Amorphous iron formation following occupancy of iron atoms in vacant sites of epsilon-iron that transformed from alpha-iron during rubbing in a low vacuum

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Abstract. The main purpose of this paper is to present two TEM diffraction patterns taken from a layer (more than 100 μm thick) of piled-up adhered wear debris on a rubbed surface. The unidirectional rubbing was made in a low vacuum, regularly separating the slider from the specimen. The specimen and the slider were α-iron. One of the diffraction patterns consists of large spots and halo rings and the other consists of small faint spots and halo rings. The latter seems to be the state just before the perfect amorphization. All the spots in the diffraction patterns correspond to the structure formed due to the occupancy of iron atoms in O and T sites of ε-iron. Neither this way of amorphization nor the occupied structure mentioned above has not been reported. Both the amorphous state and the occupied structure remain at ambient conditions. The mechanism of high-pressure generation that transformed α-iron to ε-iron and the generation of high tensile stress that breaks the atomic bonds in wear debris are presented. The latter is considered to have enabled the occupancy.

1. Introduction

This article presents the transformation from α-iron to ε-iron that exists at 13 GPa and above [1], the occupancy of iron atoms in the T and O sites of the ε-iron structure [2] and the formation of amorphous iron following it, during unidirectional rubbing in a low vacuum, regularly separating the slider from the specimen. Hereafter, the iron after the occupancy and the unidirectional rubbing mentioned above will be called the occupied iron and unidirectional discontinuous rubbing. Neither the occupied iron nor this way of amorphous-iron formation has not been reported.

The mechanism of the high-pressure generation that transformed α-iron to ε-iron and that of the generation of high tensile stress that breaks the atomic bond are also presented. The latter enabled the occupancy.

The properties of the occupied iron and the amorphous iron mentioned above should be different from those of α-iron. The rubbing is inexpensive. Therefore, we can expect their practical application.

2. Material and methods

TEM diffraction patterns were taken from the layer of piled-up adhered wear debris generated by unidirectional discontinuous rubbing in a vacuum (7-13 mPa) between α-iron slider and α-iron specimen without lubricant at room temperature with the apparatus shown in figure 1.
In this case, it was necessary to take diffraction patterns from only one of each pieces of debris to avoid the overlapping of the diffraction patterns. This is the reason why I took TEM diffraction patterns because an electron beam can be focused by the electron lenses, and, therefore, it is possible to irradiate a narrow area. The used iron was commercial pure polycrystal one (C<0.003%,Si<0.005%,Mn<0.005%, P<0.005%, S<0.0003%, Al<0.005%, in mass). The specimens and the sliders were annealed and electropolished before rubbing. The apparent maximum pressure during the sweep of the slider, the sliding speed, the frequency and the sliding distance per cycle were 7 MPa, 32mm/s, 0.19 Hz and 20.5mm, respectively. The diffraction patterns were taken from the area where the apparent pressure was highest, after 2.5 x 10^4 traversals.

Even on extremely smoothly finished surfaces, there are many minute asperities [3]. When the slider contacts with the specimen, asperities on the specimen or those on the slider contact with the friction surface of the slider or of the slider and high pressure is generated at the contact areas; these contact areas have been called true contact areas and the generated high-pressure true contact pressure [4]. In the case of unidirectional discontinuous rubbing, when the slider leaves the specimen, the temperature of the true contact areas drops, and the asperities recover their hardness. This enables the repetition of the shearing at high pressure. After numerous repetitions of the rubbing, much debris piles up on the specimen and adheres to other debris to form a layer, whose thickness reaches more than 100 μm [5]. The thinning of the specimens to take TEM diffractions was made by fine emery polishing followed by electropolishing, only from the opposite side of the rubbed surface. Some TEM diffraction patterns had to be taken without a beam stopper, because it was impossible to make wide thin TEM-specimens owing to the severe surface roughness. After thinning, the specimens were dipped into extremely pure cyclohexane for at least three months at room temperature to know the survivability of the structure and state generated by the rubbing; cyclohexane prevents oxidation from iron.

3. Structure analysis and discussion

Figure 2 shows TEM diffraction patterns taken from the layer of piled-up adhered wear debris.
As demonstrated in Table 1, figure 2 does not correspond to α-iron [6].

Table 1. Data of spots in figure 2.

| Spot number | Interplanar spacing (pm) | Reciprocal of fractional intercept | Intensity | After occupancy |
|-------------|--------------------------|-------------------------------------|-----------|----------------|
| 1           | 177                      | 2 x (2 0 8/3)                       |           |                |
| 2           | 155                      | 4 x (2 0 10) *                      |           |                |
| 3           | 122.5                    | (1 1 0)                             | 4f²       | 64f²           |
| 4           | 102                      | (3/2 0 8/3)                         |           |                |
| 5           | 96                       | (3/2 0 3)                           | 23f²      |                |
| 6           | 86                       | (2 0 8/3)                           |           | 25f²           |
| 7           | 75                       | 2 x (2 0 10) *                      |           |                |
| 8           | 71                       | (3 0 0)                             | 4f²       | 64f²           |
| 9           | 68                       | (2 1 3)                             | 3f²       | 28f²           |
| 10          | 61                       | (2 2 0)                             | 4f²       | 64f²           |
| 11          | 54                       | (3 1 3)                             | 3f²       | 32f²           |
| 12          | 46                       | (4 1 0)                             | 4f²       | 64f²           |

*Intensity of (2 0 10) is 23f².

