

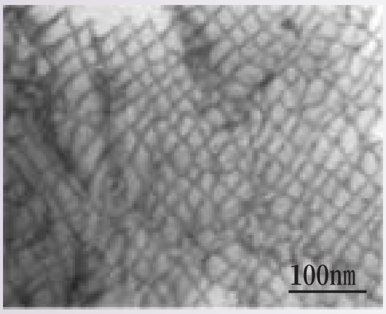

Fig.1

Transmission electron micrographs of TMS-162, which is strengthened by refining the interfacial dislocation network between precipitates and the matrix to 25nm (same value is 60nm in TMS-138).

Development history of Ni-base single crystal superalloys:
Beginning with the generation 1, which did not contain rhenium (Re), the microstructure was progressively improved in the generation 2 (3% Re), generation 3 (5〜6% Re), and generation 4 (generation 3 + platinum group elements). With each new generation, the service temperature increased by approximately 20〜25℃.

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New Cooling Technology

Fig. 2 shows a Gd_2O_2S ceramic magnetic regenerator material after surface polishing and granular processing. The newly developed material has been evaluated in Japan, the US, and various European countries, demonstrating an improvement of 20% or more in 4K refrigeration capacity. It has already passed reliability tests of 6 months or more in commercial refrigerators, and full commercialization is foreseen during fiscal year 2003. Within several years, the magnetic regenerator material developed by this NIMS research group is expected to see application in MRI devices worldwide, supporting wider use of superconductor technologies in general.

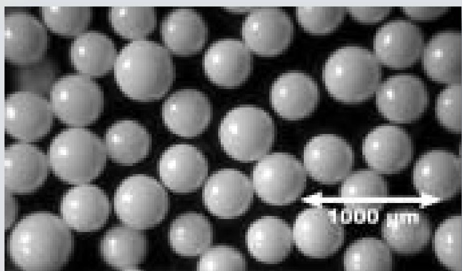

Fig.2 Ceramic magnetic regenerator material (Gd_2O_2S) (average grain size: 400 μm).

Success in Downscaling Nanostructure Fabrication Using Electron Beam Induced Deposition

—Fabrication of world's smallest nanostructures using electron beam—

Kazutaka Mitsuishi
Masayuki Shimojo
Kazuo Furuya
Nano Characterization Group
Nanomaterials Laboratory (NML)

To date, wide-ranging research on local vapor deposition of metals has been carried with a variety of metals. In this method, an organometallic gas is passed over the surface of a deposition substrate, and the gas is decomposed by irradiation with an ion or other particle beam or electron beam. In most cases, scanning electron microscopes with acceleration voltages of no more than 30kV have been used. Research has rarely been performed using higher acceleration voltages due to the effect of the gas flow in the vicinity of the plate in the high-voltage section of the electron gun where the electron beam is generated and accelerated. Moreover, up to the present, decomposition of the organometallic gas has been attributed to secondary electrons which are excited in the material by irradiated electrons, and distribution to the sub-15nm region has therefore been considered impossible.

The device employed in the present research was a 200kV field-emission type transmission electron microscope with an improved gas feed system which makes it possible to introduce very minute quantities of gas in the vicinity of the specimen. By using this device and reducing the diameter of the electron beam to suppress the spread of secondary electrons, the authors succeeded in producing a significantly smaller nanostructure, with a size greatly exceeding the conventional limits.

Examples are shown in the figures at the right. In (a), tungsten carbonyl ($W(Co)_6$) organometallic gas was passed over a silicon substrate, and the substrate was irradiated at arbitrary points by focusing the electron beam generated by the 200kV field-emission electron gun. By changing the electron beam irradiation times at individual locations during scanning, it was possible to perform vapor deposition of nanopits of various sizes with positional control. Image (b) is an example of a 2-dimensional pattern created by this method.

Image (c) is an example of a 3-dimensional nanostructure fabricated on carbon mesh. By scanning the electron beam in lines, it is possible to fabricate structures which extend into space as desired. The minimum diameter of these lines is less than 10nm.

Future work will focus on clarifying the relationship between the structure and physical properties of these nanostructures and their fabrication conditions, and will also include research on application to nanodevices.

