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Non-crystalline zirconia structure formation by severe mechanical damaging

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Zirconia containing 2.85 mol % Y_2O_3 and 1.42 mol % HfO_2 was repeatedly rubbed in one direction without lubricant at room temperature. Transmission electron diffraction (TEM diffraction) taken from the above specimen revealed a structure created as the sum of the contributions of compounds of the composing elements. Further, this also showed halo rings that suggest amorphous zirconium formation. These transformations act as mechanisms of plastic deformation during rubbing.

1. Introduction

Ceramics in general have excellent mechanical properties except low fracture toughness. Zirconia ceramics containing some metal oxides, however, have exceedingly high fracture toughness compared to other ceramics and much wear-resistant than metals and metallic alloys. Most machine elements, dies, cutting tools and others become unusable owing to wear arisen from numerous repeated frictions and oxidization. Although there are some problems such as manufacturing cost, just after their invention in 1970s, they, therefore, have been considered to be one of the most hopeful new materials to make machines more durable. The wear mechanism of zirconia by repeated rubbing, however, has not been fully clarified yet. One of the purposes of this paper, therefore, is to acquire some knowledge of the mechanism of wear by repeated rubbing of zirconia.

In repeatedly rubbed alumina, a structure consisting of the sum of the contributions from different aluminas formed [1]. A similar structure has been found in repeatedly rubbed iron oxide and is considered to be neither crystal nor quasicrystal owing to the lack of interplanar regularity [2], in spite of the existence of atom-composed planes. Furthermore, repeated rubbing generates structures whose atomic arrangement is ordered only in one direction, in alumina [3] and copper [4], respectively. Only repeated rubbing has made these structures. Mechanical and chemical properties of zirconium oxide whose atomic arrangement differs from that of already reported ones ought to be different from those reported zirconium oxide. The second purpose of this study, therefore, is to make new zirconium oxide by repeated rubbing and to modify the friction surface. During repeated rubbing, debris numerously repeats exfoliation and adhesion and are extremely damaged. The atomic arrangement inside of these debris ought to be extremely disordered. Accordingly, we can expect to obtain knowledge of extremely mechanically damaged state, in addition to the above purposes.

2. Experimental procedure

Zirconia containing 2.85 mol % yttria and 1.42 mol % hafnia was repeatedly rubbed in one direction without lubricant at room temperature in the air at the relative humidity of 50–70%. The rubbing pressure, the rubbing speed, the frequency, and the rubbing distance per traverse were 1.45 MPa (1.37–1.53 MPa), 142.9 mm/s, 0.65 Hz, and 23 mm, respectively. The rubbing apparatus is schematically shown in Fig. 1. The mode of repeated rubbing by this apparatus is different from that of most of the studies on repeated rubbing: in the latter mode, the same surface area of a slider always contacts throughout the repeated rubbing, e.g. repeated rubbing of a part of the friction surface of a rotating disc by a pin-on-disc type apparatus. In the present study, debris attached to the slider are easily caught between the specimen and the slider at the beginning of their contact and the contact area of a slider repeatedly cools down during repeated rubbing. The mode of repeated rubbing of tooth surface of gears and others resembles to that of the present study. What we call rolling friction accompanies sliding friction owing to the deformation

* The study was made when he was a postgraduate student at Yamanashi University.

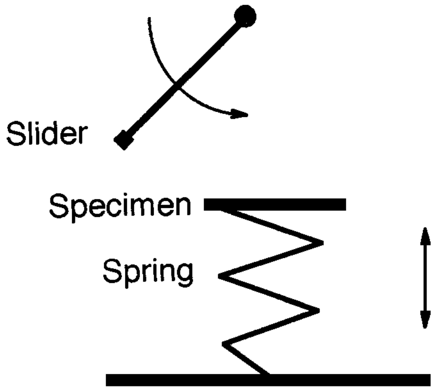

Figure 1 Scheme of the repeated rubbing apparatus.

