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BASE TECHNOLOGY APPROACHES IN MATERIALS RESEARCH FOR FUTURE NUCLEAR APPLICATIONS

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Abstract

In the development of advanced nuclear systems for future, majority of critical issues in material research and development are more or less related with the effects of neutron irradiation. The approaches to those issues in the past have been mainly concerned with interpretation of the facts and minor modification of existing materials, having been inevitably of passive nature. In combating against predicted complex effects arising from variety of critical parameters, approaches must be reviewed more strategically.

Some attempts of shifting research programs to such a direction have been made at JAERI in the Base (Common) Technology Programs either by adding to or restructuring the existing tasks. Major tasks currently in progress after the reorientation are categorized in several disciplines including new tasks for material innovation and concept development for neutron sources.

The efforts have been set forth since 1988, and a few of them are now mature to transfer to the tasks in the projects of advanced reactors. The paper reviews the status of some typical activities emphasizing the effects of the reorientation and possible extensions of the outcomes to future applications.

Key Words

New materials, material innovation, neutron effects, intense neutron sources, material database, base technology.

1. INTRODUCTION

With some limited exceptions, most materials common in nuclear technology applications have been employed from the stock-piles of those developed and used in conventional non-nuclear applications. Such convenient adoptions, either direct or through modifications of commercial materials, occasionally resulted in unexpected failures of key reactor components, which generally required costly and time-consuming remedial actions. At least to the present, however, the present fair technical maturity of power reactors might have proved such a sequence as one of the practicable strategic options in respect of its eventual safety and economic efficiency.

Austenitic stainless steels, used widely in LWRs and LMFBRs are typical examples. Some of them were originally developed and used in chemical industry to handle acids. Stress corrosion cracking of the stainless steel welds in oxygenated hot water became one of the common material failures in the early part of the history of power reactors. Further, composition of type 316 stainless steel is not always rationalized as optimum in terms of the resistance to the radiation induced void swelling, while it is widely adopted to LMFBR. Nevertheless, the AISI(SUS) 300 series of steels have been one of the basal streams of material selection in the modern nuclear reactor technology.

There have been exceptions, however, such as the well known Zircaloy and Magnox. They were developed specifically for use as nuclear fuel cladding. It is interesting to note that, those core materials reached to a maturity within a period much shorter than those for the other structural components. The successes might have partly come from the relatively frequent feed-back cycles between service experience and manufacturing in the case of fuel cladding, but more important would be that those materials were developed through tailoring for specific purposes. This fact is encouraging in terms of making a strategy of innovating new materials for future nuclear systems, and it can be an important lesson to learn.

2. NEAR TERM APPLICATIONS --- ADOPTION OF EXISTING MATERIALS BY MODIFICATION

The former type of approach, modifying existing materials to meet project 's requirements for systems applications within a given period of time, has always been important. In fact it would be only a choice in majority of the cases without very critical difficulty. There is a typical example, which has been carried out for over 15 years to the present at JAERI.

Extensive series of R&D works have been made on the structural material for the intermediate heat exchanger of an experimental HTGR, named HTTR, which is expected to be cooled with very high temperature helium to produce the out-put temperatures up to 950°C for process heating applications. There were no material that could meet the requirements among the existing alloys at the time of the project initiation(1970's). A nickel-based commercial alloy, Hastelloy X was found as the most potential for modification. The alloy has been modified to a new version Hastelloy XR[1]. To the present a significant number of experimental heats at different development stages have been melted and fabricated to tubes. Two large scale heats were manufactured in 1976 and 1977(named XR-II) and have been tested in the simulated HTGR coolant to excess of 30,000 hours referring to the basic requirements in uses for extended period of time at 950°C. Basic ideas of the improvement came from rather fundamental phases of works made during early to mid 70's. Modification of chemical composition featuring 1% of Mn with strict control of a few other minor elements was found to form uniform Cr-Mn spinel oxide film on which was extremely protective to the inert gas based low oxygen potential environments[2]. The resistance to corrosion under severe thermal cycling has been confirmed by tests up to 30,000 hours.