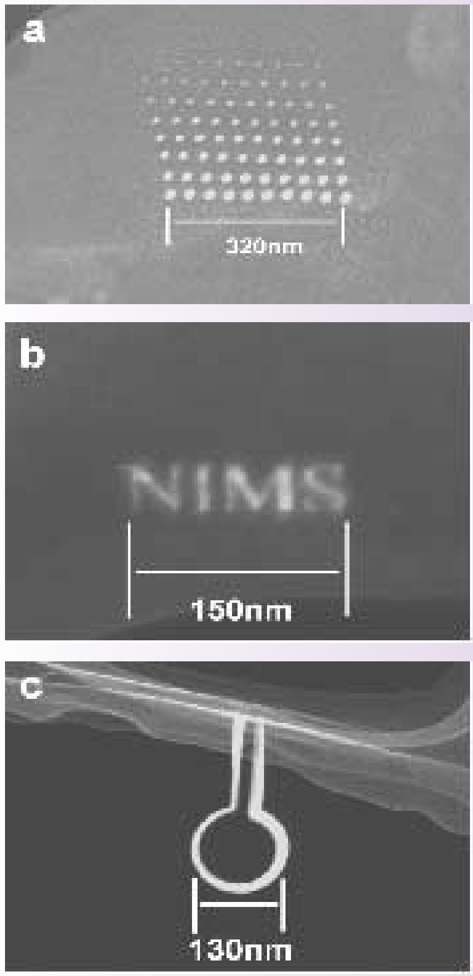

Fig. (a) Example of nano-dots fabricated under positional control, and examples of fabrication of (b) 2-dimensional and (c) 3-dimensional structures.

Publication of Data Sheet

As part of its efforts to enhance the intellectual infrastructure under its Mid-term Plan, NIMS published Creep Data Sheet, No. 49, and Long-Term Creep Test Specimen Microstructure Photographs, No. M-2.

The data sheet presents creep rupture data, high temperature tensile strength data, etc. for periods of up to approximately 30,000 hours for Ni-base high temperature alloy specimens of materials for gas turbine parts. The microstructure photo collection includes transmission electron microscope (TEM) photographs of microstructures after long-term creep tests of up to 220,000 hours, compositional analysis data on precipitates, etc. from stainless steel tubes for boiler and heat exchangers used in creep tests.

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Science & Technology Week Events

On Thursday, April 17, NIMS opened the facilities in its Sengen, Namiki, and Sakura Sites to the public, and also presented an open poster display and introduction to technology transfer at the Sengen Site.

On Sunday, April 20, the NIMS Sengen Site presented experiments which allowed young people to experience science for themselves, for example, by identifying materials through various experiments. At the Namiki Site, NIMS offered experiential learning experiments for neighboring middle-school students on topics which included the science of diamonds.

The NIMS Meguro Site was opened to the public on April 25 (Friday), allowing visitors to see the intellectual infrastructure for substance and material research, including introductions to the creep test equipment and material database.

This week-long science event provided an opportunity to inform many members of the general public of the current status of work at NIMS and achievements in NIMS research programs. At the same time, it also gave families and elementary and middle-school students a chance to experience the excitement of creating new materials.

Realization of Ultra-Miniature Light-Emitting Device

Masanori Fujimoto
WIN Research Planning Group
Taiyo Yuden Corp.

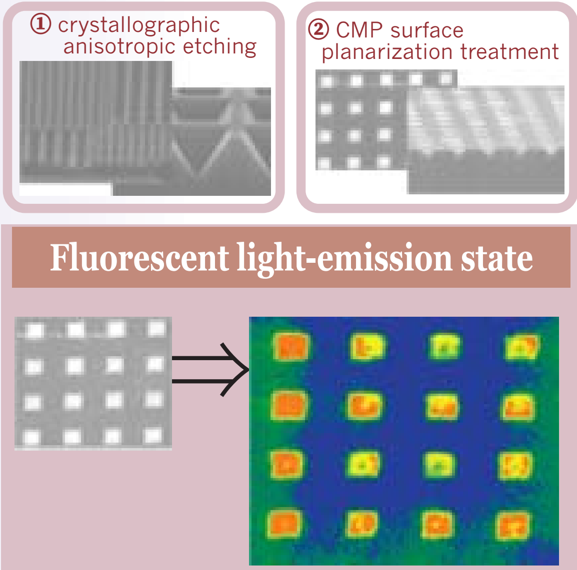
Hajime Haneda
Electroceramics Group
Advanced Materials Laboratory(AML)

Light-emitting devices such as light-emitting diodes: LED are used in high-saturation displays and similar applications, for example, in automobiles. Application to products such as displays for mobile devices, PDA (personal Digital Assistants) is also expected with further miniaturization and the development of ultra-high resolution(submicron order) display systems. However, with the conventional process, there are limits to both miniaturization and cost reduction because the fluorescent light-emitting element, which is produced by thick film printing, and the semiconductor chip drive device are fabricated individually.

