Effect of Temperature on Fretting Corrosion Behaviors between Li_2TiO_3 Pebble and F82H

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(Received 6 February 2022 / Accepted 25 April 2022)

Lithium titanate (Li_2TiO_3) pebble is a candidate tritium breeder of solid breeder blanket systems of fusion reactors. The oscillation of coolant tubes can be induced by the coolant flow. Fretting corrosion is caused between the Li_2TiO_3 pebbles and the coolant tubes which are made of reduced activation ferritic martensitic steel F82H. The purpose of the present study is to clarify the fretting behaviors at the temperatures of blanket conditions. The Li_2TiO_3 pebble produced by sol-gel method was pushed onto the surface of the oscillating F82H plate in the fretting tests which were performed for 10 min in an air atmosphere up to 573 K. The fretting scars of the Li_2TiO_3 pebble and the F82H plate were observed and analyzed by SEM/EDX and 3D laser scanning microscope. The fretting wear was mitigated at the temperatures of 373 K and 473 K due to the formation of the oxide layer, which might reduce the friction. The pebble was partially destructed by the fretting motion in the test performed at 573 K. The fretting wear of the pebble and the F82H plate was mitigated when the pebble was not fixed on the holder since the pebble could vibrate together with the oscillating plate.

Keywords: fretting, corrosion, Li_2TiO_3, F82H, RAFM, fusion blanket, oxide layer, wear, oscillation

DOI: 10.1585/pfr.17.1405075

1. Introduction

Ceramic pebbles of lithium titanate (Li_2TiO_3) are used as a candidate tritium breeder in the solid breeder blanket of fusion reactors [1–3]. The Li_2TiO_3 pebbles are closely installed in the blanket box. The coolant tubes run through the blanket box and directly contact with the pebbles. The coolant tubes are made of reduced activation ferritic martensitic (RAFM) steel F82H. The temperature of water coolant varies in the range between 553 K to 598 K in the design of the ITER test blanket module [3].

The chemical compatibility of RAFM steel with solid breeders at the operation temperatures has been studied [4–7]. Li_2TiO_3 statically and chemically reacted with Indian RAFM steel (Fe-9.02Cr-1.46W) [4] and RAFM steel ARAA (Fe-9Cr-1.2W) [5], and formed oxide layers. $Li_{2+x}TiO_{3+x}$ with Li_2ZrO_3 also chemically reacted with F82H and formed oxide layers [6].

The occurrence of fretting corrosion is induced by the vibration of coolant tubes which contact with other structures. This phenomenon is widely recognized in the field of nuclear power plants [7]. Fretting studies are being performed to clarify the mechanism and prevent the failure of the reactor components [8]. The fretting wear of alloy 690 tubes against 304 stainless steel plates was reported in the previous study [9]. Fretting studies were also performed to examine the reliability of cladding materials (e.g., APMT, SiC and Zircaloy-4 [10]).

The fretting corrosion is possibly induced between solid breeder pebbles and coolant tubes in the blanket box of fusion reactors, since coolant tubes can be vibrated due to the water coolant flow. However, the study on fretting corrosion in the solid breeder blanket systems is quite limited. The previous study performed by authors clarified the fundamental behaviors of fretting corrosion between the Li_2TiO_3 pebble and the F82H plate in an air atmosphere at room temperature (RT) [11]. However, the fretting behaviors at the blanket operation temperature of coolant tubes installed in the box were not made clear so far.

The purpose of the present study is to clarify the behaviors of fretting corrosion between Li_2TiO_3 pebble and F82H plate at the temperatures up to 573 K.

2. Experimental Conditions

2.1 Test materials

The fretting tests were performed with the plate specimens of F82H BA12 HEAT and the pebble specimens of Li_2TiO_3. Table 1 presents the chemical composition of

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Table 1 Chemical composition of F82H BA12 HEAT (unit: wt%).

Cr	W	C	Si	Mn	P	S	V	Ta	B	Ti	O	N	Al	Fe
7.88	1.78	0.099	0.10	0.45	0.011	<0.0005	0.19	0.093	0.0040	<0.001	0.0012	0.0098	0.022	Bal.