Some spots correspond to ε-iron that exist at 13GPa and above [1]. The other spots correspond to the planes whose reciprocals of fractional intercept with a, b and c axes contain at least one nonintegral.

There are vacant sites in the ε-iron structure, i.e. O sites: 2/3, 1/3, 1/4; 2/3, 1/3, 3/4 and T sites: 1/3, 2/3, 2/3, 1/8; 1/3, 2/3, 7/8; 0.0, 5/8; 0.0, 3/8 [2]. Comparison between these vacant sites and the nonintegral plane indices in Table 1 leads to the idea that the diffraction patterns were taken from the structure after the occupancy of iron atoms in the vacant sites of ε-iron. Occupancy of titanium atoms in the vacant sites of α-titanium by shearing at high pressure has been reported [7].

At the spot 1 in the pattern A, no spot ought to exist. There is no choice, therefore, but to think that the spot 1 is the superlattice of the spot 5. It has been reported that superlattice form in sheared iron up to 14 GPa [8]. For the structure mentioned above to occur, high pressure of 13 GPa and above that enable the transformation from α-iron to ε-iron must occur [1] and iron atoms must enter the inside of ε-iron structure. Generation of very high pressure by unidirectional discontinuous rubbing have been reported [9,10].

When the asperities on the slider or on the specimen contact with the other friction surface, they adhere to it and are pressed downward and laterally pulled with the movement of the slider and break to become wear debris. This mechanism has been called adhesive wear and has been accepted among tribologists [11]. For the high pressure mentioned above to be generated, the adhered asperities must be tensioned or compressed without yielding, i.e., without the movement of dislocations. The Young’s modulus (E) of hcp iron in compression increases with the pressure [12]. Therefore, its smallest value appears just after the beginning of compression, i.e., fairly higher than 600 GPa [12]. High pressure 13 GPa is generated when the adhered asperities elastically deform a little higher than 2.0%.

Without the movement of dislocations, the breaking stress of the adhered asperities is almost equal to the ideal strength, i.e., E/10 [13]. From the Hooke’s law, the elongation of the interatomic distances just before the breaking of wear debris is about 10%. Assuming that atom is a ball of radius r, the radius of ball that enter O sites and T sites before applying stress are 0.414r and 0.225r, respectively [2]. Judging from the facts mentioned above, it is impossible for iron atoms to occupy in the vacant sites of ε-iron, at this stage.

TEM diffraction patterns taken from unidirectionally discontinuously rubbed ceramics revealed a structure that comprises a part of the structure of compounds consisting of composing elements, some
of them exist at high pressure [14,15]. There was a case, however, where one of the composing elements of ceramics became an amorphous metal, besides the formation of the structure mentioned above [15]. This indicates that plural structures that comprise a part of the structure of compounds consisting of composing elements can exist. Without diffusion, it is impossible for the structure mentioned above to bond again.

Diffusion coefficients of ceramics are much lower than those of metals [16]. It can be considered, therefore, that the same phenomenon occurs with metals. Epsilon iron is composed only of iron atoms. If \( \varepsilon \)-iron breaks, diffused iron atoms occupy the widened vacant sites and as in the case of ceramics, broken atomic bonds were also bonded by diffused iron atoms. This process gives birth to the occupancy. There are many asperities on the friction surfaces. Wear debris repeat adhering to the slider and exfoliating from it, many times. Accordingly, a large number of occupied sites are generated. The halo rings in the diffraction patterns indicate the amorphous state formation.

This is as much explanation as possible, because no detailed elucidation of the mechanism of adhesive wear has been made [17].

The transformation from \( \varepsilon \)-iron to \( \alpha \)-iron is martensitic [18]. Martensitic transformation is caused by a shift in which the relative position of atoms does not change. Therefore, reverse transformation can occur. However, in the case of this study, the reverse transformation cannot occur because the relative position of atoms has changed due to the occupancy of iron atoms in the vacant sites of \( \varepsilon \)-iron.

The properties of the occupied iron and the amorphous iron ought to be different from those of \( \alpha \)-iron. Unidirectional discontinuous rubbing is inexpensive. Therefore, we can expect to use them for practical purposes.

The occupancy causes the volume decrease near friction surfaces and increases the distance between two sliding surfaces, leading to many machines unusable.

The amorphous iron mentioned above is the extreme state of mechanically damaged metal structures.

4 Conclusions

TEM diffraction patterns were taken from the layer of piled-up adhered wear debris (more than 100 \( \mu \)m thick) generated by unidirectional discontinuous rubbing between \( \alpha \)-iron specimen and \( \alpha \)-iron slider in a low vacuum. They revealed a structure in which iron atoms occupy the vacant sites of \( \varepsilon \)-iron and amorphous iron. Both remain at ambient conditions. The rubbing is inexpensive and easy. From the facts mentioned above, it is expected that they are put into practical use.

High-pressure generation that transformed \( \alpha \)-iron to \( \varepsilon \)-iron during rubbing in a low vacuum is also presented.

This article provides useful information for tribologists.

The amorphous iron formed by rubbing is the extreme state of mechanically damaged metal.

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