The modification was extended to the creep strength and welding-relevant properties through optimizing boron and carbon contents which lead to rather dramatic improvements[3]. Figure 1 shows the current status of the creep-rupture performances of the two heats of Hastelloy XR tested in simulated reactor coolant environment. It is interesting to see that the degree of improvement in the latest heat (XR-II) is more explicit as the duration of the tests extends. The improvements are attributed to the morphology of carbide precipitated during holding at elevated temperatures; namely, the M_6C dominant morphology is replaced with $M_{23}C$[4].

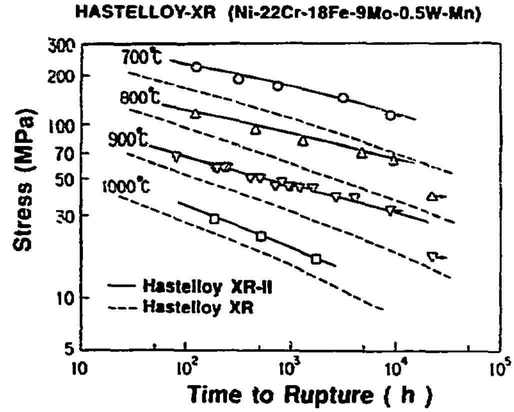


Fig. 1 Creep-rupture test results for the first generation and the recent heats of alloys modified for application to helium-based service environments

As mentioned above 2 sets of long time engineering tests have been carried out along with the steps of improvements in this series of development, because the data sets achieved for the materials before and after the modification are naturally different from each other. The HTTR, under construction, employs the latest version of the material while the structural design for the plant licensing is based on the test results of the initial version of the alloy XR, leaving the improvements as safety margins. The factors of improvements achieved relative to the starting material are ranged roughly 5 to 10 in terms of life extension.

In conclusion, it has been learned that, the type of development as described above takes significantly long time was new because the process was developed and had been used for forming glasses without melting or for producing fine powder of oxide particles of uniform size.

The point of particular attention in the process[12] proposed by Ogawa is a precise control of gel mixing through control of the iso electric point (IEP hereafter). IEP is a point where the surface charges arising from adsorption of water on a solid surface attain neutral state which can be controlled by pH of the solution. In principle, one can make various kinds of ideally homogeneous mixtures through such a single process. Figurer 6 is an example of the process of forming the carbides of transition elements. The liquids used are 3 alcohol-based solutions with suspended carbon powder, dissolved alcoxides of those transition elements and water. For boride formation, boron-bearing compounds are incorporated. The hydrolysis is made with control of pH to get for a designated IEP to form fine particles of mixed carbide and borides. The work is now ready to serve for various applications in the challenge of materials innovation.

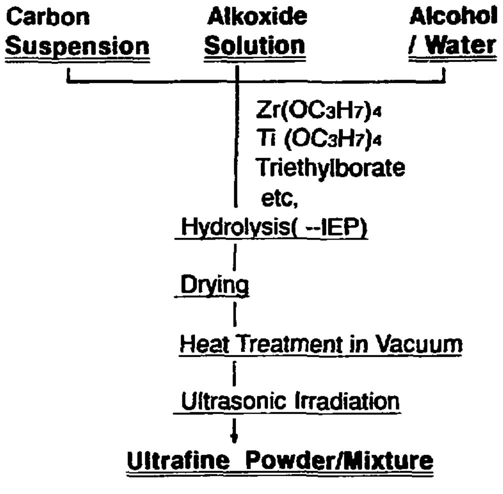


Fig. 6 Alkoxide gellation process developed for ultra-fine powder of compounds from transition elements

6.2 Molten Salts

In the study of the material to be used in liquid state, molten salts were picked up. An effort to lowering melting point of mixed inorganic salts has been attempted by Kato. The major incentive of the work was to improve chemical compatibility of molten salts with structural materials by reducing operating temperature. The corrosion attack of metals is considered as one of the major drawbacks in the molten salt technology. The issue has, indeed, blocked the perspective of utilizing the attractive substance. The attempt has been successful so far. The ternary diagram in Fig. 7 tells that the zone, circled, gives an answer that one can go as low as 320 °C[13]. Compared to the known salts like the so called FLIBE, this melting temperature is substantially low. It is predicted that the salt can be compatible in molten state with most of the stainless steels including the ferritic-martensitic versions.

