Effect of Surface Roughness on Improved Lubricity under an Ironing Condition Using a Synthetic Mica-Orga nic Intercalation Compound

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Abstract

It is well known that the surface roughness of metal substrates considerably influences the tribological properties of solid lubricants. In this study, the surfaces of metal substrates were modified by wet-blasting and polishing, and the lubrication performance of synthetic mica-organic intercalation compounds on these substrates was evaluated using an upsetting-ironing type tribometer. Wet-blasted substrates lubricated with synthetic mica exhibited the best anti-seizure ability, whereas a lubricated polished metal surface produced the worst results. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) revealed that concavities prepared by wet-blasting still remained on the ironed substrate surface, and the intercalated synthetic mica trapped in concavities was supplied to the flat areas as ironing advanced across the substrate surface. Furthermore, EDS and Fourier-transform infrared spectros copy (FTIR) analysis showed that intercalated synthetic mica extended on the ironed surface while releasing organic compounds from its interlayer spaces. As the ironing process continued to progress, the initial concavities gradually became shallow, but they did not completely flatten. Therefore, a roughened surface is more advantageous for achieving improved lubricity due to the continuous supply of solid lubricant from concavities to the flattened areas where seizure is likely to take place.

Keywords

surface roughness, mica, clay, intercalation, lubrication, cold forging

1 Introduction

Solid lubricants have long been widely used to improve lubricity and to achieve longer die life in applications such as cold forging, heading, and wire, bar and tube drawing. In general, solid lubricants are used as an additive in oil, grease, and lubrication coatings. Solid lubricants work by preventing direct contact between the metal surface and die, thereby ensuring smooth processing in the frictional interface between them [1,2].

We have already reported that the surface roughness of a metal substrate greatly influences lubrication performance of solid lubricants in cold forging processing. That is, anti-seizure properties are significantly improved with roughened metal substrate surfaces due to the improvement of the lubricant's adhesion strength to the rough surface, resulting in an excellent extension ability of solid lubricants [3]. This effect is called an “anchoring effect”, which is particularly well known in the field of anti-corrosive coatings, heat resistant coatings, and designable coatings. The anchoring effect improves lubricant performance for properties such as corrosion resistance, adhesion strength, and long-term sustainability of various functional properties [4-6].

In cold forging processing, however, a roughened surface interface is gradually flattened as the substrate stretches during processing [7]. This environment is different from those of other coatings, i.e. the improved lubrication performance due to the anchoring effect on a roughened surface does not necessarily continue until the end of the processing. This makes it difficult to understand the lubrication mechanism, so there are few studies examining the relationship between the surface flattening process and lubrication performance in cold forging processing. In general, wet-blasting, dry-blasting and acid pickling, polishing, etc. are surface roughening methods applied prior to the lubrication coating process to remove oxidized scale on metal substrates or to modify surface roughness.

Many studies discussing surface texturing techniques have been reported for applications such as sliding parts in automotive engines, machinery, steel molds, and cutting tools lubricated with oil [8-12]. These studies indicate that dimples formed on metal substrates are effective in significantly lowering the friction coefficient because they allow the oil to be retained, and a variety of optimum texturing designs for maintaining lubricity have been
proposed. As long as the textured surface does not disappear due to wear and abrasion, lubricity as a result of the dimples persists. Unfortunately, these results are not directly applicable to cold forging, since the metal substrate expands as a result of this processing technique and surface flattening also occurs.

In this study, metal substrates with a variety of different surface roughness profiles were prepared by wet-blasting and polishing. The lubrication performance of synthetic mica intercalated with a cationic organic compound was evaluated on these metal substrates using a newly devised upsetting-ironing type tribometer. In particular, lubricity as a function of initial surface roughness during successive stages of cold forging processing was analyzed using scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and Fourier-transform infrared spectroscopy (FTIR). The intercalated synthetic mica used here is a promising white alternative to black molybdenum disulfide (MoS2), eliminating the issues associated with a black solid lubricant [13].

2 Experimental methods

2.1 Preparation of barrel-shaped samples and modification of surface roughness

For testing, an Si10C barrel-shaped sample with a height of 17.60 mm, a bottom and top diameter of 15.68 mm, and a maximum side diameter of 19.67 mm was used. The barrel shape was obtained by compressing a cylinder (13.96 mm diameter and 32 mm height) in an upsetting process to a 45% reduction in height. The details of the upsetting conditions will be explained in section 2.4.

