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研究課題名（和文） 照射効果に水素を重畳させると材料劣化は促進するか、それとも抑制できるか

研究課題名（英文） Concurrent effects of hydrogen and irradiation defects in alloys

研究代表者

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研究成果の概要（和文）：　Zr合金は原子炉燃料被覆管として利用され、使用環境下で腐食、水素吸収、照射損傷といった劣化が生じる。これら個々は詳細な知見があるが、重畳効果は明らかにはなっていない。そこで本研究では、Zr合金の水素化効果と照射効果の重畳効果の明確化を目的とした。

再結晶したZry-4に水素注入し水素化物を顕微鏡観察し、加速器結合型透過電子顕微鏡内にてイオン照射組織変化をその場観察した。固溶体中の水素により照射欠陥密度の増加、つまり核形成の促進につながることを示した。また、欠陥での水素原子捕獲により欠陥成長の促進も生じることを明らかにした。照射と水素の同時効果についてさらなる調査を継続しているところである。

研究成果の学術的意義や社会的意義
ジルコニウム合金は、その種々の特性から原子炉燃料被覆管用材料として広く使用される。原子炉環境におけるこの材料の劣化挙動には腐食、水素化、照射効果があり、それぞれ多くの知見の蓄積がある。しかしこれらの重畳効果については必ずしも明らかではない。本研究はこの重畳効果（特に水素化と照射）について明らかにしたものである。

研究成果の概要（英文）：　Zr alloy is used as a reactor fuel cladding tube and causes deterioration such as corrosion, hydrogen absorption, and irradiation damage under the usage environment. Although each of these has detailed knowledge, their synergistic effect has not been clarified. Therefore, the purpose of this study was to clarify the superimposition effect of the hydrogenation effect and the irradiation effect of the Zr alloy.

Hydrogen was injected into the recrystallized Zry-4, the hydride was observed under a microscope, and changes in the ion-irradiated microstructure were observed in-situ in a transmission electron microscope interfaced with an ion accelerator. It was shown that hydrogen in the solid solution leads to an increase in irradiation defect density, enhancing nucleation. It was also clarified that the capture of hydrogen atoms in defects also enhancing defect growth. Further investigation is ongoing on the simultaneous effects of irradiation and hydrogen.

研究分野：原子力材料

キーワード：ジルカロイ合金　水素化　照射損傷　重畳効果　加速器結合型電子顕微鏡

様 式 Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

Zirconium alloys are widely used as cladding materials for Light Water Reactor fuel assemblies, due to their low thermal neutron capture cross-section, good mechanical properties, and excellent corrosion resistance at high temperatures. However, during normal operation, Zr alloys suffer from a degradation in material performance caused by waterside corrosion, hydrogen uptake and irradiation damage.

Since the Zr claddings are water-cooled, oxygen from the water bonds with the outer layer of the cladding to create Zr oxides, releasing H atoms to the cladding. When the H concentration surpasses the terminal solid solubility limit of the Zr, hydrides are formed which lead to embrittlement and fracture through delayed hydride cracking (DHC). There are four known hydride phases in the Zr-H system: $ZrH_{0.5}$－ζ, ZrH－γ, $ZrH_{1.5\text{-}1.7}$－δ, and ZrH_2－ε, and the four phases of Zr hydrides have different crystal structures. δ hydride and ε hydride are stable Face-Centered Cubic (FCC) and Face-Centered Tetragonal (FCT) phases, respectively. γ hydrides are FCT and ζ hydrides are trigonal. The ζ phase is metastable and is believed to be a transitional phase between α-Zr and δ or γ hydrides. The δ and γ hydrides are the phases most liable for embrittlement and fracture of materials. Although they differ in crystallography, both the δ and γ phases grow in similar directions within the Zr matrix. The direction of growth has been determined to be [11$\bar{2}$0]. The fraction of δ or γ hydrides is related to the H concentration and cooling rate of the Zr. A higher H concentration and/or a slower cooling rate will lead to production of more δ hydrides, and the opposite will lead to more γ hydrides 1).