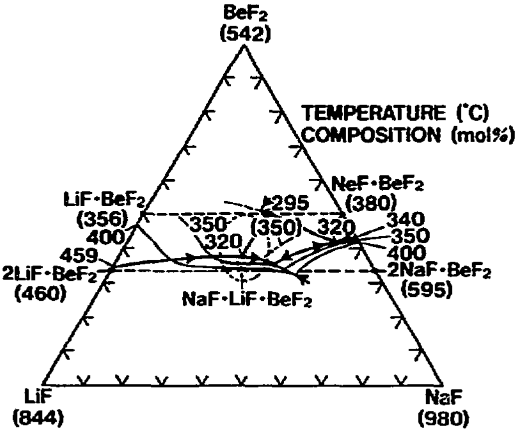


Fig. 7 Salts with low melting temperatures developed for nuclear applications

One of the possible applications of the salt in future nuclear technology may be as a fluid for a liquid target in the nuclear waste transmutation in the technology of incineration using particle accelerators. The open molecular structure which was depicted by the molecular dynamics simulation technique by Ohno et al, has confirmed that this substance can dissolve large amount of transuranium (TRU) species to be processed in the transmutation treatment.

4.2 Performances in Radiation Environments*

The situation changes rather drastically when the service environment is accompanied with strong radiation. The existing ceramic materials are more or less sensitive to neutron damage. BeO, for example, is degraded its mechanical properties sharply at a fast neutron fluence level of only 10^{24}n/m^2, which is very low relative to the damaging levels for metals[8].

Another important aspect of the radiation effect on ceramics is shifts of some physical properties such as electrical conductivity occurring during irradiation in the otherwise electrical insulators. Recently, Noda and his group observed the effect of irradiation on the electrical conductivity of sintered alumina through an in-situ measurement with 14 MeV neutrons, the energy level corresponding to the fusion neutrons[9]. The flux from the facility FNS was as low as 1.5 x 10^{15}n/m^{2}s, while the change observed was appreciable. The shift was almost totally reversible with "on" or "off" irradiation at the levels of flux and fluence tested. Such a kind of excitation effect has been known with ionization radiations such as γ ray. Intensive research must be invested with high energy neutrons, because various types of insulators and functional ceramics are expected to be employed for nuclear fusion applications.

5. STRATEGY FOR INNOVATION

To this point only a few symbolical facts have been referred to in identifying a back ground for orienting a research strategy to the future. It is clear that there are strong demands for a break-through. To respond such a situation, it is a simplest prescription to state that, wide variety of basic research on large number of disciplines must be invested. However, we have to be aware of the fatal limitations in time and resources. Even though fund were supposed to be made available, population of professional people, facilities of particular function and their capacity that are available, etc. can by no means be provided in a consistent basis to protect programs from the risks of possible limitless diversion.

The key issues or targets identified are; innovation of materials which fulfills basic requirements common in the materials for nuclear applications, the next step is to give a specific ability to withstand some critical service conditions with accompanying radiation. Among those the environments with intense neutrons are most critical.

5.1 The Base Technology Program Concept

A strategic concept was developed based on the facts that some well focused basic research works are urgently needed, and that the key issues have been identified to a fair extent. Recognizing the neutron effects as the central key issue, an extensive survey was attempted reviewing proposed research programs with respect to wide variety of issues covering the subjects of fundamental scientific to applied phase. After the reviewing the feasibility and priority were judged, and the items of common interests from the view points both of scientific and engineering aspects were selected. Considering the reality with respect to the potential availability of various kinds of resources, a model of research structure was proposed. Along with this direction the existing research system was restructured by shifting the grouping of divisions, experts and research equipments. The ultimate structure of the "Base Technology Shift" is depicted in Fig.3.