Prior to coating the metal with lubricant, the surface roughness of the barrel-shaped sample was modified by wet-blasting with 150 μm stainless grit, or polishing with #2000-grade SiC emery paper followed by polishing with 0.5 μm alumina particles. Wet-blasting was conducted using a spray pressure of 0.25 MPa for 60 s (COCOTTE, MACOHO Co., Niigata, Japan). Figure 1 shows the surface roughness profile of the original specimen (untreated surface) compared to the surface after wet blasting (wet-blasted surface) and polishing (polished surface).

2.2 Preparation of intercalated synthetic mica

It is well known in clay science that some layered clay minerals have a certain cation exchange capacity (CEC), which represents the amount of exchangeable inorganic cations (e.g., Na+, K+, etc.) that are held between the silicate layers in a 1 kg sample. Soluble organic cations can be incorporated into the interlayer space [14,15]. For this study, we used a synthetic mica (CEC = 12 mol/kg, exchangeable cation; Na+) as a solid lubricant (host), whose particle diameter measured by laser diffraction was 6.4 μm (D50). Figure 2 shows the chemical structure of synthetic mica. Dioctadecyl dimethyl ammonium chloride (DDA-Cl) was selected as an intercalating agent (guest), details of which are provided in Table 1.

To perform the intercalation reaction with a high yield, an excess amount of DDA+ equivalent to 150% of the mica’s CEC and 5 × 10^{-3} kg of the synthetic mica were added to 0.1 kg of deionized water, which was then magnetically stirred at 90°C for 1 h. After the reaction, the treated synthetic mica was separated by filtration under reduced pressure, thoroughly washed with deionized water, and then dried at 110°C.

Table 1 Name and chemical formula of intercalating agent

| Name (abbreviation) | Chemical formula |
|---------------------|------------------|
| D dioctadecyl dimethyl ammonium chloride (DDA-Cl) | (CO₂H₂)|₃(N(CH₃)₂Cl) |

To analyze the degree of intercalation, the interlayer distance of the synthetic mica was measured using X-ray diffraction (XRD, Xpert-MPD, PANalytical Co., Almelo, The Netherlands) with CuKα radiation. Using Bragg’s law (see Eq. (1)), the interlayer distance was calculated as the d-spacing, where λ is the X-ray wavelength (1.542 Å), θ the scattering angle and n a positive integer.

\[ 2dn\sin\theta = n\lambda \] (1)

2.3 Lubrication coatings and treatment process

To evaluate the lubricity of the intercalated mica on the metal barrel, a water-based non-reactive lubrication coating solution was prepared. This coating solution consisted of the intercalated synthetic mica and a cellulose-based organic binder, whose weight ratio was adjusted to 95 : 5. Each ingredient was dissolved or dispersed in deionized water to a total concentration of 10%. The lubrication coating was then formed on metal surfaces by dipping and drying at 100°C. The weight of each coating was measured at 3 × 10^{-4} to 10^{-3} kg/m² by a gravimetric method,

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which corresponds to a coating thickness of 10-15 μm as measured by an electromagnetic thickness tester. This treatment process is described in more detail below.

Treatment process for lubrication coating on the metal barrel:
Step 1. Cleaning: 10 min immersion of barrel in 2 × 10⁻² kg/dm³ of alkaline degreasing agent (Fine Cleaner E6400, Nihon Parkerizing Co., Tokyo, Japan) at 60°C.
Step 2. Water rinse: 30 s immersion in tap water at R.T.
Step 3. Lubrication coating: 30 s immersion at 60°C.
Step 4. Drying: 10 min at 100°C.

2.4 Evaluation of lubricity

To evaluate the lubricity of the intercalated mica coatings, an ironing test was carried out using a newly devised upsetting-ironing type tribometer on a 1,000 kN multi-action press (Shinohara Press Maintenance Co., Chiba, Japan). Figure 3 shows a schematic illustration of the tribometer, which consists of an upper punch, lower punch and three bearing balls [2,16]. Table 2 provides details of the experimental conditions.