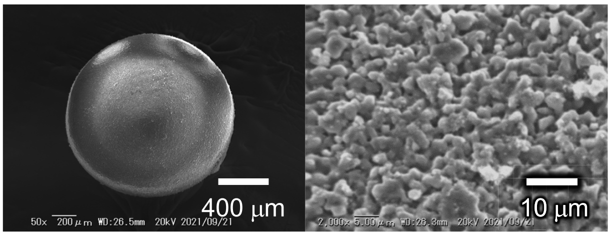

Fig. 1 SEM images of Li_2TiO_3 pebble before fretting test, (a) low-magnification SEM image and (b) high-magnification SEM image.

Table 2 Experimental conditions of fretting tests.

Load [N]	1.0
Frequency [Hz]	50
Amplitude [µm]	120
Time [min]	10
Temperature [K]	296, 373, 473, 573

F82H BA12 HEAT. The rectangular plate specimens of F82H which had a size of 16 mm × 16 mm × 2 mm were mirror polished. The Li_2TiO_3 pebbles were produced by sol-gel method. Figure 1 (a) shows the scanning electron microscope (SEM) images of the Li_2TiO_3 pebble before the fretting test. The diameter of the pebbles is approximately 1.2 mm. The Li_2TiO_3 pebbles have a porous structure to promote the release of tritium [12]. The grain size of the pebbles is less than 10 µm as shown in Fig. 1 (b).

2.2 Experimental apparatus

Figure 2 (a) shows the schematic diagram of the fretting test apparatus. The rotating motion of the motor was converted into the oscillation of the sliding table by the eccentric unit and connecting rod. The sliding table then oscillated horizontally [11]. The load was adjusted by changing the weight installed on the tray, which was balanced with the other side through the string and pulley as shown in Fig. 2 (b). Figure 2 (c) shows the schematic diagram of the test section. The ceramic heater was installed under the plate specimen to control the temperature of the specimen, and the specimen temperature was measured by a thermocouple.

The pebbles may be firmly stuck in the blanket box due to the tightly packed condition. In this condition, the fretting is caused between the pebbles fixed and the oscillating structural materials. The other possibility is that the pebbles may rotate according to the oscillation of the structural materials. Therefore, the tests were conducted under two different conditions as shown in Figs. 2 (d) and (e). Figure 2 (d) shows the schematic diagram of the pebble specimen holder in which the pebble fixed with glue was pushed onto the plate specimen in point contact. The fretting tests were also performed in the condition where the pebble was not fixed with the holder and could rotate and vibrate in the holder according to the motion of the oscillating plate specimen as shown in Fig. 2 (e).

2.3 Experimental conditions

Table 2 presents the experimental conditions of fretting tests. The fretting tests were performed at 296 K, 373 K, 473 K and 573 K. The fretting test at each temperature condition was repeated two or three times.

The fretting behaviors in an air atmosphere were investigated in the current work. The solid breeder blanket is operated under the environment of helium (He) including a small amount of hydrogen [13]. The oxidation behavior of RAFM steel F82H which has similar chemical composition with JLF-1 under the blanket condition has been investigated in the previous study [14]. The formation of Fe_2O_3 oxide layer on F82H was recognized in the oxidation test performed under He + 1 vol% hydrogen at 573 K for 100 hours [14]. The thickness of the oxide layer was approximately 50 nm. The surface oxidation of F82H under He + 1 vol% hydrogen was induced possibly due to the presence of a small amount of water vapor. The fretting behaviors involving the oxidation in an air atmosphere were investigated in the current work. The results of current fretting tests indicated the formation of Fe-Cr-O on the surface of F824 as described in a latter chapter. Thus, the present study could partially simulate the oxidation behavior under the blanket condition. The oxidation depth of the fretted area was not measured in the current work, since the fretted area was rough and very narrow. The oxidation depth in the current work could be thinner than the thickness of oxide layer formed under He + 1 vol% hydrogen [14]. The oxidation is promoted at the fretting area [15].

The load applied between the Li_2TiO_3 pebble specimen and the F82H plate specimen was 1.0 N. The static force applied to a single pebble in the blanket box may be less than this load. Previous studies indicated that wear was promoted when the load was larger [16].

The fretting debris [11] produced during the tests was collected to be microscopically observed and analyzed by SEM with energy dispersive X-ray spectroscopy (EDX).