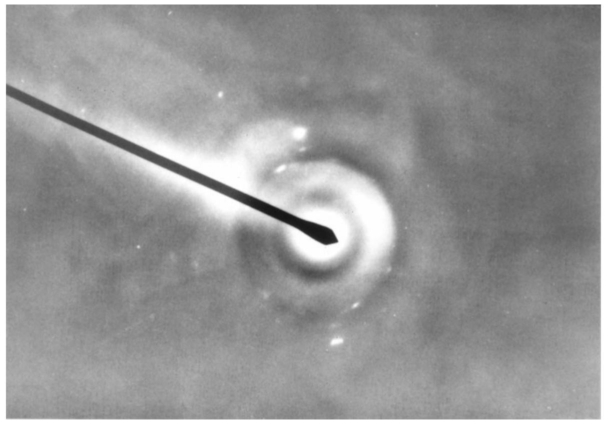

Figure 2 Transmission electron diffraction pattern from repeatedly rubbed zirconia (3×10^4 traversals).

of contact areas. Therefore, the mode of sliding friction arisen from rolling friction with high normal load resembles to that of the present experiment. Rolling friction with high normal load is frequently found in machinery, e.g., wheels of cars on rails.

After repeated rubbing, we examined specimens under a transmission electron microscope (TEM) with a lapse of about one month. Specimens for TEM were thinned by bombarding 99.999 vol % argon ion accelerated at 4 keV at an angle of $\pi/15$ rad only from the opposite side to the friction surface. Probably due to residual stress and scratches arisen from rubbing, the thinnest area of the specimens, that is, the central area where ion beam most severely radiated, frequently broke into pieces. Repeatedly rubbed surface is not smooth. Accordingly, we had no choice but to observe luckily unbroken thin areas near the center hole of the specimens. The thin areas in this case correspond to those under scratches formed by rubbing. Accordingly, it was impossible to observe a structure in the areas between scratches. Halo rings and some spots were extremely faint under TEM and almost escaped observation. Accordingly, long exposure time (about 5 min) was needed to photograph the diffraction pattern.

The observed diffraction spots by TEM were indexed when both the interplanar spacing and the interplanar angles correspond to parts of structures of compounds consisting of the composing elements of specimens, within the limits of 0.5 nm and 52 mrad (3°), respectively.

Some specimens were analyzed with X-ray photoelectron spectroscopy (XPS). No segregation of elements was detected.

3. Results and discussion

Fig. 2 shows a transmission electron diffraction pattern (TEM diffraction pattern) taken from a specimen in the state of steady state wear (after 30,000 traversals). Like TEM diffraction patterns taken from repeatedly severely rubbed materials [1–5], it is extremely disordered, asymmetric with respect to the direct spot and in spite of severe damaging, the spots are not elongated but round. The spot arrangement, on the whole, does not correspond to any compound containing zirconium. The arrangement, however, partly corresponds to compounds of composing elements (Fig. 3a–i).

We often see plural spot groups that partly correspond to the identical compound. Spots that belong to different groups sometimes lie on the identical straight lines (hereafter these straight lines will be called connecting lines). Not only spots corresponding to the same compound but also those corresponding to the different ones also lie on identical connecting lines (Fig. 4), although their slopes do not always coincide with those in Fig. 3. No dislocation was observed in the area from where Fig. 2 was taken, despite the repeated severe rubbing (Fig. 5). It may be said that repeated rubbing of zirconia generated a new structure that consists of parts of the structures of compounds of the composing elements. Although this structure has atom-composed planes, it may not be considered as crystal owing to the lack of interplanar regularity. Similar structures have been found in repeatedly rubbed alumina [1] and iron oxide [2].

The compound in Fig. 3c, that is, O in Fig. 4 has been found at atmospheric pressure after quenching zirconia kept at ultrahigh pressures [6]. This indicates ultrahigh pressure generation during repeated rubbing and remaining of the ultrahigh pressure state at atmospheric pressure, although the generation may be restricted in narrow regions. TEM diffraction patterns suggesting ultrahigh pressure generation by repeated rubbing has been presented in iron oxide [1] and iron [4], with a long lapse of time after finishing the repeated friction. Ultrahigh pressure state also lasts in sheared glass [7], although the reason has not been fully clarified yet.