As part of the project "Research on creation of new functional materials using ceramic integration*1 technology" (joint research project with Taiyo Yuden Corp.), the Electroceramics Group focused its attention on nano-order silicon refinement processing technology, and on zinc oxide (ZnO), which is among the materials used in low-voltage ultraviolet light-emitting elements for automobiles, but is more economical than other UV-emitting materials such as GaN. As a result, the Group successfully developed a nano-order, high resolution ZnO light-emitting array. Generally, the term "light-emitting array" indicates a group of light-emitting elements arranged in rows. In contrast to this, the device produced in this research work is more 2-dimensionalized and has a lattice-type structure. The key points in realizing this device were ① crystallographic anisotropic etching, utilizing the (111) plane of square pyramid in the (100) plane silicon substrate during formation of refined inverse pyramid shaped cavities on the silicon surface, and ② use of a surface planarization treatment method which approaches the near-electron level by the polishing technique referred to as CMP (chemical mechanical polishing leveling treatment). (See figure.) The UV light generated during electron beam irradiation with an scanning electron microscope was detected, showing that the fluorescent light-emission state of these photo elements was fluorescent light emission with a wavelength of 390nm.

This light-emitting element is expected to be applied to displays which require miniaturization and higher resolution, for example, for use in cell phones and PDA. In the future, high expectations are also placed on application to ultra-miniature varistors, ultra-miniature piezoelectric arrays, and other devices integrated with silicon.

(These research results have also been published in various newspapers, including the Nikkan Kogyo Shimbun, Japan Industrial Journal, and Nikkei Sangyo Shimbun.)



This light-emission experiment confirmed fluorescence with a wavelength of 390nm by a high density, 25 million/cm^2 array of nanopits (AML).

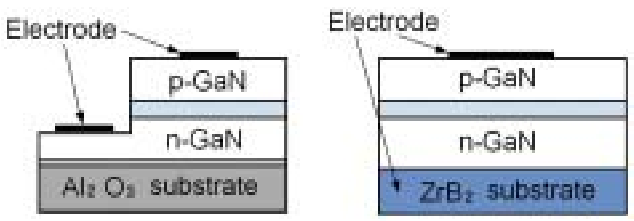
Fig. Results and key points of technology of development.

*1 Ceramic integration: New material and design technology for integration of various types of functional materials aimed at the development of more technically advanced functional ceramics, realizing multi-functional materials by integration.

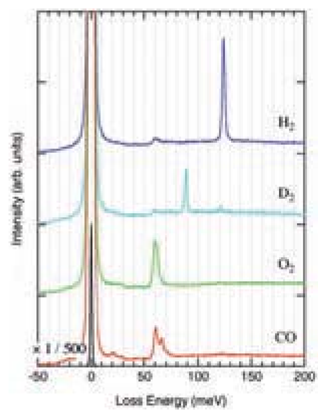
Boride Group／Director,Shigeki Otani

The boride group performs research on refractory borides, which consist of two- or three-dimensional boron-networks. The borides have high melting points, 2000-3500℃, and characteristic bulk and surface properties. Therefore, we develop technology for growing the large crystals with high quality and search new phenomena regarding the bulk and surface properties. We also developed a substrate for Group III nitride semiconductors.

High quality GaN films is epitaxially grown on the ZrB_2 substrate because of good matching of lattice constants and thermal expansion. In addition, the ZrB_2 substrate with metallic electrical conductivity works as an electrode and has the advantage of simplifying the device structure. The high thermal conductivity of ZrB_2 makes it suitable for high power devices.



GaN semiconductor device on the sapphire and ZrB2 substrates.



High-resolution electron energy loss spectra for gas adsorption on ZrB_2(0001).

In order to understand and to control an initial interface, we investigated the gas adsorption on ZrB_2 (0001) by using one of the highest resolution electron-energy-loss spectrometers in the world. One strong vibrational loss peak is observed for H_2, D_2 and O_2 adsorption, and two for CO adsorption, respectively. The molecules dissociate on the surface to individual atomic adsorbates at the room temperature.

1st NIMS International Conference (NIMSIC - 1)

—Material solutions for photonics—

Kenji Kitamura
Opto-Single Crystal Group
Advanced Materials Laboratory

The 1st NIMS International Conference (NIMSIC - 1) was held March 17 to 19, 2003. The Conference provided a forum for productive exchanges of information between NIMS researchers and joint researchers and invited researchers from Japan and other countries. Conferences will be held in a different field each year, and will explore research methodologies and directions for the future.