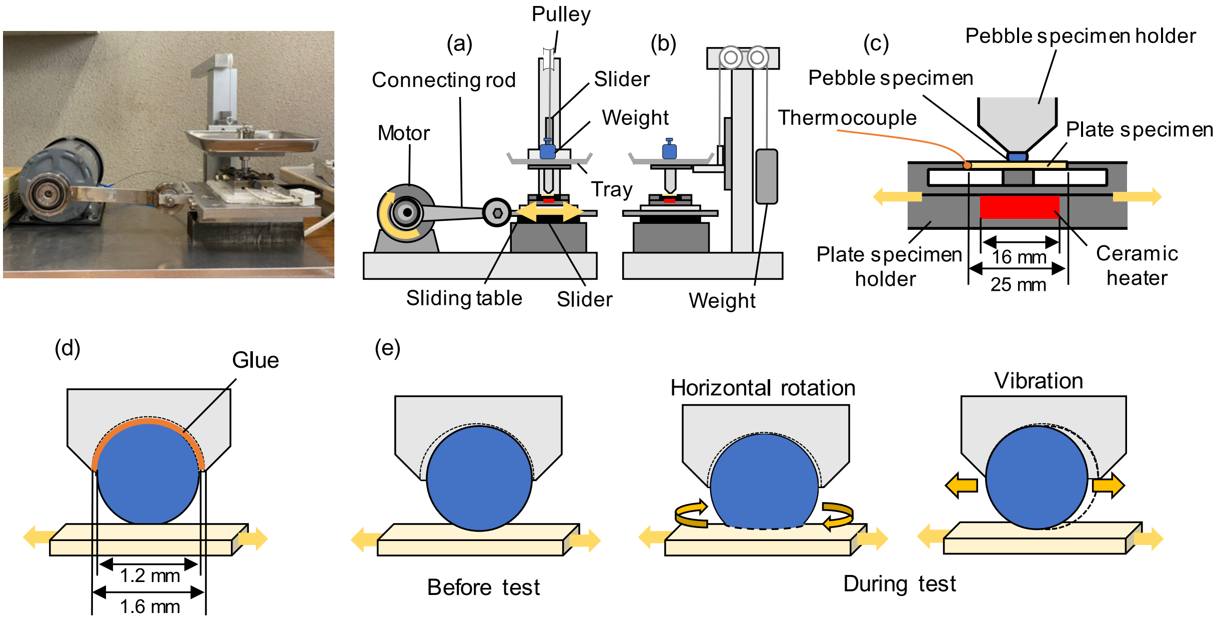

Fig. 2 Schematic illustrations of fretting test apparatus, (a) front view, (b) side view, (c) test section of fretting test apparatus, (d) pebble specimen holder with fixing pebble and (e) pebble specimen holder without fixing pebble.

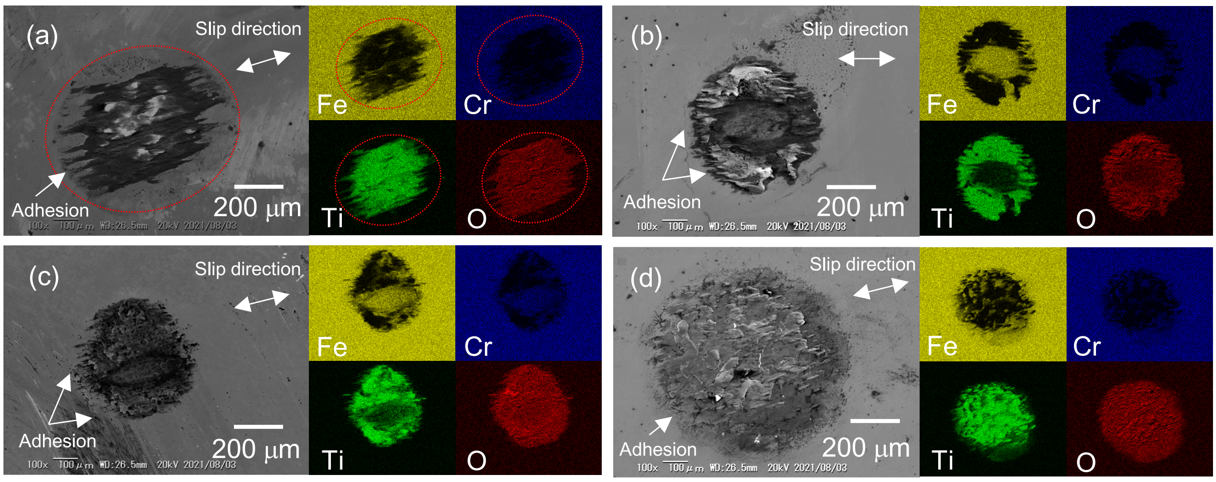

Fig. 3 SEM images and results of EDX mapping analysis of fretted area on F82H specimens formed in tests at (a) 296 K, (b) 373 K, (c) 473 K and (d) 573 K.