The disciplines selected as essential to the institutes base materials technology research for nuclear applications were; material innovation, sophistication of methodology and techniques for testing, qualification and demonstration. The development of integrated databases on material performances and characters was suggested to be accelerated to be given a centralized function. The eventual strategy selected by the planning committee of the JAERI, organized in 1987, was essentially a shift of priority of research to more disciplinary-oriented researches keeping coordination with the specific needs generated by the project for nuclear systems developments. The tasks being inplemented are classified as;

1. Designing and processing of New Materials
2. Characterization of innovated materials for application
3. Testings for reliability qualification and life-prediction
4. Integrated materials database
5. Methodology of testing and analyzing materials
6. Developing concepts of neutron facilities for materials testing.

There are a few added features, which the conventional program structure did not carry explicitly. Regarding the importance of radiation effects, comprehensive irradiation test facilities are centralized. A series of ion accelerators had

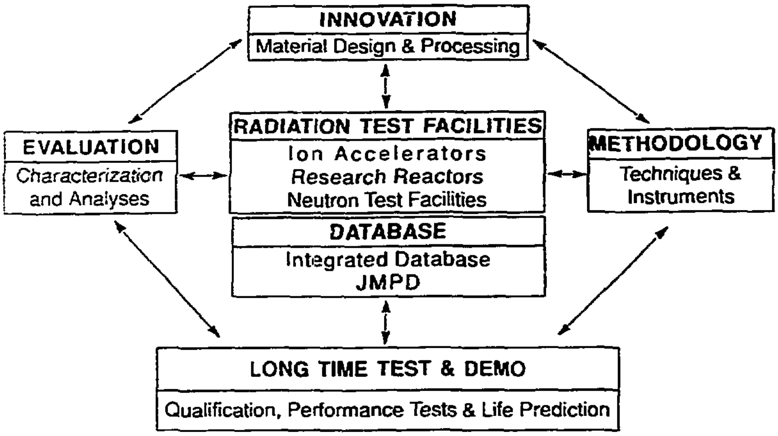


Fig. 3 Structure of the Base Technology Program at JAERI

been brought into construction already at Takasaki Research Establishment of JAERI before the base technology program was proposed. A new neutron test facility, ESNIT described later, is now in conceptual design stage

5.2 Issues in Ceramics Research

There are some fatal problems in the use of ceramics in nuclear components for services under radiation. Among several factors, the undefined nature of the boundary zones formed by sintering powder particles with binder mixtures can be a typical source of great uncertainty to the performance and reliability, and the analyses of the associated degradation mechanisms with complex synergy of radiation and atomic transport require deep scientific understanding. The two irradiation induced effects shown in Fig.4 are the main sources of the problems. Beside the well known basic issues of ceramics material, such as the limitations in product size, joining or welding, non destructive flaw detection, etc. the well know, high sensitivity to the effects of radiation such as the losses of toughness, dimensional stability and thermal conductivity are typical drawbacks under the conditions of

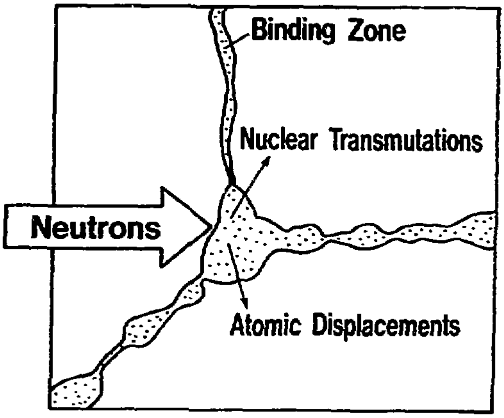


Fig. 4 Schematic of the elements of property degradation induced in sintered ceramics by irradiation of high energy neutrons

relatively heavy neutron irradiation.