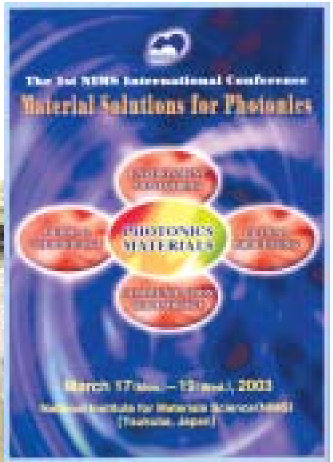
This year's conference focused on the research field of photonic materials, an area in which NIMS is continuing to achieve new results. One purpose of the meeting was to examine methodologies in NIMS materials research with the aim of contributing to the photonics industry, where leading-edge science and technology play a key role.

Four keynote addresses were presented, covering the life sciences, IT, the environment, and nanotechnology/materials, which are the four priority fields under the 2nd Period Basic Plan for Science and Technology. The Conference itself was divided into five sessions. Invited Japanese and international researchers who have achieved outstanding results in the respective areas presented a review and discussion of topics in advanced research, and NIMS representatives reported on the status of research by this organization. NIMS researchers also made poster presentations accompanying each of the sessions.

This 1st NIMS International Conference registered a total of 153 participants, and included 4 keynote addresses (one by an invited international researcher), 39 presentations by invited researchers (including 13 international and 9 NIMS researchers), and 43 poster presentations.

Most of the poster presentations were by NIMS or joint researchers, and the high level of enthusiasm and strong potential of NIMS were evident from the number. The Conference also helped to foster cooperation between researchers belonging to different units within NIMS. Thus, in a number of respects, this was an extremely significant event.

Participants at poster session.



Cover of Conference Proceedings.

SESSION TOPICS

Session 1: Wide gap semiconductors for LED
Research reports on application of metal oxide semiconductors represented by ZnO, diamonds, etc. to wide band gap semiconductors for LED.

Session 2: Ferroelectric materials
Presentations on experiments in wavelength conversion by polarization inversion structures, leading-edge devices, signal processing devices for the telecommunications wavelength range, etc., with emphasis on devices which use strong dielectrics, particularly LN/LT.

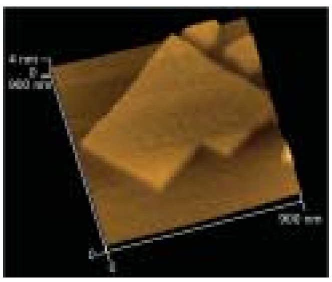
Session 3: Photonic crystals for colloids
Research reports with particular emphasis on approaches from colloid crystals in which colloid grains grow as self-generating arrays in liquids.

Session 4: Non-linear glass and optical fibers
In particular, reports on high-density resonance response in metal nanocrystals and the non-linear strengthening effect of local fields, optical transmissivity history response associated with phase changes in oxide nanocrystals, etc.

Session 5: Business prospects in photonics
Reports on photonics startups, including background and problems, based on various actual examples, by invited representatives of venture companies in the field of photonics.

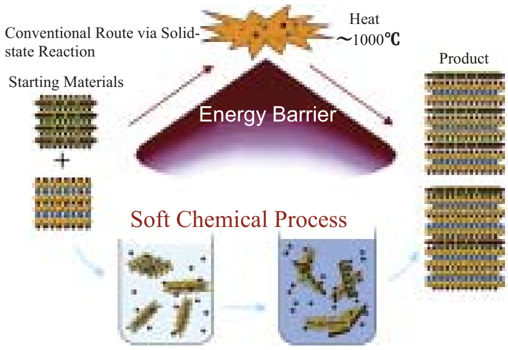
Soft Chemistry／Director,Takayoshi Sasaki

In the Soft Chemistry Group, titanium oxides, cobalt oxides and their related compounds are synthesized through various soft chemical processings including exfoliation into nanosheet materials, their reassembling, intercalation reactions, and ion-exchange reactions. The synthesized materials are characterized and explored in terms of their chemical and physical properties. Based on the technologies mentioned above, our group is now developing nanosized functional oxides with a novel shape, electrode materials for high-performance batteries, and photocatalyst materials.



Functional oxide nanosheets.

Oxide nanosheets are derived by chemically exfoliating a layered host into single layers. The nanosheet crystallite is characterized by its high two-dimensionality associated with a thickness comparable to molecules. The nanosheets often exhibit novel physicochemical properties that are not observed in other materials. They can be also used as a building block to construct larger nanostructured systems.



Conceptual explanation of soft-chemical synthesis.

Soft-chemical synthesis is defined as a ceramics fabrication process using chemical reaction technology at low temperatures,such as aqueous solution reactions. Those processes can yield special composition, structure and features of materials that are not synthesized by conventional methods with thermal treatment at high temperatures.

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