The F82H plate specimens were then cleaned for 5 min by ultrasonic cleaning with acetone. The fretted areas of F82H plates and Li_2TiO_3 pebbles were observed and analyzed by SEM/EDX and 3D laser scanning microscope (LSM).

3. Results and Discussions

3.1 Fretting behaviors between oscillating F82H plate and Li_2TiO_3 pebble fixed on holder

3.1.1 Test at 296 K

Figure 3 (a) shows the SEM image and the results of EDX mapping analysis of the fretted area formed on the F82H plate in the test at 296 K. The oval fretting scar which had a diameter of approximately 754 μm was observed on the F82H specimen. The local maximum depth of the fretting scar formed on the F82H specimen was 47.99 μm as shown in Fig. 4.

The Li_2TiO_3 pebble was worn due to the fretting wear as shown in Fig. 5 (a). The diameter of the worn area was approximately 716 μm. The worn area had a rugged surface, and the maximum height of the irregularities was approximately 50 μm. This corresponds to the local maximum depth of the fretting scar on the F82H specimen as shown in Fig. 4. Therefore, the deep scar on the F82H specimen might be made by the fretting with the pebble which had the rugged surface. The volumetric loss of the

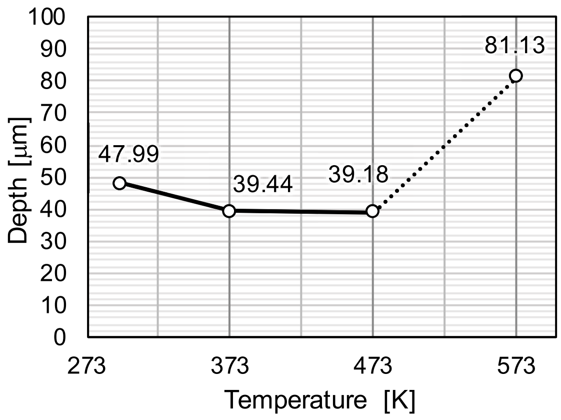

Fig. 4 Local maximum depth of fretting scars formed on F82H specimens.

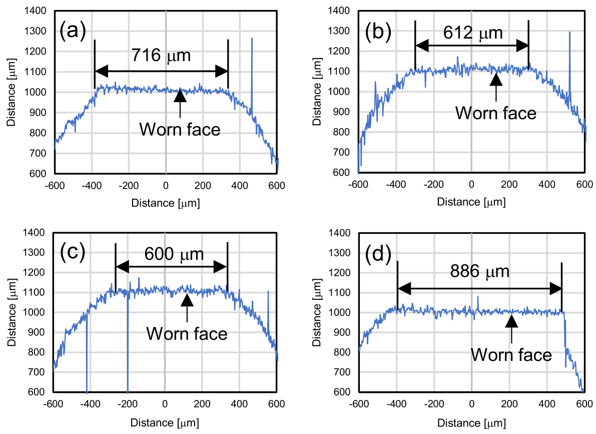

Fig. 5 Cross-sectional profiles of Li_2TiO_3 pebbles tested at (a) 296 K, (b) 373 K, (c) 473 K and (d) 573 K.

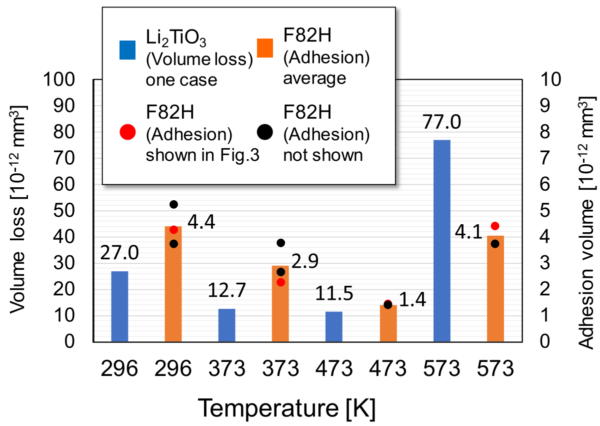

Fig. 6 Volumetric loss of Li_2TiO_3 pebbles and adhesion volume on fretted areas of F82H specimens.