Regarding the above stated issues, significant part of the conventional technology base for designing and processing ceramics must be subject to change in the nuclear applications. The initial step taken by the program was to challenge the molecular dynamics simulation approach to theoretical design of new materials, which is followed by molecular beam epitaxy type processing experiments and properties measurements. Survey on variety of innovative processes to manufacture ceramics materials have been attempted in which attention has been focused to create materials with defined chemical composition(purity) and microstructures.

In practice the following aspects have been considered;

(1) The materials must be as pure as possible to secure well defined conditions.
(2) Types of suitable molecular structures must be identified for potential high-resistance to radiation.
(3) The fatal brittleness may be covered partly by forming materials to fiber.
(4) In some limited cases use of tailored elements such as stable isotopes may be helpful to reduce farmful nuclear transmutants.
(5) Chemical compatibility with other substances like metals should be taken into accounts.

6. RECENT OUTCOMES FROM THE NEW PROGRAM

The base technology program has spent approximately 4 years since its beginning. Within Tokai area, the program has been run with the total annual cost of approximately 2,500 M.Yen for 7 laboratories in 2 departments with about 50 researchers. The works are actively under way.

In this review only a few examples are introduced to show what are going on mainly with nonmetallic materials and the development of neutron source concepts because of their critical nature relative to metals and alloys research.

6.1 Ceramic Materials

There is a good example of partial modification of anexisting process that has lead to a remarkable progress. A method of producing high purity, high strength SiC fiber developed by Seguchi and his group[10]. A simplified flow diagram is shown in Fig. 5. They employed gamm-ray and electron irradiation instead of oxidation for curing in the conventional process[11] of converting polymer fiber to SiC known as "Nikalon". The Material prepared is close to oxygen free condition and basically free from other impurities common in sintered materials. The low oxygen versions showed remarkable high temperature stability retaining very high tensile strength even after exposure tests at 1500 °C. The material has drawn attention in respect of its potential for possible resistance to radiation and application as a reinforcing element of composite materials.

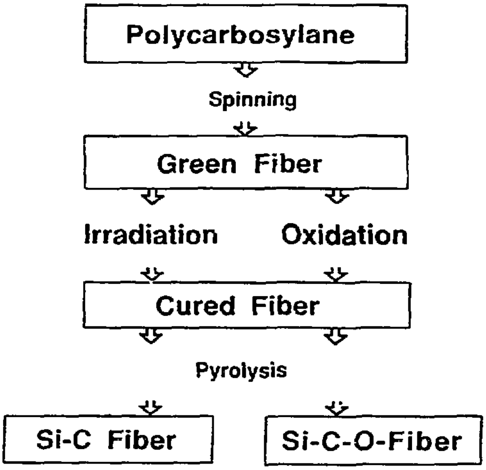
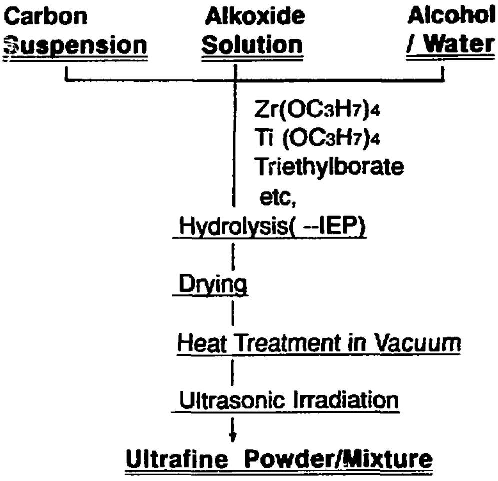


Fig. 5 High purity SiC fiber produced from polymer by curing with gamma ray

The second example has a more fundamental starting point. Ogawa considered the potential features of the compounds of transition elements. In contrast to the popular materials like SiC, Si_3N_4, of which atomic bonds are of covalent nature, transition elements such as Ti and Zr form stable compounds such as carbides, nitrides, etc with significant fraction of ionic bonds.