Originally, this tribometer was developed to simulate the processing for severe cold forging of components such as pinion gears, bevel gears, tripods, etc. that are forged by a combination of upsetting and ironing processes. The same combination was employed in this tribometer. During testing, the lubrication coating on the side surface of the billet is first subjected to free expansion during upsetting, and the damaged coating is then squeezed in an ironing process by pushing down three fixed bearing balls simultaneously from the top of the billet. In more detail, a cylindrical billet is first processed into a barrel-shaped sample during the upsetting process. The barrel sample height is 17.60 mm, which is determined by the cylindrical billet height and height reduction in the upsetting process (32.00 mm × (1 − 0.45)). The barrel sample bottom diameter is 15.68 mm, which corresponds to the diameter of the lower punch. The barrel sample maximum diameter is 19.67 mm, which is an actual measured value at the cross section of the middle point (8.8 mm)

of the barrel sample height. The difference between the bottom radius and the maximum side radius is 2.0 mm, which corresponds to a maximum overhanging height on the side of the barrel sample and a maximum ploughing depth in the ironing process.

In this study, however, we chose to cancel the influence of the upsetting process on the surface roughness. For this reason, the modification of the surface roughness and the lubrication coating process were carried out on the barrel-shaped sample after the upsetting process. That is, the lubrication coating only undergoes an ironing process.

By employing a point-tracking technique using a finite element method (FEM, software; DEFORM-3D) where the frictional shear factor (μ) is set at 0.15, the surface expansion ratio of the ironed surface after the ironing process was calculated to be over 150 times the initial area (see Fig. 4) [16,17]. The point-tracking technique is one of the FEM's functions where initial points marked on a barrel sample are displayed on the corresponding sites of the ironed surface. The surface expansion ratio can be calculated by the distribution patterns of the points.

![Fig. 3 Schematic illustration of an upsetting-ironing type tribometer [2,16]](image)

![Fig. 4 Relation between ironing stroke and surface expansion ratio in the ironing process, as calculated by FEM [16,17]](image)

| Table 2 Test conditions for an upsetting-ironing type tribometer |
|---|---|---|
| Billet | Material | S10C (JIS : 0.10% carbon steel) |
| | Diameter | 13.96 mm |
| | Height | 32.00 mm |
| Upsetting conditions | Reduction in height | 45.0% |
| | Speed | 10.00 mm/s |
| | Temperature | RT |
| Ironing conditions | Material of bearing ball | SUJ2 (JIS : 1% Cr bearing steel) |
| | Diameter of bearing ball | 10.00 mm |
| | Speed | 60.0 mm/s |
| | Temperature | RT |
The maximum contact pressure between the bearing ball and the billet was also estimated to be ~2 GPa and the maximum temperature was estimated at 170°C by the FEM analysis.

Lubrication performance was evaluated from the ironing load curve and degree of seizure on the ironed surface. The critical surface expansion ratio determines the anti-seizure ability or the extension ability of the lubricant, and, was measured by visually assessing the stroke position at the onset of seizure combined with the FEM-analyzed relationship between the stroke position and surface expansion ratio, as shown in Fig. 4.

2.5 Surface analysis

To investigate the condition of the ironed surface, the residual coating was observed using field emission scanning electron microscopy (FE-SEM, SU8020, Hitachi Co., Tokyo, Japan) equipped with energy dispersive X-ray spectrometry (EDS, EMAX Evolution, Horiba Co., Kyoto, Japan) with an acceleration voltage of 5 kV. A surface roughness meter (SURFCOM NEX, TOKYO SEIMITSU CO., LTD., Tokyo, Japan) and laser microscope (VK-8700, KEYENCE CORP., Osaka, Japan) were used to measure the 2D (2 dimensional) and 3D surface roughness profile.

2.6 Analysis of extension behavior of an intercalated synthetic mica

To investigate the extension behavior of synthetic mica in the process of its cleavage, a cylinder-on-disk tribometer using a Bowden-type friction abrasion analyzer (Type14FW, HEIDON Co., Tokyo, Japan) was used. The test conditions are outlined in Fig. 5. In this test, intercalated synthetic mica with an area of 5 × 10 mm was coated on one end of an SPCC-SB substrate (70 × 150 mm), where the amount of the coating was adjusted to 3 × 10⁻⁵-4 × 10⁻³ kg/m² or 10-15 μm in thickness, as measured by the same method described in section 2.3. An SUJ2 cylinder (5 mm diameter ×10 mm height) with a load of 80 N was placed on top of the mica coating and stretched 50 mm towards the non-coated area of the substrate at 10 mm/s, one time only and in one direction only. The stretched mica was analyzed using Fourier-transform infrared spectroscopy (FTIR, Type-610, JASCO Co., Tokyo, Japan) at sliding distances of 1, 20, and 40 mm.

