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The Impact of Water on the Tribological Behavior of Lubricating Grease Based on Calcium Carbonate Polymorphs

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Abstract: In this article, calcium sulfonate complex grease with different polymorphs was acquired. With reference to the improved rolling stability test method, 5% and 10% water were added to the calcium sulfonate composite grease respectively. The influence of water on the flow and deformation characteristics of grease under external force was characterized by rheological analysis. Moreover, the influence of water on the tribological behaviors of grease was evaluated at 30 and 80 °C. The results indicate that water could affect the flow and deformation characteristics of calcium sulfonate complex grease in vaterite polymorph (CSCG-V) more than calcium sulfonate complex grease in calcite polymorph (CSCG-C), and CSCG-V could combine with water to form a more stable grease under external force. Tribological results also clearly show that CSCG-C with water shows better tribological properties than CSCG-V with water under harsh conditions. There was no significant difference in the components of the films that consisted of $CaCO_3$ and CaO regardless of grease within or without water. The improvement of tribological properties of CSCG-C with 5% and 10% water benefited from the influence of water on the film forming capacity of calcium carbonate on the steel surface.

Keywords: calcium sulfonate complex grease; water influence; rheological analysis; tribological behaviors

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1. Introduction

According to the definition of National Lubricating Grease Institute (NLGI), grease is a solid or semi-solid product formed by dispersing one or more thickeners into one or more lubricating base oils. Due to its special physical and rheological structure, grease is an indispensable lubricant to reduce wear and prolong life for bearings [1–8]. At the same time, grease also acts as an additional sealant to prevent the entry of solid pollutants and water. However, grease will inevitably be polluted by water in some special application, which will more or less affect its lubrication performance and may lead to bearing failure [9–14]. Especially for the rolling bearing of hot-rolled steel, the roll grease will be rinsed by a large amount of water since a large amount of water is required to cool the roll. In addition to the water environment, these greases also involve high loads and high temperatures, which may lead to boundary lubrication region. Therefore, the successful operation of the bearing system under harsh conditions depends on the performance of the surface and the ability to form a wear-resistant and low shear boundary film between the surface and the environment. As a grease with excellent wear protection and water resistance, high performance calcium sulfonate complex grease (CSCG,) provides one of the solutions for the above strict boundary lubrication environment [15–19]. Calcium sulfonate complex grease is composed of calcium sulfonate, crystalline calcium carbonate, and complex thickener. The crystalline calcium carbonate and calcium sulfonate adsorb each other to form colloidal particles or micelles with larger particle size. The colloidal particles or micelles form a staggered network skeleton by molecular force and ionic force, so that the oil is fixed in the gap of the structure skeleton. Such CSCG with special thickener have unique mechanical stability, good anti-wear (AW) and four-ball extreme pressure (EP) performance without additives. Further, calcium sulfonate can wrap part of the water to form micelles in the case of water, reducing the influence of water on the extreme pressure performance, shear resistance, and rust resistance of lubricating grease. Therefore, the application effect of CSCG at high temperature, with more water, a heavy load, and impact load is very excellent.

Meanwhile, it is well known that crystalline calcium carbonate in CSCG mainly exists in the form of calcite [20]. Previous literature has also reported that stable calcite calcium carbonate is the main reason why calcium sulfonate grease has excellent tribological properties, and further accurately confirmed the existence of calcium carbonate in the films of surface [21]. In addition, during the preparation and production of CSCG, crystalline calcite is usually generated from precursor amorphous calcium carbonate through vaterite [22]. Unstable vaterite can be easily transformed into stable calcite, depending on appropriate external conditions [21,23]. In most cases, the crystalline calcium carbonate in CSCG forms a crystal form dominated by vaterite due to some improper conversion operations. As shown in an earlier study [21], the CSCG with calcite shows excellent lubrication performance than CSCG with vaterite under boundary lubrication conditions. The results in SRV tests showed that the CSCG with calcite processed stable and smooth friction curves from 200 to 500 N, while the CSCG with vaterite showed many fluctuations, even sharply rising to seize during the tests. However, calcium sulfonate grease is inevitably mixed with water in practical application. The existence of this water not only affects its rheological behavior, but also affects its tribological behavior. Seldom studies have focused on the influence of water on the rheological behavior of grease, although the impact of water on the rheological behavior of greases has been reported more in recent years. Cyriac, F. et.al. researched the impact of water on the yield stress and startup torque of lubricating greases [10]. The results show that small quantities of water (10%) have no influence on the startup torque of calcium sulfonate complex. Cyriac, F. et.al. also confirmed the impact of water on the rheology of lubricating greases [11]. The results show that the zero-shear viscosity of calcium sulfonate complex greases increased with water concentration. Lugt. P.M. reported the shear stability of dry and water-contaminated calcium sulfonate complex lubricating greases. For water-contaminated greases, no water separation was found during the prolonged aging [13]. Therefore, the effect of calcium carbonate polymorph in CSCG on tribological properties is not clear, especially under the influence of water. Moreover, the rheological behavior influenced by water affecting the tribological behavior during the rubbing process remains unclear. Furthermore, the crystalline form of calcium carbonate still needs to be explained in the water environment.