We can see two faint broad halo rings in Fig. 2. Interplanar spacings corresponding to the radii are 254.7 and 143.5 pm. The ratio of the smaller radius to the larger one is about 0.56. As shown in Table I, this coincides with that of "polish pattern" (diffraction patterns taken from rubbed metals, which consist of two halo rings). The interplanar spacings that correspond to the most intense and the second intense diffraction from β zirconium are 250.7 and 144.7 pm [8]. Those from ω zirconium are 253 and 145.7 pm [9]. These values are close to the corresponding interplanar spacings of the halo rings and the ratios are 0.58 in both cases. The formation of halo rings has also been found in repeatedly rubbed alumina [3]. In this case, deoxidization from alumina was observed. Amorphous formation by rubbing has been reported in iron [5, 10, 11],

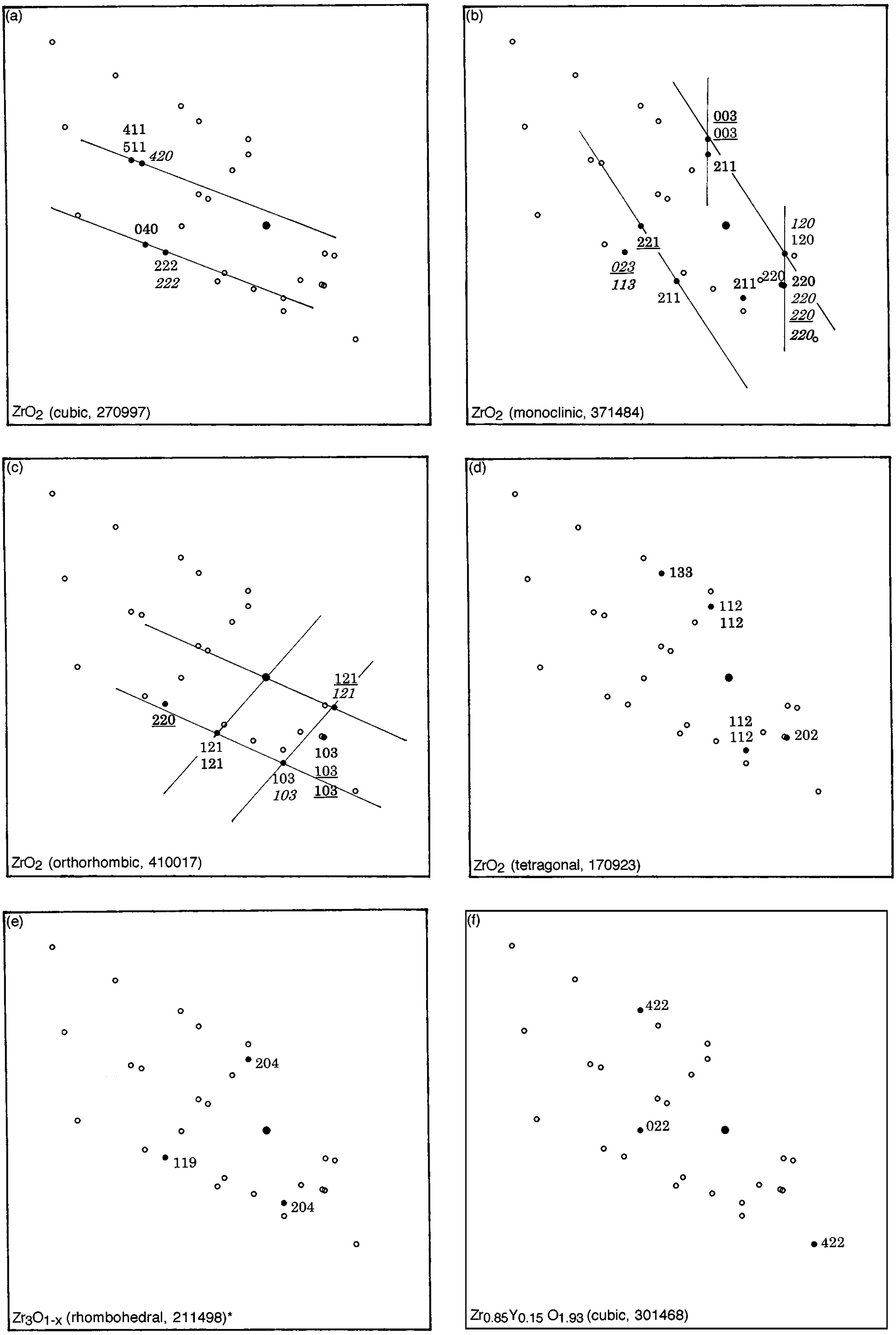

Figure 3 Schematic diagrams of spot arrangement in Fig. 3: ● coincident (not only interplanar spacing but also interplanar angle) spots, ○ uncoincided spots. Different figure style was used to distinguish spot groups that differently correspond to the identical compound. Figures in parentheses are JCPDS card numbers. *In accordance with JCPDS card, lattice planes are indexed as hexagonal system. (*Continued*)

