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PRIORITIES IN R&D FOR CERAMIC MATERIALS

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INTRODUCTION

Priority for R & D of materials has been dramatically changed by realization of environmental crisis. Technology friendly to public people is also needed, since some of recent advanced technology has led to techno-stress due to too much complicated control system. Materials for the technology must be designed to meet requirements, reasonable fabrication cost, high reliability during use, capability for recycling and easy handling . Taking into account of the requirements, the present author proposes intelligent materials with mechanisms such as self-diagnosis, self-recovery, self-adjustment and capability for tuning. These intelligent mechanisms are classified into two levels; primary intelligence (self-diagnosis, self-recovery and self-adjustment) and advanced one(tuning capability for saving complexity and/or recycling).

INTELLIGENT MATERIALS MINIMIZING COMPLEXITY OF DEVICES

Although computers with integrated circuits are normally used to control operations or to make judgments, neither these nor any other devices containing electrical connections can be introduced into hazardous environments. Even under non-hazardous conditions, where computers are used for complicated functions the result is often a tangle of electrical leads, a situation called as " spaghetti syndromes". Some operations or judgments therefore need to be carried out within materials. We need chip intelligent materials to save complicated and unstable circuits.

PTC thermistor provides an example of intelligence in materials. From the viewpoint of heater performance PTC thermistor is more intelligent than NTC

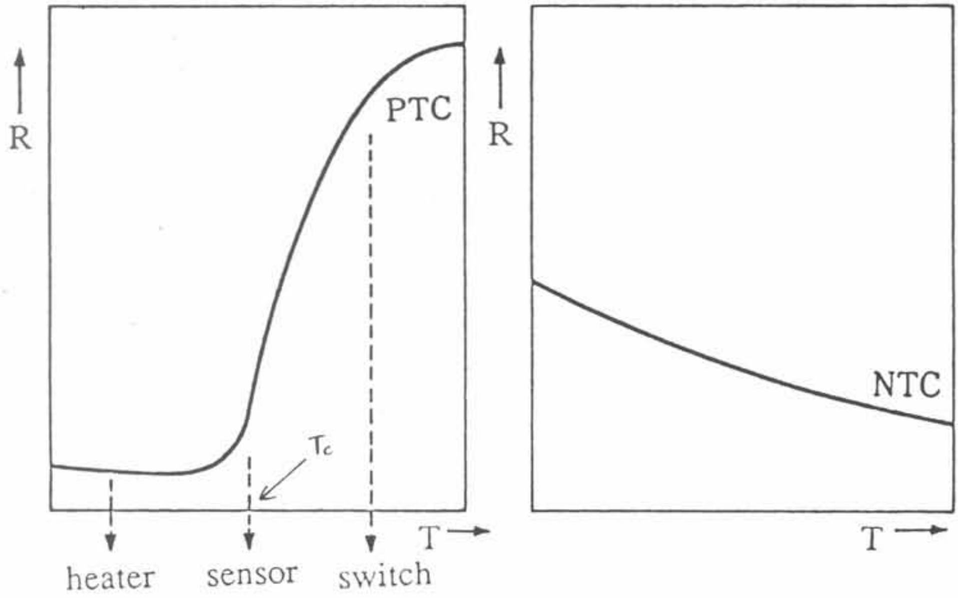
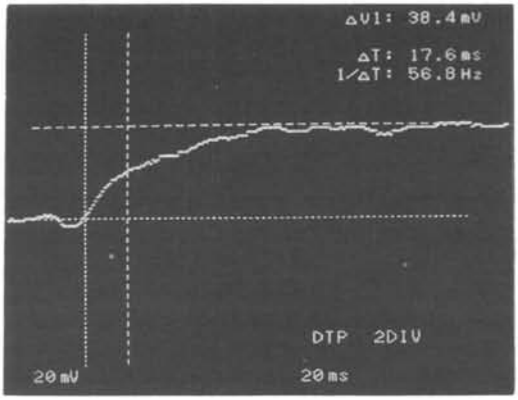