3 Results and discussion

3.1 Synthetic mica characterization

Figure 6 shows XRD patterns of the synthetic mica before and after the intercalation with DDA⁺. In the pattern of non-intercalated synthetic mica, a clear peak was detected at a d-spacing of 12.6 Å, which corresponds to the interlayer spacing of pristine synthetic mica, where exchangeable Na⁺ ions remain between the silicate layers. The intercalated synthetic mica, on the other hand, exhibited a maximum peak at a d-spacing of 36.1 Å. Figure 7 shows that the volume of synthetic mica significantly increased due to the intercalation reaction. This result indicates that the interlayer region of synthetic mica was enlarged by the incorporation of DDA⁺, which replaced the accessible Na⁺ by an ion exchange reaction.

![Fig. 6 XRD patterns of synthetic mica before and after intercalation](image)

![Fig. 7 Appearance of synthetic mica before and after intercalation](image)

![Fig. 8 Illustration of the structural model for synthetic mica before and after intercalation](image)
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Figure 8 shows the possible DDA⁺ formation in the interlayer region. DDA⁺ is incorporated between the silicate layers, most likely in a vertical formation. The reason for this will explained later in this discussion. The thickness of the silicate layer and the length of the C18 paraffin chain of DDA⁺ have been reported to be 9.6 Å [18] and 25.9 Å [19], respectively. If DDA⁺ occupied a vertical formation, the theoretical d-spacing of 35.5 Å (9.6 + 25.9) agrees well with the measured value of 36.1 Å.

3.2 Lubricity of a intercalated synthetic mica measured by upsetting-ironing type tribometer

Figure 9 shows the ironing load-stroke curves for the lubrication coatings formed on the metal barrels, as measured by an upsetting-ironing type tribometer. Before discussing these results, it is important to note that the ironing load increases immediately after the ironing stroke starts, reaching a maximum value at an ironing stroke of 6-7 mm. This is because the contact area between bearing balls and billet is maximized at this point. The ironing load then decreases with the decrease in contact area between them. Thus, both the deformation resistance of the billet and the friction coefficient of the ironed surfaces influence the ironing load. In other words, if the billet remains the same, then a lower ironing load indicates a better lubrication coating. In this way, the lubrication performance of the different coatings can be evaluated and compared.

The test was conducted three times for one condition, but because the repeatability was excellent, the representative data is shown in Figs. 9 and 10. It is evident in Fig. 9 that the ironing load of wet-blasted surface was lower than those of other types of surfaces in the last half of the stroke. This result means that the intercalated synthetic mica formed on the wet-blasted substrate extended more efficiently and effectively along with surface expansion than those of the other samples. On the other hand, the ironing load of the polished substrate was the highest, which is likely due to the poor extension ability of synthetic mica. As shown in Fig. 10, the average values for the critical surface expansion ratios, which were calculated by the method explained in section 2.4, were 45.2 (untreated substrate), 128.7 (wet-blasted substrate) and 23.1 (polished substrate), respectively. This trend of the critical expansion ratio correlates well with the ironing load curve results, revealing that greater initial surface roughness was more advantageous for achieving improved lubricity.

3.3 Surface roughness and SEM images of ironed surface

Figure 11 shows the 3D surface profile of the ironed surface after removing the residual coating by ultrasonic alkaline cleaning. Initial surface roughnesses Rₐ of untreated, wet-blasted and polished substrates were 3.07, 5.21 and 1.22 μm, respectively. This figure shows that Rₐ of each sample decreased with the advancement of the ironing stroke due to surface expansion, but the results were different depending on the initial surface roughness. That is, a wet-blasted surface with an initially greater value of Rₐ is gradually flattened more than an untreated and polished surface. At the ironing stroke of 8 mm, all three Rₐ values were basically the same, regardless of the initial Rₐ value. However, the Rₐ value at ironing strokes of 2 and 4 mm still maintained the same relative relationship to each other that was present prior to ironing, indicating that the roughened surface did not disappear as soon as ironing began.

To further investigate the surface profile of the ironed surface, sample surfaces subjected to an ironing stroke of 8 mm were observed using SEM. It is evident from Fig. 12 that more concavities, which were stretched towards the ironing direction, were observed in the wet-blasted surface than the other surfaces. This result indicates that the initial roughened surface gradually becomes shallower along with surface expansion, but it is not completely flattened. These remaining concavities may play an important role in improving lubrication performance.