Regarding the irradiation damage, under neutron irradiation, lattice atoms are displaced from their original sites, resulting in the formation of collision cascade. The accumulation of irradiation-induced defects in the material during service is dictated by the processes of defect generation, annihilation, recombination, and clustering. The neutron irradiation induced microstructure in Zr alloys is dominated by dislocation loops. The <a> type loops formed in the early stage of irradiation are both vacancy- and interstitial-type dislocation loops on the hcp lattice’s prism planes, and the <c> type loops formed in higher dose conditions are a lower density of vacancy-type dislocation loops on the basal planes. These dislocation loops structures can lead to irradiation-induced hardening and irradiation growth 2-3).

２．研究の目的

Although a large number of studies for understanding the degradation of Zr base cladding materials by irradiation damage and hydrogen uptake have been extensively reported, so far, there are few papers reported on the concurrent effect of hydrogenation and irradiation. Obviously, in the practical reactor operation environment, the effects of hydrogenation and irradiation can have an impact on the degradation behavior of fuel claddings at the same time. To clarify the degradation behaviors in Zr-alloys under nuclear reactor environments, Kano et al. investigated the concurrent effect of neutron irradiation and hydrogen absorption in Zry-2 by mechanical testing. The results showed that the magnitude of irradiation-induced hardening and embrittlement was suppressed by a 100 ppm H charge, which indicating that the mechanical properties of Zr alloys could be affected by hydrogen in the matrix and irradiation-induced defects at the same time 4). Therefore, it is significant to study how the hydrogen and hydrides in the matrix and irradiation-induced defects affects each other and how they affect the properties of materials.

Vizcaino et al. found that the TSSD of hydrogen in Zry-4 were higher after neutron irradiation than in the unirradiated specimens. After these irradiated specimens were annealed, and the TSSD of irradiated specimens tended to the unirradiated values, suggesting that the irradiation-induced defects trapped the hydrogen atoms and slowed down their release 5). Shinohara et al. confirmed by in-situ TEM observation that hydrogen would be trapped by irradiation defects. They performed in-situ observation in un-irradiated and Ni-ion-pre-irradiated Zry-4 during hydrogen ion implantation and found that in pre-irradiated specimens both irradiation defects and hydrides grew linearly, and the growth rate of hydrides in un-irradiated specimens higher than that in pre-irradiated specimens, which means the amount of hydrogen absorbed by defect clusters 6).

Tournadre et al. investigated the hydrogen impact on <c> dislocation loops in M5. They found that the growth of the <c> loop nuclei could be enhanced by the trapping of hydrogen atoms in solid solution on the defects, and that the remaining <c+a> dislocations after the precipitated hydrides dissolution could act as nucleation sites for <c> loops [7].

From previous studies on the effects between the irradiation damage and hydrogenation, we can find that hydrogen in the matrix can be trapped at the irradiation defects. In the last paper, it is found that <c> loops can also be affected by hydrogen in solid solution and hydrides. However, these studies remain insufficient to reveal their effects on each other and to give any evidence on the change of mechanical property in Zr alloys. Therefore, it is necessary to further investigate the effects of hydrogenation and irradiation.

In this research, the effects of hydrogen in solid solution state in Zry-4 on the irradiation dislocation loops at a low irradiation dose will be investigated. Since hydrogen could be trapped at defects, it can affect the formation and growth of dislocation loops, e.g., the density and size of dislocation loops.

The purpose of this study is to investigate the effects of hydrogen in solid solution on the formation and growth of dislocation loops under ion irradiation in Zry-4.

３．研究の方法

3.1 Material

In this study, a cold-worked and stress-relieved (CWSR) Zircaloy-4 tube (Zr-1.3Sn-0.2Fe-0.1Cr, in wt%) was used as the original material to prepare the experimental specimens. The Zircaloy-4 cladding tube was cut into two parts, and subsequently rolled into two sheets at room temperature. To obtain the recrystallized microstructure, they were finally annealed at 973K for 5 h under high vacuum as low as 10^{-5} Pa. Then the specimens were cut into disks of 3 mm diameter for TEM observation and hydrogen charging. The microstructure of recrystallized Zircaloy-4 observed by TEM. A typical recrystallized structure with well-equiaxed grains was observed and the mean grain size was about 5 μm.