Because of such a difference the latter compounds are expected to have higher compatibility with metals and easier microstructural control relative to the former. These materials may provide some chances of challenging to clear the requirements specific to nuclear applications. In practice he attempted to apply the process of the so called "alcoxide gellation" to form carbides of transition elements. The attempt was new because the process was developed and had been used for forming glasses without melting or for producing fine powder of oxide particles of uniform size.

The point of particular attention in the process[12] proposed by Ogawa is a precise control of gel mixing through control of the iso electric point (IEP hereafter). IEP is a point where the surface charges arising from adsorption of water on a solid surface attain neutral state which can be controlled by pH of the solution. In principle, one can make various kinds of ideally homogeneous mixtures through such a single process. Figurer 6 is an example of the process of forming the carbides of transition elements. The liquids used are 3 alcohol-based solutions with suspended carbon powder, dissolved alcoxides of those transition elements and water. For boride formation, boron-bearing compounds are incorporated. The hydrolysis is made with control of pH to get for a designated IEP to form fine particles of mixed carbide and borides. The work is now ready to serve for various applications in the challenge of materials innovation.



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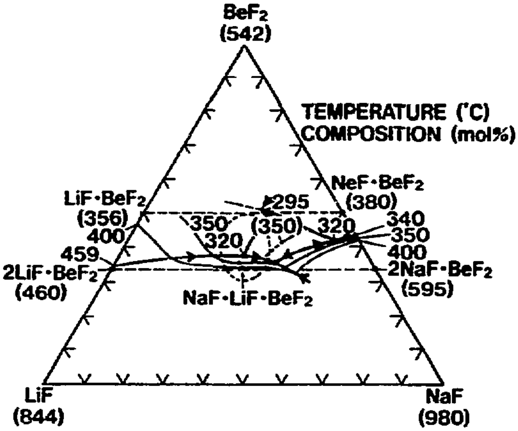

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7. NEW NEUTRON IRRADIATION TEST MEANS FOR ADVANCED RESEARCH

Among various test means in the field of studies on irradiation effects on materials, accelerator based neutron test facilities are expected to play an essential role parallel with nuclear reactors.

The reason why the system is considered as one of the key tools for future neutron tests is most easily understood by looking at the issues of the irradiation effects in fusion power development, which is unique in the energy (14MeV) spectrum. In quantitative approaches it can not be substituted with any other convenient simulation means. The requirements, that need to be fulfilled in the experimenter's points of view cover mainly the following items:

1) neutron energy spectrum
2) flux
3) fluence
4) test volume
5) precise control of test condition
6) accessibility for in-situ experimentation

7.1 High Energy Neutron Test Facility

There have been several concepts for producing neutrons with energy levels higher than fission neutrons and best simulating fusion reactor environments. An international assessment group organized by the IEA implementing agreement on fusion materials has recently concluded that the accelerator based sources are most feasible for construction in the next decade[14]. There are two most potential candidate concepts at the moment. The d-Li source[15] utilize the neutron generation by injecting accelerated deuterons to flowing liquid lithium to cause the stripping reaction. This type of source has been considered as technically most mature due to the development by the FMIT project in USA made about 7 years ago[16]. An alternative concept has been proposed recently in Germany in which tritons are incident to water jet. The latter has an advantageous feature in the energy spectrum structure relative to the d-Li type but with less attractive in potential ability of providing adequate test volume. Regarding the premature state of technology of the latter, the d-Li system is considered currently as only one realistic candidate[17].

In 1987 when the base technology program was under plan, a consensus was converged to the urgent need of a new means of neutron testing to cover limited functions of research reactors. The concept of the Energy Selective Neutron Irradiation Test Facility, ESNIT, was referring to the results achieved by the FMIT project. It paid special attention to the linear dependence of the average (or peaking) neutron energy from d-Li source on the energy of the incident deuteron beam[18].