Although initial surface roughness is apparently the most influential factor for improving lubrication, the remaining concavities that are still present after wet-blasting and ironing suggest that surface hardening may also be a factor. In our previous study, a wet-blasted substrate had a surface layer several microns thick with a compressive residual stress of 253 MPa, compared to 108 MPa for an untreated substrate [20]. Although the thickness of the hardened layer is extremely thin compared to the ironing depth (2 mm), the difference between these values cannot be ignored. As it is presently difficult to clarify the extent to which the surface hardened layer contributes to the delay of surface flattening, further detailed investigation is needed.

3.4 Analysis of ironed surfaces by SEM/EDS

To investigate the status of residual mica on the ironed faces, EDS area analysis was conducted. Figure 13 shows the relationship between ironing stroke and characteristic X-ray peak intensity of Si, as well as the intensity ratio of Ic/Ibs, where the
peak intensity of Si and C are attributed to synthetic mica and the organic cation of DDA⁺, respectively. As shown in Fig. 13(left), the Si peak intensities detected from untreated, wet-blasted and polished surfaces decreased along with ironing stroke. This is because the synthetic mica extended and thinned along with surface expansion, but the magnitude of this was dependent on the surface roughness. That is, Si peak intensity on the wet-blasted surface was greater than for the other surfaces. This means that metal substrates with a greater surface roughness trapped more residual synthetic mica.

On the other hand, the intensity ratio of I⁺/I⁺⁺, shown in Fig. 13(right), increased along with the ironing stroke, indicating that the intercalated synthetic mica extended while changing the chemical composition ratio of synthetic mica and DDA⁺. It is

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| Ironing stroke | Surface expansion ratio | Untreated surface | Wet-blasted surface | Polished surface |
|----------------|------------------------|-------------------|--------------------|-----------------|
| mm (initial)   | × 1.0                  | Rₐ 3.07µm         | Rₐ 0.71µm          | Rₐ 0.15µm       |
| 2mm            | × 1.3                  | Rₐ 0.84µm         | Rₐ 0.23µm          |                 |
| 4mm            | × 2.5                  | Rₐ 0.45µm         |                    |                 |
| 8mm            | × 4.5                  | Rₐ 0.15µm         |                    |                 |

Fig. 11 3D surface profiles of ironed surfaces after removing residual coatings

![Fig. 12 SEM images of an ironed surface at an ironing stroke of 8 mm after removing residual coatings](image)

Fig. 12 SEM images of an ironed surface at an ironing stroke of 8 mm after removing residual coatings

![Fig. 13 Si peak intensities and intensity ratio of I⁺/I⁺⁺ measured by EDS area analysis: The data of the polished sample at an ironing stroke of 14 mm was omitted because deep and widespread seizure already occurred, hindering analysis accuracy.](image)

Fig. 13 Si peak intensities and intensity ratio of I⁺/I⁺⁺ measured by EDS area analysis: The data of the polished sample at an ironing stroke of 14 mm was omitted because deep and widespread seizure already occurred, hindering analysis accuracy.
assumed that DDA+ was separated from synthetic mica and extended more preferentially than synthetic mica when it was cleaved by shear stress.

To analyze more details about the distribution pattern of the intercalated synthetic mica, SEM/EDS analysis was performed at a higher magnification. Figure 14 shows the SEM images of the ironed surface at an ironing stroke of 8 mm. Although each surface pattern contained both flattened areas and concavities, the ratio of concavities to the flattened area in the wet-blasted surface was greater than those of untreated and polished surfaces. The shape of concavities on the wet-blasted surface appeared to have been stretched towards the ironing direction, while the surface profile of the polished substrate showed that a large part of the ironed surface was flattened, apart from the seizure line visible in the center of the picture.

Table 3 showed EDS point analysis of Si and the intensity ratio of k/Cs in flattened and concavity areas. It was found that the concavities still hold a greater amount of intercalated synthetic mica since the k/Cs values were close to the initial ratio before ironing. A smaller amount of the intercalated synthetic mica remains in the flattened areas, as indicated by a higher k/Cs value. This result suggests that the intercalated synthetic mica trapped in concavities still remain in nearly an uncleaved state because there is little ironing load on the inside of the concavities. Since ironing load is mainly loaded on the flattened area, we believe that the intercalated synthetic mica in this area was cleaved and thinly stretched by shear stress, while the chemical composition changed to an organic-rich ratio due to the difference in extension ability between synthetic mica and DDA+.