3.2 Hydrogen charging

Hydrogen charging is performed with a gaseous hydrogen charging method using 3.5% H_2-Ar gas. Before gas mixture into the furnace chamber, the samples were heated to 673 K under a high vacuum around 10^{-4} Pa. Then the gas mixture was introduced into the furnace chamber to a certain pressure level for a certain time, depending on the target hydrogen concentration of specimens.

Hydrogen concentration of the specimens was measured quantitatively by hydrogen analyzer LECO RH-404. Hydride morphology was examined by using a laser confocal microscope. The microstructure of hydride was observed by a JEOL-2100 transmission electron microscope (TEM) operated at 200 kV. The specimens for TEM were prepared by twin jet electro-polishing.

3.3 In-situ TEM heating and ion irradiation

The in-situ TEM heating and ion irradiation experiments were performed at the High Fluence Irradiation Facility at the University of Tokyo (HIT) with a JEM-2000FX TEM system operating at 200 kV. In the in-situ experiments, the specimens of Zry-H (50-ppm) were selected as hydrogen charged specimen to perform the experiment.

For the in-situ heating experiment, the specimen was heated up to 673 K by a GATAN double-tilt heating holder with a water-cooling system.

For the in-situ irradiation experiment, the specimen of no hydrogen charging (Zry) and the hydrogen charged specimen (Zry-H, 50 ppm H) were irradiated with 1 MeV Fe^+ ions at 633 K and irradiated. The dose rate and the total dose were calculated using SRIM-2013 code. SRIM calculations were done with an incident angle of 30° (an intersection angle of 60° with the surface of the foil specimen) and a displacement energy of 40 eV. The average dose was calculated as 0.74 dpa, and the specimens were irradiated for 60 min at a dose rate of 2.1×10^{-4} dpa/s. For the in-situ ion irradiation, it was estimated that most of the Fe^+ ions penetrated the observation area of the specimen, and the influence of the accumulation of Fe^+ ions in the specimen for TEM observation is negligible.

４．研究成果

4.1 Hydride morphology by laser microscopy observation

Figure 1 showed the hydride morphology in disk specimens with 49, 167 and 270 ppm hydrogen concentration. The higher amount of hydrogen absorbed, then the more hydrides were observed. It is found that hydrides are basically precipitated along the circumferential direction.

4.2 Hydride microstructure by TEM observation

The hydride microstructures in recrystallized Zry-4 specimens were analyzed by TEM, and it is confirmed that the appeared hydrides are corresponding to the δ-hydrides. To further investigate the effect of hydrogen concentration on the hydride size, the size distribution of hydrides was analyzed for all the specimens with different hydrogen concentration respectively.

It is seen that the hydrides introduced by electro-polishing possess a small size; revealing that, in the case of hydrogen charged specimens, most of the hydrides of 50-200 nm are formed due to electro-polishing, instead of hydrogen charging. Based on this result, in Zry-4 (49-ppm H), the size of formed hydrides is mainly in the range of 200-1000 nm, and most of hydrides are intragranular hydrides. In this specimen, the longest hydride was observed to exhibit a length of about 3 μm. Figure 4.7 (c) shows that in Zry-4 (167-ppm H), the size of formed hydrides is mainly in the range of 1000-3000 nm, and most of hydrides of 1000-3000 nm are intragranular hydrides with one ends at the grain boundary. The largest hydride observed was about 5.5 μm. In Zry-4 (270-ppm H), the size of formed hydrides is mainly more than 3000 nm, and most of hydrides more than 3000 nm are intragranular hydrides and transgranular hydrides. The largest hydride observed was about 8 μm.