In this work, the impact of water on the tribological behavior of lubricating grease based on polymorphs of calcite and vaterite is researched. The rheological behavior influenced by water is investigated, and the relevant tribological mechanism affected by calcium carbonate polymorphs is discussed.

2. Experimental Section

2.1. Materials and Preparation

Mineral base oil (trade name as 150BS) was acquired from Integrated Refinery and Petrochemical Complex. (Rayong, Thailand). Over based calcium sulphonate (OBCS) with a total base number of 400 mg KOH g^{-1} was purchased from Richful Lube Additive Co., Ltd. (Xinxiang, China). Dodecyl stearic acid with an acid number of 183 mg KOH g^{-1} was purchased from Dongying Shuili Chemical Co., Ltd. (Dongying, China). Other common reagents, such as acetic acid (purity: 99.7%), butanol (purity: 99.5%), calcium hydroxide (purity: 96.2%), and boric acid (purity: 99.6%), were acquired from local markets.

CSCG with calcite (coded as CSCG-C) was prepared as follows [12,16]. An appropriate proportion of 150BS base oil (100 g), over based calcium sulphonate (150 g), and water (15 g) each was added to the beaker and stirred for 15 min. When the mixture was heated to 70 °C, acetic acid solution (3 g acetic acid and 3 g water) and butanol solution (3 g butanol and 3 g water) were slowly added, and the mixture was held for a period of time. Then, the mixture was heated to 85–95 °C, and the transformation reaction was finished according to the peak at 863 cm^{-1} in Fourier transform infrared spectroscopy (FTIR) was replaced with the peak at 883 cm^{-1}. FTIR spectra over time to show the conversion from peak at 863 to 883 cm^{-1} was show in Figure 1. After the transformation was complete, the other proportions of 150BS base oil (100 g), calcium hydroxide solution (7 g calcium hydroxide and 7 g water), boric acid (9 g), and dodecyl stearic acid (13 g) were added in the mixture. The mixture was then heated to about 105 °C, and the complex reaction was maintained for about 30 min. While the complex reaction completed, the mixture was heated to a higher temperature to remove the alcohols and water, before the grease was collected as a brown transparent semi-solid.