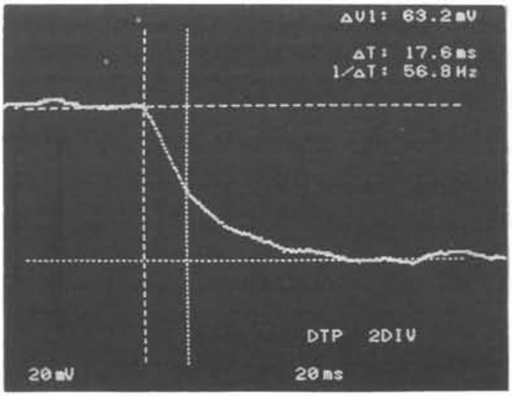
Figure 1 Two types of ceramic thermistor

one. The resistivity of NTC thermistor decreases with temperature. Increase in temperature gives rise to increase in electric current. This is a positive feedback, difficult to control. When an NTC thermistor is used as a heating element, we have to equip a temperature control circuit. On the other hand, PTC thermistor is a heater below the Curie Temperature(T_C), it is a critical temperature sensor, and it is a switch too since above the temperature the resistivity increases tremendously. It is a multi-functional material. However, it is intelligent not from the multi-functions but from the self adjusting mechanism. The temperature vs. resistivity characteristics gives rise to strong negative feedback mechanism. We do not have to equip any electric circuits to control temperature. Figure 1 gives a comparison between PTC thermistor and NTC one.

There are three types of infrared(IR) sensors; quantum, pyroelectric and thermistor. Each has advantages and disadvantages. Although the quantum type excels in response and sensitivity, it needs cooling system difficult to control. The pyroelectric type is less expensive than the quantum one and its sensitivity is high. It, however, cannot detect a stationary object. In order to detect immobile



(a)



(b)

Fig.2. The oscillograph of the typical E_{out}-time curve when the IR radiation from the human hand (Fig.2(a)) and the IR radiation from the ice block (Fig.2(b) were radiated to the PAN-based carbon fiber (resistivity: 275 Ωcm, number: 50, length: 1 mm).

targets, it requires an additional mechanism such as a chopper. Complication in mechanism and in circuit increases. Although the thermistor type is not expensive, neither response nor sensitivity is enough. It can detect a stationary object. The author's group has improved the response speed of the thermistor type sensor using SiC fibers, or carbon fibers[1]. Fibrous SiC(or carbon) can follow a temperature change very quickly, because, being fibrous, it is very low in heat capacity. The mechanism and circuit are simple. Examples of response are shown in Figure 2[2].

NON-LINEAR INTERACTIONS AS ORIGINS OF INTELLIGENCE

It is usually said that interfaces are origin of novel functions. The present author has classified two dimensional structures from the viewpoints : interface being between similar or different materials, being closed or open(contact), and phenomena across or along the interfaces[3]. Among them interesting are open interfaces between different materials. Novel functions arise from nonlinear interactions between two different materials with opposite properties. Open interface means that there are contact points between different materials and channels along the interface for chemical species can migrate out or in.

The author's group has constructed a new type of ceramic humidity sensor [4]. This sensor made of p/n contact, CuO (or NiO) p-type semiconductor and ZnO n-type, measures current across the interface required for electrolyzing water adsorbed around the contact points [5]. This has saved a circuit or treatment to remove water molecules adsorbed around the contact points. Figure 3 shows the voltage-current characteristic changes with humidity. The mechanism of this device has been analyzed as follows. The amount of water

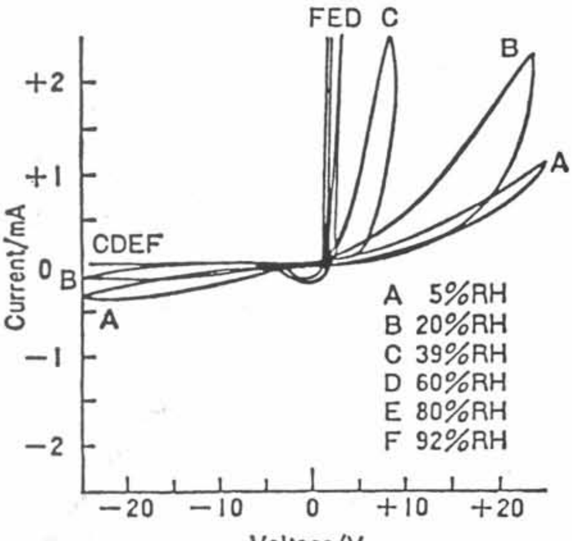


Figure 3. Humidity dependent voltage-current characteristic changes of an intelligent humidity sensor made of hetero-contacts between CuO and ZnO (RH=relative humidity)