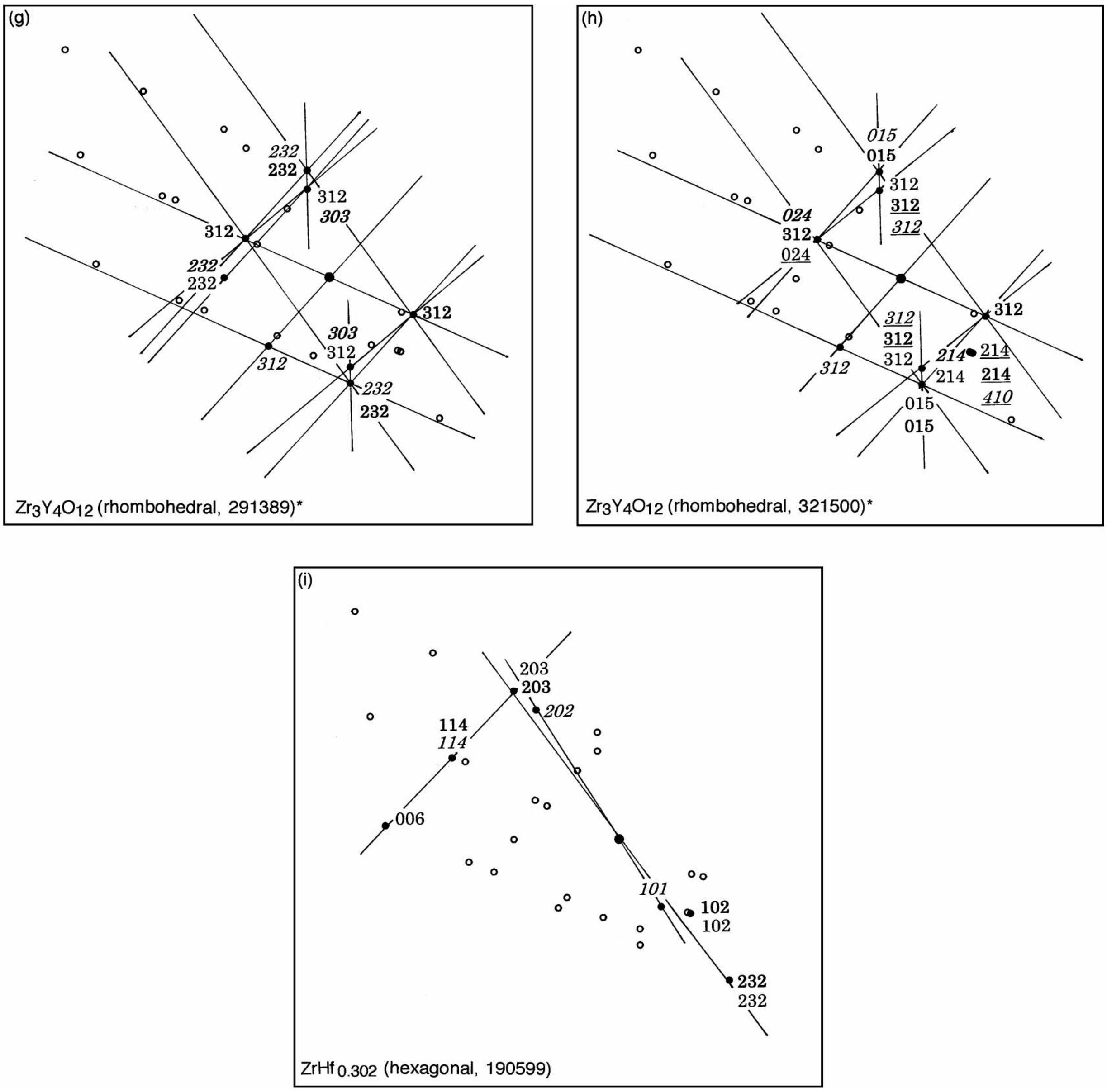

Figure 3 (*Continued*).