7.2 ESNIT Program and Development of Small Specimen Test Technique

The total system of a typical d-Li neutron irradiation test facility is composed of a linear deuteron accelerator, liquid lithium target, irradiation and post irradiation test systems. One of the features in the design policy of the ESNIT is the realism in its beam current specification, 50mA. The conservatism comes from an optimization through a series of trade-off considerations, while the concept leaves a sufficient capacity of upgrading to 100 mA in future at the stage of engineering design. There are very generic trade-offs concerning the technical and financial risks against the benefits of flux and test volume. However, it is important for this kind of system to have a timely start by the very beginning of the 21st century as there is a large area of uncertainly about the knowledge on the materials response to high energy / high flux neutrons. Many efforts in assessing the facts through either experiments with simulation techniques or theoretical modeling can only be verified through experiments facilitated with well defined intense high- energy neutron test environments.

There is a common critical issue of the test volume limitation, which is fatal in the accelerator driven neutron sources. To the level of fundamental research and material development, the issue of the limited test volume is expected to be solved, to a considerable extent, by use of the small specimen test technique. The current state of art of the technique covers several mechanical property test items that have been developed systematically in last several years. With exceptions of some intrinsic limitations, a significant part of the post irradiation test items can now be covered by these techniques. The use of those techniques increases the essential test capacity readily by to some thousand times relative to the standard size regimes. A complete solution of the test volume can be made in future by increasing the capacity of the system with increased accelerator beam current (250 ~ 500mA) combined with appropriate multi target system. The details of the specification and the status of the ESNIT by Noda appears in the paper for the present proceedings.

8. SUMMARY

1) Understanding neutron irradiation effects and developing materials tailored to withstand those effects are stressed to be the key issues to the future.
2) The need of developing materials that can be used in high energy neutron field corresponding to fusion reactor first wall is identified as the area where a technology breakthrough is urgently required.
3) Incentives and structure of the Base Technology Program being implemented at JAERI are described with emphases on activities of innovating new non-metallic materials and the concept development of a neutron test facility.

References

[1] M. Shindo and T. Kondo, Proc. Conf. Gas-Cooled Reactors Today, Bristol, UK, BNES(1982)179

[2] M. Shindo and T. Kondo, Testu To Hagane(J. Iron and Steel Inst. Japan)68(1982)1638

[3] H. Nakajima et al., unpublished

[4] Proc. 1st. International Conf. on Creep(1986)97, also see K. Watanbe et al., J. Nuclear Materials, 185(1991)8

[5] R. Tanaka and T. Kondo, Nuclear Tech. 66(1984)75

[6] T. Kondo et al., Japanese Patent, No. 2-175829 (1990)

[7] H. Ohno and T. Kondo, Proc. 1st. International SAMPE Symposium, Chiba, Japan(1989)1622

[8] B. S. Hickman, STUDIES IN RADIATION EFFECTS/ Physical and Chemical, Vol. A G. J. Diens Ed.,Gordon-Breach, New York(1966)72

[9] K. Noda, unpublished

[10] M. Takeda et al., 15th. Ann. Conf. on Composites and Adv. Ceramics, USA, Am. Cer. Soc.,Jan. 14,(1991)

[11] S. Yajima et al., Chemical Letter, 931(1975)

[12] T. Ogawa and K. Fukuda, Proc. 1st. Europiean East-West Symposium on Materials and Progress, Helsinki, Finland,June(1990)

[13] Y. Kato, unpublished

[14] D. G. Doran and J. E. Leiss, J. Fusion Energy, 8(1989)137

[15] P. Grand et al., Nuclear Tech., 29(1976)327

[16] A. L. Trego et al., Nuclear Tech., 4(1983)695

[17] T. Kondo, D. G. Doran, K. Ehrlich and F. W. Wiffen, J. Nuclear Materials, (in press)

[18] T. Kondo, H. Ohno, M. Mizumoto and M. Odera, J. Fusion Energy, 8(1989)229 also see K. Noda et al., J. Nuclear Materials, 179/181(1991)1147