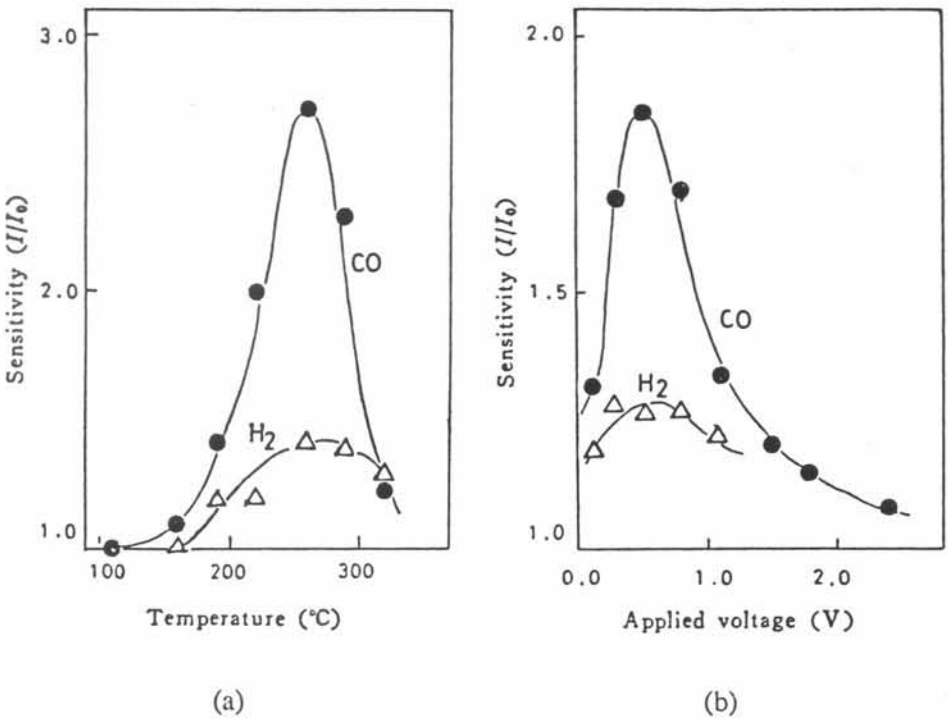


Figure 4. The gas sensitivity of CuO/ZnO hetero-contact
(gas concentrations are 8000ppm)

(a) The temperature dependence of the gas sensitivity
(Applied voltage is +0.5V)
(b) The relation between the gas sensitivity and the applied voltage
(Measuring temperature is 260 °C)

adsorption in the vicinity of the hetero contacts changes with humidity. Electron holes are injected from the p-type semiconductor electrode into the adsorbed water molecules, giving rise to protons in the adsorbed water phase. The positive charge is liberated at the surface or the n-type semiconductor electrode. As a consequence of this process the adsorbed water is electrolyzed. During measurements the cleaning process is always working, since the cleaning of self-recovery treatment is itself the working mechanism.

If we look at also the same hetero contact from the viewpoint of gas sensor performance as shown in Figure 4, it is able to detect carbon monoxide selectively from hydrogen gas[6]. The selectivity towards carbon monoxide arises from selective adsorption of carbon monoxide at the CuO surface. The sensitivity changes with the bias applied across the p/n contact as shown in Figure 4(b). The maximum sensitivity is obtained when the CuO side is positively biased at about 0.5V. Although sensitivity decreases above the bias selectivity becomes uniform for all kinds of flammable gaseous species. This effect constitutes a tuning.