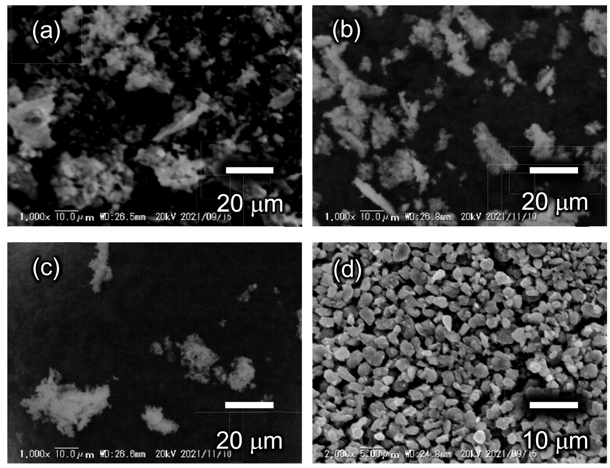

Fig. 7 SEM images of fretting debris, (a) test at 296 K, (b) test at 373 K, (c) test at 473 K and (d) test at 573 K.

pebble was estimated as 27.0×10^{-12} m^3 from the wear condition and shown in Fig. 6.

The adhesion was recognized around the center of the fretted area, and Ti and O were detected in the adhesion by EDX as shown in Fig. 3 (a). Therefore, the adhesion could be the attachment of debris produced by the fretting wear of the Li_2TiO_3 pebble. The volumetric loss of F82H by fretting wear and adhesion volume of debris are shown in Fig. 6. The volume of adhesion which is shown in Fig. 3 is indicated by red closed circle. The volume of adhesion was 4.28×10^{-12} m^3 as shown in Fig. 6. This adhesion volume corresponds to approximately 16% of the volumetric loss of the Li_2TiO_3 pebble. Figure 7 (a) shows the SEM image of the fretting debris. The debris was produced by the wear of Li_2TiO_3 pebble.

3.1.2 Test at 373 K

The diameter of the fretting scar formed on the F82H specimen was approximately 557 μm as shown in Fig. 3 (b). The diameter of the fretting scar at 373 K was approximately 26% smaller than that at RT. The local maximum depth in the fretted area formed on F82H was 39.44 μm as shown in Fig. 4. The depth was approximately 18% smaller than that at RT.

The worn area formed on the pebble had a diameter of approximately 612 μm as shown in Fig. 5 (b). This diameter was approximately 15% smaller than that at RT. The volumetric loss of Li_2TiO_3 pebble was 12.7×10^{-12} m^3 as shown in Fig. 6. This loss was much smaller than that at RT. These results indicated that the fretting wear of the pebble was mitigated at 373 K.

The adhesion was observed at both sides of the fretted area along the oscillation direction as shown in Fig. 3 (b). The adhesion volume on the fretted area was 2.2 $\times 10^{-12}$ m^3 as shown in Fig. 6, and this value was much smaller than that at RT. Ti was detected in the outer region of the fretted area, though it was not detected in the center region as shown in Fig. 3 (b). The debris might be formed and discharged to both sides and pressed by the pebble. O was detected with Fe and Cr in the center region of the fretted area. The formation of the Fe-Cr oxide layer was induced only on the fretted area.

3.1.3 Test at 473 K

The diameter of the fretting scar formed on the F82H specimen was approximately 524 μm as shown in Fig. 3 (c). The diameter was slightly smaller than that at 373 K. The local maximum depth of the fretting scar was 39.18 μm as shown in Fig. 4. The depth was almost the same with that at 373 K. The fretting damage of the F82H specimen was nearly the same with that at 373 K.

The adhesion of debris was detected on both sides of the fretted area, though it was not recognized in the center region as shown in Fig. 3 (c). This feature was the same with the case at 373 K. The adhesion volume was 1.4×10^{-12} m^3 as shown in Fig. 6. The adhesion was approximately 36% smaller than that at 373 K. The surface was oxidized locally in the center region of the fretted area.

The diameter of the worn area formed on the pebble was approximately 600 μm as shown in Fig. 5 (c). This diameter was slightly smaller than that at 373 K. The volumetric loss of Li_2TiO_3 pebble was 11.5×10^{-12} m^3. The loss was almost the same as that at 373 K.