In conclusion, hydrogen concentration plays a role in influencing the size of formed hydrides. Specimens with higher hydrogen concentration tends to form hydrides with a greater size.

4.3 In-situ TEM heating observation

From in-situ heating observation, it can be obviously confirmed that as the temperature increases, the hydride gradually dissolved, and that the solid H atoms from the dissolved small hydrides during heating process, re-precipitated as a large hydride during the cooling process. Figure 6 shows hydrides dissolved completely at 673K, and after cooling, a large hydride was precipitated.

4.4 In-situ TEM irradiation observation

In the in-situ irradiation experiments, the specimen of Zry and Zry-H were irradiated at 633 K for 60 min with a dose rate of 2.1×10^{-4} dpa/s. Mean defect size and area defect density are plotted as a function of dose which is shown quantitatively in Figure 2 and 3, respectively.

By comparing the Zry specimen with the Zry-H specimen, it is found that the defect density in the hydrogen charged specimen was always higher than that in the specimen without H. This is probably because a vacancy can combine with several hydrogen atoms and form a thermodynamically stable hydrogen-vacancy complex, which can be expressed as $Va+nH\rightarrow VaH_n$. The hydrogen-vacancy complex is supposed to have a higher migration potential of than that of vacancy only, which shows that the hydrogen-vacancy complex has a lower diffusion ability than that of vacancy [8).]Therefore, compared with vacancies, the hydrogen-vacancy complex shows a good thermal stability and low migration rate, so they are difficult to be annihilated by diffusion, which can greatly enhance the nucleation of defects and stabilize the defects.

In Zry-H specimen, it is also found that the size of defects depended on the distance from the hydride, the closer to the hydride, the larger the size. It might be because the hydride dissolution forms a solubility gradient of hydrogen, and defects can trap hydrogen, thus enhancing the growth of defects. Also, the defects at the area of the dissolved hydride were larger in size, probably due to the dislocations left by the dissolution of the original hydride.

By comparing the un-irradiated Zry-H with the irradiated Zry-H specimen, it is found that the hydride precipitated in the unirradiated Zry-H, but not in the irradiated Zry-H, which may indicate that the irradiation increases the solid solubility of H in Zry, due to hydrogen could be trapped at the irradiation-induced defects.

The results above are summarized as follows:

(1) Hydrogen concentration plays a role in influencing the size of formed hydrides.

(2) The hydrogen in solid solution from the dissolved hydrides during heating process could be re-precipitated during the cooling process.

(3) Hydrogen in solid solution can increase the density of irradiation-induced defects, probably due to the formation of more stable hydrogen-vacancy complex, which enhance the nucleation of defects.

(4) The trapping of hydrogen atoms at defects and the remaining dislocations after the hydride dissolution could cause relatively large-size defects.

(5) Irradiation can suppress the precipitation of hydrides, probably because irradiation-induced defects increase the solid solubility of hydrogen in Zircaloys by trapping hydrogen atoms.

Reference

1) J. Nucl. Mater., 466 (2015) 12-20 .
2) Eng. Fail. Anal, 18 (2011) 1921-1942 .
3) J. Nucl. Mater, 425 (2012) 76-82 .
4) EnvDeg 2019, Boston, MA, August18-22, 2019.
5) J. Nucl. Mater, 304 (2002) 96-106 .
6) J Nucl Sci Technol, 46 (2009) 564-571 .
7) J. Nucl. Mater, 441 (2013) 222-231 .
8) ACTA METALLURGICA SINICA, 54 (2018) 1683-1692.