RECYCLE DESIGN OF MATERIALS AND STRUCTURES

Motivation for development of materials changes with era or style of industry. Until very recently materials suitable to large scale production have been enthusiastically developed. This is not friendly at all to environment, however. This style of industry consumes much resources and energy, and leaves plenty amount of waste. Next stage of development of materials, called as novel materials era, was to seek better performances such as durability, strength, toughness, etc. Although it might have helped saving energy and resources, it also gave rise to difficulties in recycling. Performances improved at the stage are rejecting recycling. Materials scientists are now asked to solve contradictions between recycling capability and durability of materials.

Public mentality has been changing for recycling. Users will not buy products unless return of waste guaranteed. Industry executives are afraid they are sending out future debts when selling their products. As for future products, we should design breaking-down mechanisms on mechanical level for recycling beforehand. We need also recycle design on chemical level such as little dopants or alloy. We can only develop how to re-use materials already produced on chemical or mechanical level.

Dispersed fiber reinforced composite materials have very serious disadvantages. Glass fibers separated from the composite are prickly. Much attention has to be paid to collect those fibers. Sometimes it may lead to a serious cost as collecting asbestos. Carbon fibers are electrically conductive. If deposited onto electric apparatus or devices they may cause short-circuits, which will give rise to fatal troubles. From the points of feasibility to recycling, those fibers are recommended to be woven as net shape.

Architectural design concept has been also changing. It used to be to seek lower cost for construction. Pre-fabrication methods have been developed. It has become to minimize the cost of construction and maintenance. Today is the era we must consider recycling of materials. Therefore, we must optimize the total cost of fabrication, maintenance and recycling. We have to take into account of the cost for breaking down beforehand the construction. it is very difficult to find places to deposit the architectural waste. The solution is to find the methods to recycle the architectural waste into raw materials again. This requires the design for recycling beforehand construction.

INTEGRATION OF STRUCTURAL AND FUNCTIONAL MATERIAL

It is not easy to assure reliability of materials or structures. Fracture takes place without any notice yet. One of the ways to solve the problem is to install self-diagnosing functions in materials themselves during use and materials design for recycling beforehand manufacturing. If we can obtain a certain signal prior to fatal fracture, we may be able to avoid accidents. The signal must be distinct, methods to detect must be simple.

The design of the materials with self-diagnosing function is based upon hybridization of material A, electrically conductive with lower limit of elongation, with material B, insulating with higher limit of elongation. A typical example of the combination is CFGFRP, carbon fiber glass fiber reinforced plastic[7]. The material has primarily been developed for an alternative of iron bar to reinforce concrete structures. Mechanical behaviors of CFGFRP are very similar to iron bars; even after rigid carbon fibers fractured tough glass fibers can still absorb fracture energy. A typical example of the load - strain - change of electrical resistance characteristic of the materials is shown in Figure 5. A remarkable increase in resistance is observed with onset of fracture of carbon fibers while the materials are still alive. This corresponds to a health examination. Although residual strain can hardly be noticed with specimen after stress is removed, the residual resistance change is remarkable, too. This method, therefore, tells also a past disease.