3.5 Analysis of an extended intercalated synthetic mica by FTIR

Before discussing the extension behavior of the synthetic mica, IR spectra of the synthetic mica before and after intercalation with DDA+ was measured to investigate the difference between their IR absorption bands. Figure 15 shows IR spectra ranging from 800 to 1300 cm⁻¹, corresponding to absorption bands of Si-O stretching. In the IR spectrum of non-intercalated synthetic mica, an absorption band was detected at a wavenumber of 1007 cm⁻¹. Intercalated synthetic mica, on the other hand, exhibited an absorption band at 1077 and 1112 cm⁻¹ in addition to 1007 cm⁻¹. In the IR spectrum of non-intercalated synthetic mica, the absorption bands of 1077 and 1112 cm⁻¹, which were clearly detected in the intercalated synthetic mica, seem to be hidden in the broad shoulder. This result indicates that the prominent emergence of absorption bands at 1077 and 1112 cm⁻¹ is caused by the expansion of d-spacing by the intercalation reaction.

According to the previous studies, the band at 1007 cm⁻¹ corresponds to in-plane Si-O stretching vibration, and the other bands at 1077 and 1112 cm⁻¹ are related to out-of-plane Si-O stretching vibration [21-23]. In more detail, in-plane Si-O stretching vibration means vibration of Si-O-Si linkages at the surface of mica's tetrahedral layer, with their transition moment (the direction of dipole oscillation during the vibration) lying in the plane of the layer. On the other hand, out-of-plane Si-O stretching vibration means vibration of Si-O bonds directed towards octahedrally coordinated magnesium ions at the center of the layer, with their transition moment perpendicular to the layer [24]. It would be helpful to refer to the chemical structure of synthetic mica shown in Fig. 2 for this explanation. Suppression

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**Table 3** Si peak intensities and intensity ratio of k/Cs measured by EDS point analysis

| Surface profile     | Analytical area | Intensity / cps | Intensity ratio |
|---------------------|----------------|-----------------|----------------|
|                     | C      | Si      | k/Cs |
| Untreated surface   | Flat area | 29.36 | 4.13 | 7.11 |
|                     | Concavity area | 281.38 | 95.05 | 2.96 |
| Wet-blasted surface | Flat area | 25.54 | 3.47 | 7.36 |
|                     | Concavity area | 249.65 | 87.36 | 2.86 |
| Polished surface    | Flat area | 21.88 | 2.22 | 9.86 |
|                     | Concavity area | 30.54 | 10.55 | 2.89 |
of the in-plane Si-O stretching vibration is called the “metal surface selection rule”, which states that only vibrational transition dipole moments oriented normal to the surface will absorb light [25-27]. Similarly, it is considered that promotion of the out-of-plane Si-O stretching vibration follows the same rule. It is easy to understand that the increase in d-spacing of the silicate layers by the intercalation reaction promotes the vibration of the Si-O bonds in the silicate layers due to the release or the weakening of the interactions between the silicate layers.

In this study, the absorbance ratio of $A_{\text{out-of-plane}}/A_{\text{in-plane}}$, which are detected around 1080 and 1000 cm$^{-1}$, is introduced to evaluate the degree of cleavage for intercalated synthetic mica at the frictional interface. This absorbance ratio most likely decreases with the progress of sliding due to its cleavage and reduction in d-spacing. Figure 16 shows IR spectra of residual intercalated synthetic mica stretched by a cylinder-on-disk tribometer along with the absorbing ratio of $A_{\text{out-of-plane}}/A_{\text{in-plane}}$. As anticipated, the ratio of $A_{\text{out-of-plane}}/A_{\text{in-plane}}$ decreased along with the sliding distance, indicating that intercalated synthetic mica cleaved and extended with the decrease in d-spacing.

As explained in the previous section, the intensity ratio of $I_c/I_b$ measured by EDS increased in the process of ironing (see Fig. 13). The results of Figs. 13, 15 and 16 reveal a lubrication mechanism. When intercalated synthetic mica cleaved and stretched, the d-spacing decreased (FTIR) and the chemical composition of intercalated synthetic mica became DDA-rich, due to both the release of DDA+ from the interlayer region and DDA’s better extension ability than synthetic mica. In more detail, the released organic cation readsores to the negatively charged mica’s surface, but the cation is soon detached by the bearing ball’s shear stress, and extends further in the ironing direction. At this point in the process, we believe that the extension rate of the released organic cation is greater than that of mica. As a result, the chemical composition of the residual intercalated synthetic mica shifts to a DDA-rich one.