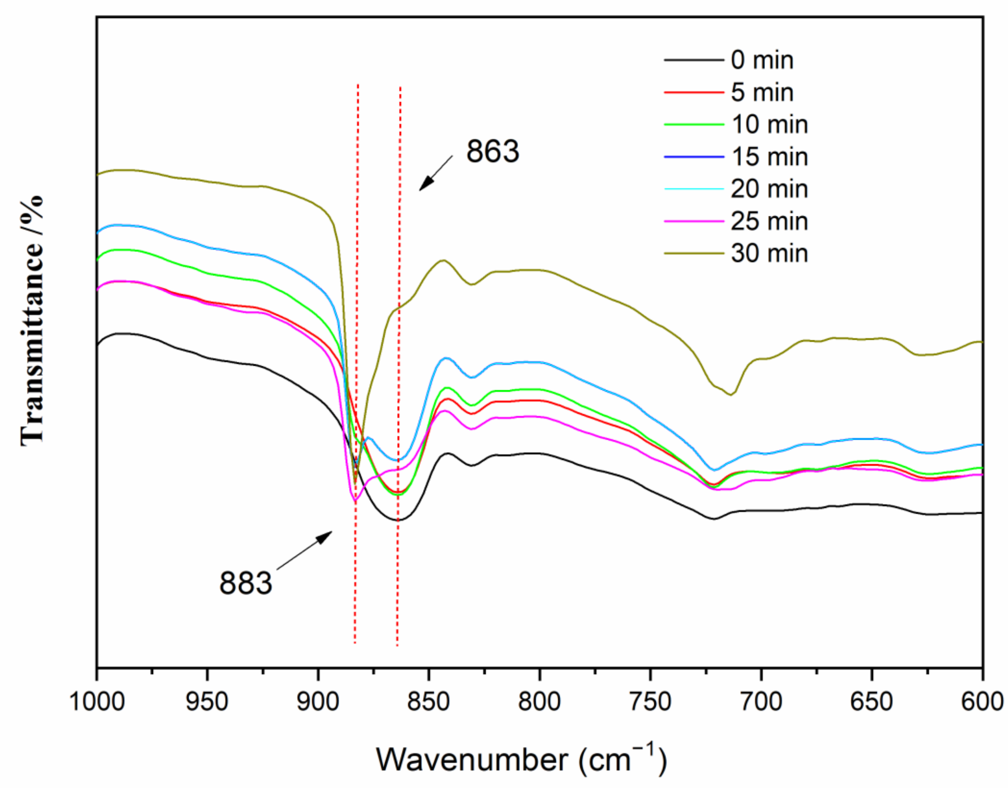

Figure 1. FTIR spectra over time to show the conversion from peak at 863 to 883 cm^{-1}.

In addition, CSCG with vaterite (coded as CSCG-V) was commercially purchased from Qingdao Lubemater Co., Ltd. (Qingdao, China). CSCG-V with 5%, 10% water and CSCG-C with 5%, 10% water were prepared by referring the improved test methods of roll stability according to ASTM D 1831, except for the modification that the duration and temperature are 24 h and 80 °C. It should also be noted that for the convenience of comparison and description, CSCG-V with 0% water is equivalent to CSCG-V, and CSCG-C with 0% water is equivalent to CSCG-C in the following.

2.2. Sample Characterization

Typical properties of CSCG, such as cone penetration and dropping point, were determined according to ASTM D1403, ASTM D566. Four-ball EP tests including last non-seizure load (N) and weld point (N) were confirmed according to ASTM D 2596. The calcium carbonate polymorphs were determined by the FTIR with a Bruker infrared spectrometer TENSOR 27 (Bruker, Billerica, MA, USA). Rheological behaviors of the tested CSCG were assessed using an Anton Paar MCR 302 rheometer (Anton Paar GmbH, Graz, Austria) with a plate-to-plate configuration (1 mm gap and 24.985 mm diameter). The storage modulus and loss modulus for evaluating the structure strength of the tested

CSCG were evaluated at a fixed stable angular frequency (ω = 10 rad/s) with the shear strain increased from 0.01 to 100 s^{-1} under the temperatures of 30 °C and 80 °C. Shear measurements were performed at 100 s^{-1} at 30 °C and 80 °C to reveal the apparent viscosity change of the tested CSCG under the shear.

2.3. Tribological Performance

In order to investigate the tribological performance of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water, a series of tribological tests were carried out using an Optimol SRV-V tester (Optimol, Munich, Germany) with a ball-on- disc configuration at a stroke of 1 mm. The material of the ball (ø10 mm) and the disc (ø24.00 × 7.88 mm) are AISI 52100 steel with hardness of 61–65 HRC. The fixed friction test conditions are as follows: Load (100–500 N), Duration (30 min), Speed (10–50 Hz), and Temperature (30 °C or 80 °C). The friction coefficients with resolution of 0.001 of repeated tests were recorded, and the wear volumes of the test disks were measured by MicroXAM 3D profiler (KLA-Tencor, Milpitas, CA, USA). Scanning electron microscopy (SEM: JSM-5600LV, JEOL, Tokyo, Japan) with resolution of 3.5 nm was used to characterize the wear scars of the upper test disks, and X-ray photoelectron spectroscopy (XPS: PHI-5702, Physical Electronics, Chanhassen, MN, USA) was used to analyze the elemental composition on the wear scar. The resolution used was ±0.3 eV with the binding energy of contaminated carbon (C 1s: 284.8 eV) as reference.