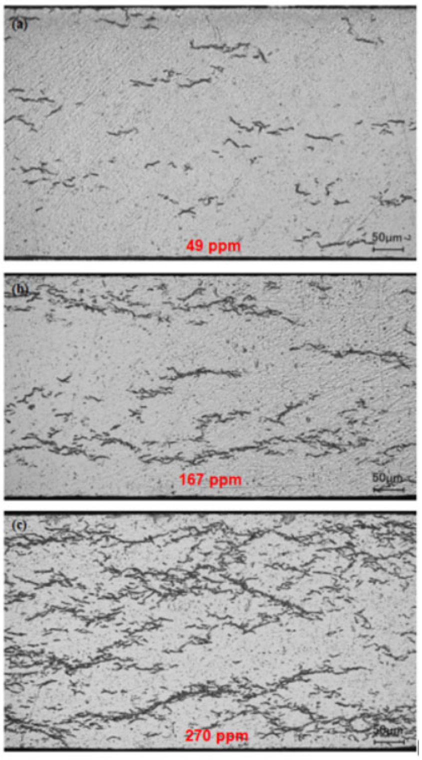

Figure 1. Hydride morphology of Zircaloy-4 disk specimens in radial-circumferential plane.

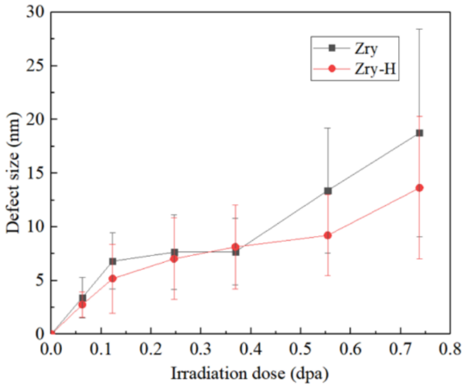

Figure 2. Mean defect size plotted as a function of irradiation dose in Zry and Zry-H specimens.

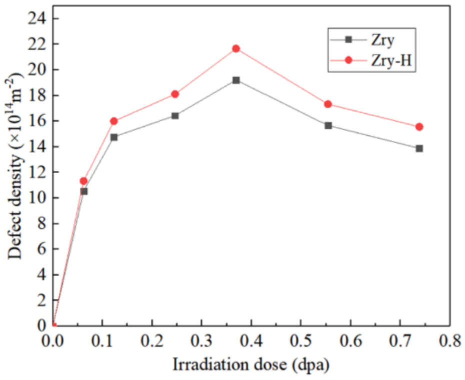

Figure 3. Area defect density plotted as a function of irradiation dose in Zry and Zry-H specimens.

５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　6件／うち国際共著　2件／うちオープンアクセス　0件）

１．著者名 H.L.Yang,S.Kano,J.McGrady,D.Y.Chen,K.Murakami,H.Abe	４．巻 542
２．論文標題 Microstructural evolution and hardening effect in low-dose self-ion irradiated Zr-Nb alloys	５．発行年 2020年
３．雑誌名 Journal of Nuclear Materials	６．最初と最後の頁 152523
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jnucmat.2020.152523	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 H.L.YangaS.Kano,J.J.Shen,J.McGrady,Y.F.Li,D.Y.Chen,K.Murakami,H.Abe	４．巻 531
２．論文標題 Investigation of anisotropic hardening response in a 12Cr-ODS ferritic steel subjected to 2.8 MeV Fe2+ irradiation	５．発行年 2020年
３．雑誌名 Journal of Nuclear Materials	６．最初と最後の頁 152016
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jnucmat.2020.152016	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 H.L. Yang, S. Kano, J. Shen, J. McGrady, Y.F. Li, D.Y. Chen, K. Murakami, H. Abe	４．巻 531
２．論文標題 Investigation of anisotropic hardening response in a 12Cr-ODS ferritic steel subjected to 2.8 MeV Fe2+ irradiation	５．発行年 2020年
３．雑誌名 J. Nucl. Mater.,	６．最初と最後の頁 152016
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jnucmat.2020.152016	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 H. L. Yang, S. Kano, J. McGrady, J. J. Shen, Y. Matsukawa, D. Y. Chen, K. Murakami, H. Abe	４．巻 162
２．論文標題 Surface orientation dependence of irradiation-induced hardening in a polycrystalline zirconium alloy	５．発行年 2019年
３．雑誌名 Scripta Mater.	６．最初と最後の頁 209-213
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.scriptamat.2018.11.029	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Sho Kano, Huilong Yang, Jingjie Shen, Zishou Zhao, John McGrady, Dai Hamaguchi, Masami Ando, Hiroyasu Tanigawa, Hiroaki Abe	4．巻 502
2．論文標題 Investigation of instability of M23C6 particles in F82H steel under electron and ion irradiation conditions	5．発行年 2018年
3．雑誌名 J. Nucl. Mater	6．最初と最後の頁 263-269
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jnucmat.2018.02.004	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