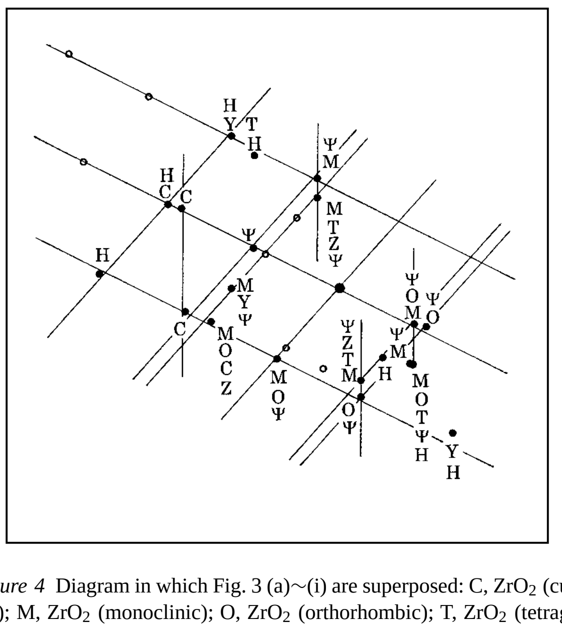

Figure 4 Diagram in which Fig. 3 (a)∼(i) are superposed: C, ZrO_2 (cubic); M, ZrO_2 (monoclinic); O, ZrO_2 (orthorhombic); T, ZrO_2 (tetragonal); Z, Zr_3O_{1-x}; Y, $Zr_{0.85}Y_{0.15}O_{1.93}$; Ψ, $Zr_3Y_4O_{12}$ (291389) and $Zr_3Y_4O_{12}$ (321500); H, $ZrHf_{0.302}$. Figures in parentheses are JCPDS card numbers.

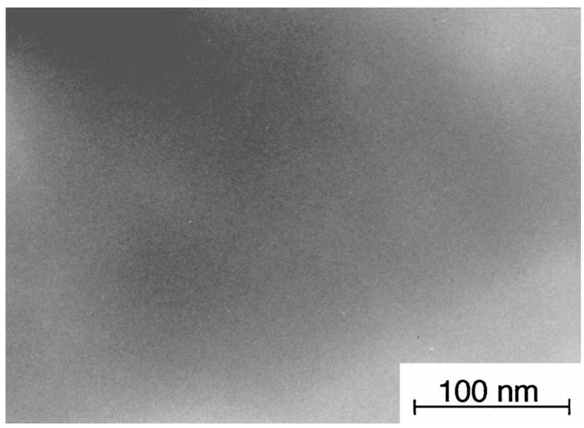

Figure 5 Transmission electron micrograph of the area where Fig. 2 was taken.

copper [4, 10–12] and other metals [10–12]. The above facts, therefore, may suggest the formation of zirconium amorphous.

These transformations act as one of the mechanisms of plastic deformation during repeated rubbing.

TABLE I Ratio of interplanar spacings of halo rings in polish patterns

Material	Interplanar spacing (pm)		Ratio	Ref.
	Ring1	Ring2	Ring2/Ring1	
ZrO_2	254.7	143.5	0.56	
β Zr	250.7	144.7	0.58	8
ω Zr	253	145.7	0.58	9
Au	223	127	0.57	10
Ag	224	125	0.56	10
	228	124	0.54	11
Cu	197	116	0.59	10
	224	125	0.56	11
	226	122	0.54	12
Fe	197	116	0.59	10
	225	125	0.56	11
Ni	199	116	0.58	10
	223	126	0.57	11

4. Conclusions

Zirconia containing small amount of yttria and hafnia was repeatedly rubbed without lubricant. TEM diffraction taken from repeatedly rubbed specimens revealed a structure that comprises a part of the structure of compounds consisting of composing elements. Despite the existence of atom-composed planes, this structure may not be considered as a crystal owing to the lack of interplanar regularity. It is neither quasicrystalline nor amorphous. Further, the pattern showed two halo rings that correspond to the most intense and the second intense rings from β zirconium and those form ω zirconium. We can not, therefore, deny the possibility of zirconium amorphous formation.

These transformations act as mechanisms of plastic deformation during repeated rubbing.

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