These results indicated that the fretting damages of the F82H plate and the Li_2TiO_3 pebble were mitigated at the temperatures of 373 K and 473 K. The previous study [17] indicated that the fretting damage could be mitigated when the hardness and coefficient of friction of the material surface were reduced due to the formation of the oxide layer. The fretting damages in the present work were also mitigated at higher temperatures due to the formation of the oxide layer.

3.1.4 Test at 573 K

The diameter of the fretting scar formed on the F82H specimen was approximately 821 μm as shown in Fig. 3 (d). The diameter was approximately 57% larger than that at 473 K. The local maximum depth was 81.13 μm as shown in Fig. 4. The depth was approximately two times deeper than that at 473 K. These results indicated that the damage of the plate specimen was more severe than that at other temperatures.

The diameter of the worn face formed on the pebble was approximately 886 μm as shown in Fig. 5 (d). The diameter was approximately 48% larger than that at 473 K. The volumetric loss of the Li_2TiO_3 pebble was 77.0×10^{-12} m^3 as shown in Fig. 6. The loss was almost seven times greater than that at 473 K. These results indicated that the damage of the pebble at 573 K was more severe than that at other temperatures.

The adhesion of debris was recognized on the fretted areas of the plate specimen as shown in Fig. 3 (d). The adhesion volume was 4.4×10^{-12} m^3 as shown in Fig. 6. The volume was approximately three times larger than that at 473 K. The size of the debris at 573 K was approximately 2.5 μm as shown in Fig. 7 (d). The debris was much larger than that at other temperatures. The round shape was also different from the debris produced at other temperatures. The Li_2TiO_3 pebbles have a porous structure, and the grain size was approximately 5 μm as shown in Fig. 1 (b). The fretting debris might be produced by the crash of the matrix that porously composed the pebble at 573 K. The pebble was partially destructed during the test. This would increase the contact area of the pebble on the plate specimen. The partial destruction promoted the fretting damage of the plate specimen.

3.2 Fretting behaviors between F82H and Li_2TiO_3 pebble without fixing

The Li_2TiO_3 pebble could vibrate together with the oscillating plate, since there was a small gap between the pebble and the holder. The vibration might be induced by the friction between the pebble and the oscillating plate at room temperature. The wear of the pebble was not caused when the pebble vibrated together with the oscillating plate.

The friction between the metals became smaller when the oxide formed on the metals [17]. The friction might be smaller in the tests at 373 K and 473 K since the fretted area on the F82H surface was locally oxidized as shown in Figs. 3 (b) and (c). Then, the vibration of the pebble was not induced due to the small friction. The pebble was then worn by the fretting motion in the same way as the tests in which the pebbles were fixed on the holder.

Figure 8 shows the consecutive photos and illustrations of fretting between Li_2TiO_3 pebble and F82H plate in the test at 473 K. The horizontal rotation of the pebble specimen was recognized in the tests at 373 K and 473 K. The pebble was marked with a solid circle in black color, and the slow motion of the black mark indicated that the pebble rotated horizontally on the oscillating plate specimen.

Figure 9 shows the adhesion volume on the fretted area of the F82H specimen in the tests. The adhesion volume increased at 373 K and 473 K, though the adhesion was suppressed at 573 K. Less adhesion was due to less fretting wear of the pebble. The fretting wear was suppressed possibly due to the vibration of the pebble together with the oscillating plate specimen at 573 K. The contact area of the pebble might be destructed and/or deformed on the oscillating plate in the initial stage of the test at 573 K as illustrated in Fig. 8 (g). The deformed area had a flat face with a porous structure and the friction might be promoted. The pebble then vibrated together with the oscillating plate as the same as that at RT. The fretting wear was then mitigated by the vibration. The horizontal rotation of the pebble at 373 K and 473 K did not suppress the fretting wear.