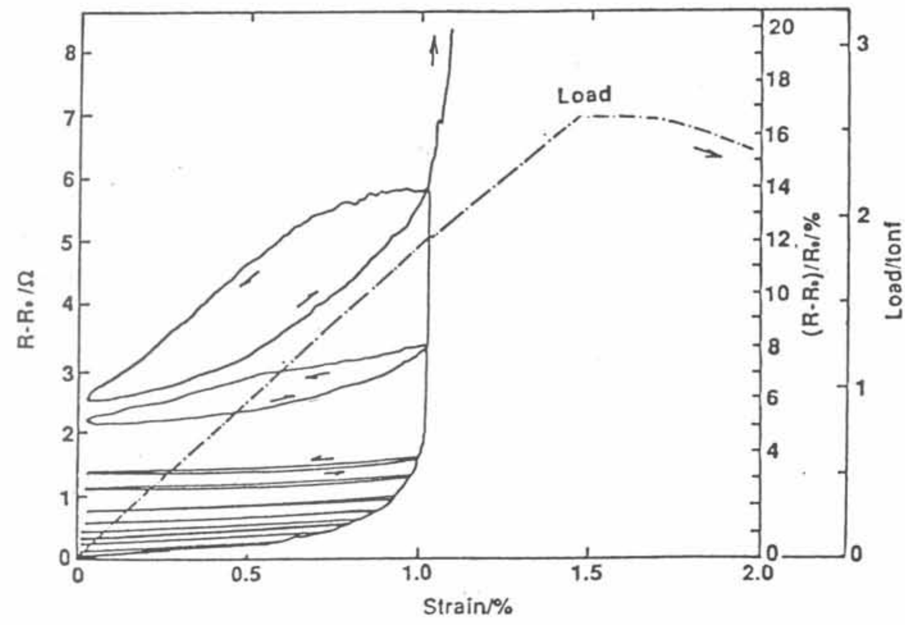


Figure 5. Load - Strain - ΔR - Characteristic of CFGFRP (C = PAN-HMCF)

The material, CFGFRP, can give rise to distinct signals without addition of complicated sensor systems. Maintenance of large scale structure, architecture or aircraft, is expected to be easier. This shows a healthy direction of technology.

The case of CFGFRP is integration of functional and structural materials. This kind of combination/hybridization is effective for integration of intelligent structural materials and functional ones, when material A is conductive, more fragile and high modulus and material B is insulative, tougher and lower modulus. When media is light, glass fiber is material A and iron is used as material B.

Integration of structural and functional ceramics has already been observed in stabilized zirconia(refractories/solid electrolytes), alumina(cutting tools/IC substrates), SiC sintered bodies(H, T materials/IC substrates), SiC fibers (reinforcement/IR detectors) and carbon fibers (reinforcement/IR detectors, Self diagnosis with GF). This direction can save complicated electrical circuits(spaghetti syndrome) and simplify structures of materials. People may consider active control is more advanced than passive control. This is not necessarily right. Active control usually requires complicated circuits and help of electricity. From the viewpoints of intelligence or wisdom passive control may be considered more intelligent or wiser since it does not require outer feedback control system. It works self-consistently : no necessity of electricity assistance. The typical examples are photochromic glass and vibration damper already adopted for buildings which works even during electricity down. The author proposes an index to measure figure of merit of intelligence. I = number of merit / number of component. Simpler structures with less components are considered to be more advanced.

CONCLUSION

For human beings to enjoy fruits of advanced technology required is to develop materials intelligent enough to minimize complexity of devices. Too complicated systems become to be used only by limited people. Limited technologies may lead to serious friction between developed and under-developing countries. This trend is not friendly to people at all. Environmental issues must also be taken into consideration when designing fabrication processes. Intelligent materials are required to make technology friendly to environment and people.

REFERENCES

1. N. Muto, M. Miyayama, H. Yanagida, T. Kajiwara, N. Mori, H. Ichikawa and H. Harada, J. Ceram. Soc. Jpn., 97, 1302-1305(1989)

2. N. Muto, M. Miyayama, H. Yanagida, N. Mori, T. Kajiwara, Y. Imai, A. Urano and H. Ichikawa, Sensors and Materials 2[6], 313-320(1991)

3. H. Yanagida, Kagaku to Kogyo, 39[11], 831-833(1986)

4. K. Kawakami and H. Yanagida, Yogyo Kyokaishi 87, 112-115(1979)

5. Y. Nakamura, M. Ikejiri, M. Miyayama, K. Koumoto and H. Yanagida, Nippon Kagaku Kaishi 1985, 1154-1159(1985)

6. Y. Nakamura, Y. Tsurutani, M. Miyayama, O. Okada, K. Koumoto and H. Yanagida, Nippon Kagaku Kaishi, 1987, 477-482(1987)

7. N. Muto, H. Yanagida, M. Miyayama, T. Nakatsuji, M. Sugita and Y. Ohtsuka, J. Ceram. Soc. Jpn., 100[4], 585-588(1992)