For these results, the transitions of $A_{\text{out-of-plane}}/A_{\text{in-plane}}$ and $I_c/I_b$ values on the frictional surface are considered useful indicators for evaluating the residual status of the lubricant, especially for this hybrid type solid lubricant. Different from single component solid lubricants such as MoS$_2$, Ca compounds, and zinc phosphate, the lubrication mechanism of the intercalated synthetic mica is quite complex. Therefore, it is important to monitor the change of the chemical composition, because it can directly affect the lubrication performance along with the progress of sliding.

3.6 Lubrication mechanism of synthetic mica during the surface flattening process

Consider the frictional environment during the ironing process; the surface of the substrate is stretched, with a huge area expansion occurring as the processing progresses. For this reason, the lubrication film is rapidly stretched and becomes thinner as the area is expanded, eventually leading to seizure. As shown in Figs. 11 and 12, the concavities were stretched towards the ironing direction and the depth of concavities became shallower as the ironing stroke advanced. However, the substrate prepared by wet-blasting contained more concavities than those of untreated and polished substrates, even when the ironing progressed to some extent. Based on these experimental results, Fig. 17 shows our proposed mechanism for the relationship between the surface flattening process and the lubrication mechanism of the intercalated synthetic mica.

Referring to the coating film on the flat area of the polished substrate in Figs. 11 and 12, the surface directly encountered by the bearing ball is rapidly cleaved and stretched towards the ironing direction by shear stress, becoming thinner, so that seizure finally takes place beyond the limit of the film’s extension ability. However, when the substrate is roughened, the coating component trapped in concavities is expected to remain almost intact because it is not fully subjected to the shear stress. The lubrication component extruded outside of the concavities along with dimple shallowing is supplied to the flattened area. The lubricants supplied to the flattened area can help sustain film thickness to a certain extent until concavities completely disappear. This is the main reason why the lubrication coating formed on the wet-blasted substrate exhibited a delay in the ironing point at which seizure takes place, compared to that of the polished substrate.

Furthermore, from the result of SEM/EDS and FTIR analysis, intercalated synthetic mica releases organic cations from the interlayer region when it cleaves, and the cations exposed on the surface undergo shear stress. The released organic cations then extend towards the ironing direction more preferentially than that of cleaved mica due to its excellent extension ability. The released organic cations readsores by electrostatic attraction through the positive-charged DDA+ ammonium group to the negatively charged sites on mica’s surface, so that the chemical composition of the residual intercalated synthetic mica shifts to a DDA-rich ratio by repeatedly desorbing and readsores many

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**Fig. 16** FTIR spectra and absorbing ratio $A_{\text{out-of-plane}}/A_{\text{in-plane}}$ of stretched intercalated synthetic mica by cylinder-on-disk tribometer
times as the ironing process proceeds. Although it is difficult to directly measure the zeta potential of the residual mica, it is presumed that a negative charge on mica’s surface in the latter half of the ironing stroke is probably neutralized more than prior to ironing. The concept of this self-supplying function of the lubricant, brought about by surface roughening is important and effective, especially when considering the frictional interface in cold forging.

4 Conclusions

The effect of surface roughness of metal substrates on lubricity of a synthetic mica-organic intercalation compound was evaluated using a newly devised upsetting-ironing tribometer, and the lubrication mechanism was investigated by surface analysis. The experimental results have led to the following conclusions:

1. An intercalated synthetic mica coated on the surface of a wet-blasted metal substrate showed the best anti-seizure ability, compared to the worst results found with the same coating on a polished substrate.

2. The initial $R_s$ value gradually decreased with the progress of ironing due to surface expansion, but the wet-blasted substrate, which had the greatest $R_s$ value, was not completely flattened. More concavities were observed on the wet-blasted substrate than those of non-treated and polished substrates, even after ironing.

3. Surface analysis showed that the concavities held uncleaved intercalated synthetic mica, and surface flattening from the ironing process caused the release of DDA⁺ from the mica trapped in the concavities. Furthermore, it is assumed that the released DDA⁺ contributed to the improved anti-seizure ability. This is considered to be the main reason why the intercalated synthetic mica on the roughened metal substrate prepared by wet-blasting performed better than those on untreated and polished substrates.

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