3. Results and Discussion

3.1. Physiochemical Properties of CSCG

In order to determine the calcium carbonate polymorphs in CSCG, FTIR spectroscopy was used. As shown in Figure 2, the calcite was confirmed at 883 cm^{-1} in CSCG, proving the totally transformation when CSCG-C was prepared [24–26]. At the same time, the spectrum of the CSCG-V was characterized by the vaterite based on the sharp peak at 878 cm^{-1} [27]. As-investigated CSCG-V with 5% or 10% water and CSCG-C with 5% or 10% water also showed the same characteristic peaks in FTIR, indicating treatment with water did not obviously affect the crystalline form of calcium carbonate in CSCG-V and CSCG-C. Significantly, CSCG-V with 10% seems to be the part of calcium carbonate that is converted into hydrated calcium carbonate, since the peak intensity differed obviously. In addition, due to the influence of other hydroxyl groups, the absorption peak of water is not obvious, and the wide peak around 3400 represents the existence of free water.

Cone penetration is an index used to measure the consistency and hardness of lubricating grease. Testing the change of cone penetration after adding water can show the change trend of consistency of calcium sulfonate grease after encountering water. The relative data was listed in Table 1. As can be seen from the Table 1, there was little difference in cone penetration between CSCG-V and CSCG-C, indicating the little difference in consistency between CSCG-V and CSCG-C. After water treatment, the cone penetration of CSCG-V with 5%, 10% water became relatively soft, while the cone penetration of CSCG-C with 5%, 10% water presented no obvious change in consistency. It should also be noted that the addition of water (5% or 10%) did not significantly change the consistency of CSCG-V and CSCG-C. Thus, this change is in line with the special properties of calcium sulfonate grease, which could absorb a lot of water without much change in consistency. In addition, four-ball EP test of CSCG-V and CSCG-C are same without water. However, the last non-seizure load and weld point were greatly reduced in CSCG-V +5% water and CSCG-V +10% water, respectively. On the contrary, the last non-seizure load and weld point of CSCG-C +5% water were not much reduced, even equivalent to the extreme pressure performance of CSCG-C as for CSCG-C +10% water. This phenomenon shows that CSCG-C with water behaved better in terms oof Four-ball EP capacity compared to CSCG-V with water. Moreover, the grease without water was also treated with the roll stability. The consistency change of CSCG-C and CSCG-V was +2 and +6, respectively.