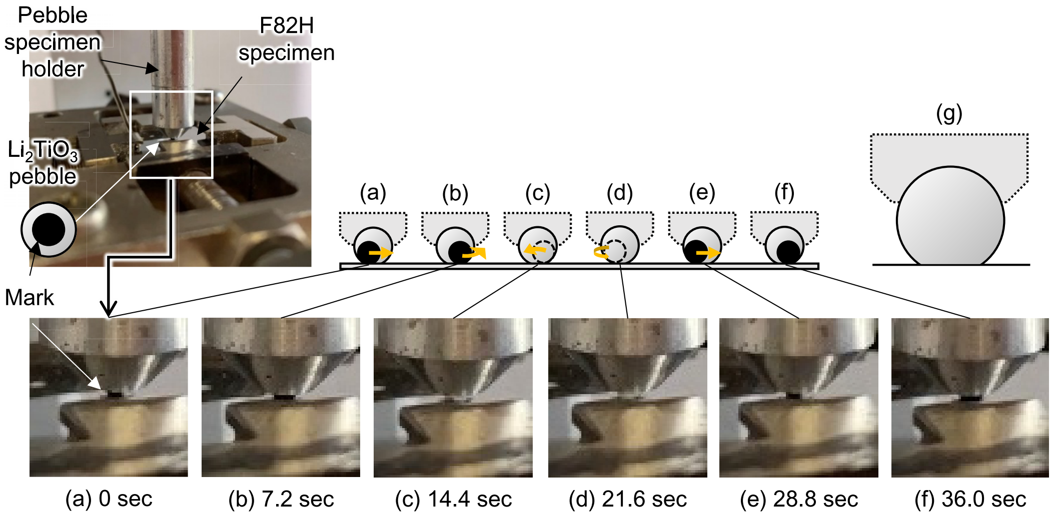

Fig. 8 Consecutive photos and illustrations of fretting between Li_2TiO_3 pebble and F82H plate in fretting test without fixing, (a) 0 sec, (b) after 7.2 seconds at 473 K, (c) after 14.4 seconds at 473 K, (d) after 21.6 seconds at 473 K, (e) after 28.8 seconds at 473 K, (f) after 36.0 seconds at 473 K and (g) shape of pebble in initial stage of test at 573 K.

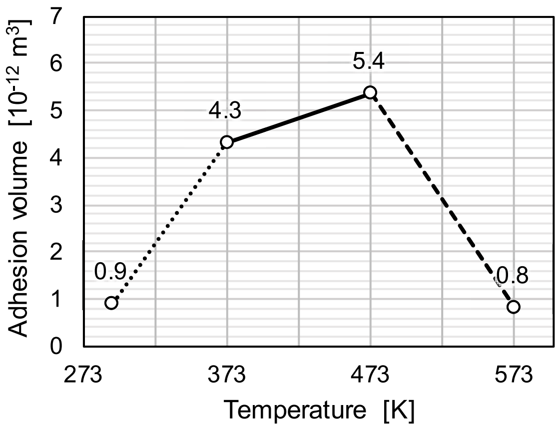

Fig. 9 Adhesion volume of fretting debris on fretted areas of F82H specimens in fretting tests performed without fixing of pebble on pebble specimen holder.

4. Conclusion

Major conclusions are as follows.

1. The fretting tests were performed as the Li_2TiO_3 pebble fixed was pushed onto the oscillating F82H plate up to 573 K. The result of the test at room temperature indicated that the fretting wear was caused both on the pebble and the plate. The damages were mitigated at the temperatures of 373 K and 473 K since the friction between the materials was reduced due to the formation of the oxide layer on the F82H plate. The pebble was partially destructed according to the fretting motion in the test at 573 K. The partial destruction promoted the fretting damage of the plate specimen.
2. The Li_2TiO_3 pebble could vibrate in the gap between the pebble and the pebble holder according to the oscillation of the plate specimen at room temperature when the pebble was not fixed on the holder. The pebble rotated horizontally on the oscillating plate during the fretting tests at 373 K and 473 K. The pebble was partially destructed in the fretting motion at 573 K, and this damage promoted the friction between the pebble and the plate. The pebble could then vibrate in the holder together with the oscillating plate, and the fretting damage was mitigated.

Acknowledgments

Authors would acknowledge Dr. Tada of Open Facility Center, Materials Analysis Division, Tokyo Institute of Technology for his technical assistance on SEM/EDX analysis, and Ms. Mochinaga of Tokyo Institute of Technology for her technical assistance on 3D laser scanning microscope. Authors would acknowledge Mr. Doi and Mr. Hara of Laboratory for Zero-Carbon Energy, Tokyo Institute of Technology for their technical assistance on manufacturing experimental apparatus. Authors would acknowledge Dr. Nozawa of QST for providing the F82H specimens. This work was partially supported by QST Research Collaboration for Fusion DEMO under the Joint Work contract 03K216.

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