1．著者名 Sho Kano, Huilong Yang, Jingjie Shen, Zishou Zhao, John McGrady, Dai Hamaguchi, Masami Ando, Hiroyasu Tanigawa, Hiroaki Abe	4．巻 17
2．論文標題 Instability of MX and M23C6 type precipitates in F82H steels under 2.8 MeV Fe2+ irradiation at 673 K	5．発行年 2018年
3．雑誌名 Nucl. Mater. & Energy	6．最初と最後の頁 56-61
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.nme.2018.08.001	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計8件（うち招待講演　3件／うち国際学会　8件）

1．発表者名 Sho Kano, H. Yang, H.Abe, Y. Watanabe, M. Ando, D. Hamaguchi, T. Nozawa, H. Tanigawa, K. Yoshida, T. Shibayama
2．発表標題 Radiation-Induced Amorphization of M23C6 in Reduced Activation Ferritic/Martensitic Steels: An atomic-Scale Observation
3．学会等名 GIMRT Joint International Symposium on Radiation Effects in Materials and Actinide Science: GIMRT-REMAS2020（国際学会）
4．発表年 2020年

1．発表者名 Hiroaki Abe, Sho Kano, Huilong Yang, John McGrady, Sun-ryun Oh, Feng Li, Hidehiro Yasuda
2．発表標題 On the stability of oxide/carbide nm-scale particles in ODS and F82H steels under irradiation; a review of in-situ observation studies in HVEM
3．学会等名 The Nineteenth International Conference on Fusion Reactor Materials (ICFRM19)（招待講演）（国際学会）
4．発表年 2019年

１．発表者名
H.L. Yang, S. Kano, J.J. Shen, D.Y. Chen, K. Murakami, H. Abe,

２．発表標題
Efefct of crytal orientation on hardness of Fe2+ irradiated 12Cr-ODS steel

３．学会等名
The Nineteenth International Conference on Fusion Reactor Materials (ICFRM19)（国際学会）

４．発表年
2019年

１．発表者名
Sho Kano, Huilong Yang, John McGrady, Wang Guangchen, Toru Higuchi, Hiroaki Abe

２．発表標題
Synergistic effects of irradiation and hydrogenation on microstructural and mechanical properties of Zr based fuel cladding alloys

３．学会等名
19th international conference Environmental Degradation of Materials in Nuclear Power System-Water Reactors, Boston USA, (2019).（国際学会）

４．発表年
2019年

１．発表者名
Hiroaki Abe

２．発表標題
Development of Advanced Nuclear Fuels and Structural Materials

３．学会等名
The 4th TU-UT Joint Multidisciplinary Symposium（招待講演）（国際学会）

４．発表年
2019年

１．発表者名
Hiroaki ABE, S. Kano, H.L. Yang, John McGrady, Q. Tang, N. Nikolova

２．発表標題
Development of Advanced Expansion Due to Compression (A-EDC) Test for Mechanical Property Evaluations of Nuclear Fuel Cladding

３．学会等名
The Asian Zirconium Workshop (AZW2019)（招待講演）（国際学会）

４．発表年
2019年

１．発表者名
H.L. Yang, S. Kano, J. McGrady, K. Murakami, H. Abe

２．発表標題
Crystal orientation dependence of irradiation-induced hardening in Zr-Nb alloys

３．学会等名
The Nuclear Materials Conferene 2018 (NuMat2018), Seattle USA, (2018)（国際学会）

４．発表年
2018年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

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７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関