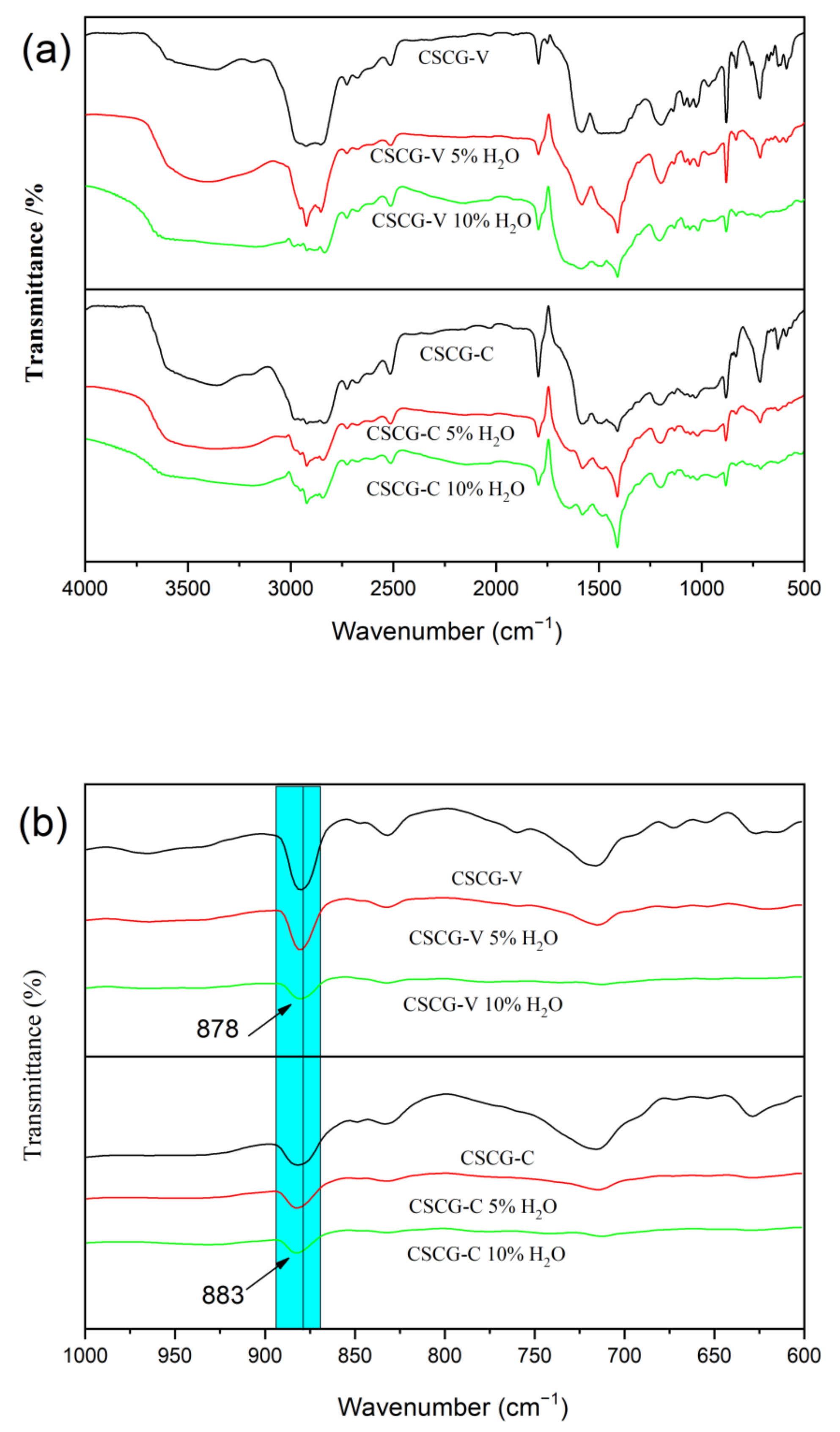

Figure 2. FTIR spectra of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water ((**a**), full spectra; (**b**), enlarged spectra).

Table 1. Typical properties of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water.

Grease Property	CSCG-V	CSCG-V +5% Water	CSCG-V +10% Water	CSCG-C	CSCG-C +5% Water	CSCG-C +10% Water	Test Standard
Base oil	150BS	150BS	150BS	150BS	150BS	150BS	
Cone penetration (0.1 mm)	256 ± 3	267 ± 6	261 ± 6	261 ± 3	254 ± 6	253 ± 6	ASTM D 217
Dropping point (°C)	320 ± 5	320 ± 5	320 ± 5	320 ± 5	320 ± 5	320 ± 5	ASTM D 566
Four-ball EP test *							
Last non-seizure load (N)	980	618	548	980	882	980	ASTM D 2596
Weld point (N)	3920	3087	2450	3920	3087	3920	

* The test standard deviation of Last non-seizure load and Weld point shall not exceed the first level load increment.

3.2. Rheological Analysis

In oscillatory shear measurements, the storage modulus (G″) and loss modulus (G′) as a function of shear strain are shown in Figure 3. When the two moduli are no longer constant, they reach the end of the linear viscoelastic regime (LVE). From this point, the structure of grease will be irreparably damaged. If storage modulus (G′) and loss modulus (G″) have an intersection outside the LVE regime, this point is called the transformation point. This point indicates the grease starts to change from grease-like to fluid-like. Thus, the shear stress at transformation point could reflect structural strength of grease [28–30]. As for each CSCG, structural strength decreased when the temperature reached from 30 °C to 80 °C. Meanwhile, the trend of structural strength is opposite to the recoverability of grease, which means that grease with high structural strength is more difficult to return to its initial state after mechanical shear. Whether 30 °C or 80 °C, CSCG-V show high structural strength than CSCG-C, indicating CSCG-V was more difficult to flow under shear. Compared with CSCG-V, CSCG-V with 5%, 10% water presented a more stable grease structure since the transformation point of CSCG-V with 5%, 10% water is far from that of CSCG-V. Hence, it could be concluded that vaterite calcium carbonate can combine with water to form a stronger structure. On the contrary, CSCG-C with 5%, 10% water behave closer to a grease structure, respectively. These results mean that water could affect the structure and properties of CSCG-V more than CSCG-C, and it is more difficult to flow when it contains water due to the increase of its shear stress at the flow transformation point. In addition, the viscosity of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water under a high 100 s^{-1} shear rate was shown on Figure 4. As for each CSCG, the viscosity decreased when the temperature increased from 30 °C to 80 °C. Whether 30 °C or 80 °C, CSCG with water showed a slight decrease in viscosity compared with CSCG. This can be explicated by shear thinning behavior, in that the thicker CSCG could not be structurally integrated at high shear rate, resulting in the viscous behavior of CSCG being more like base oil.

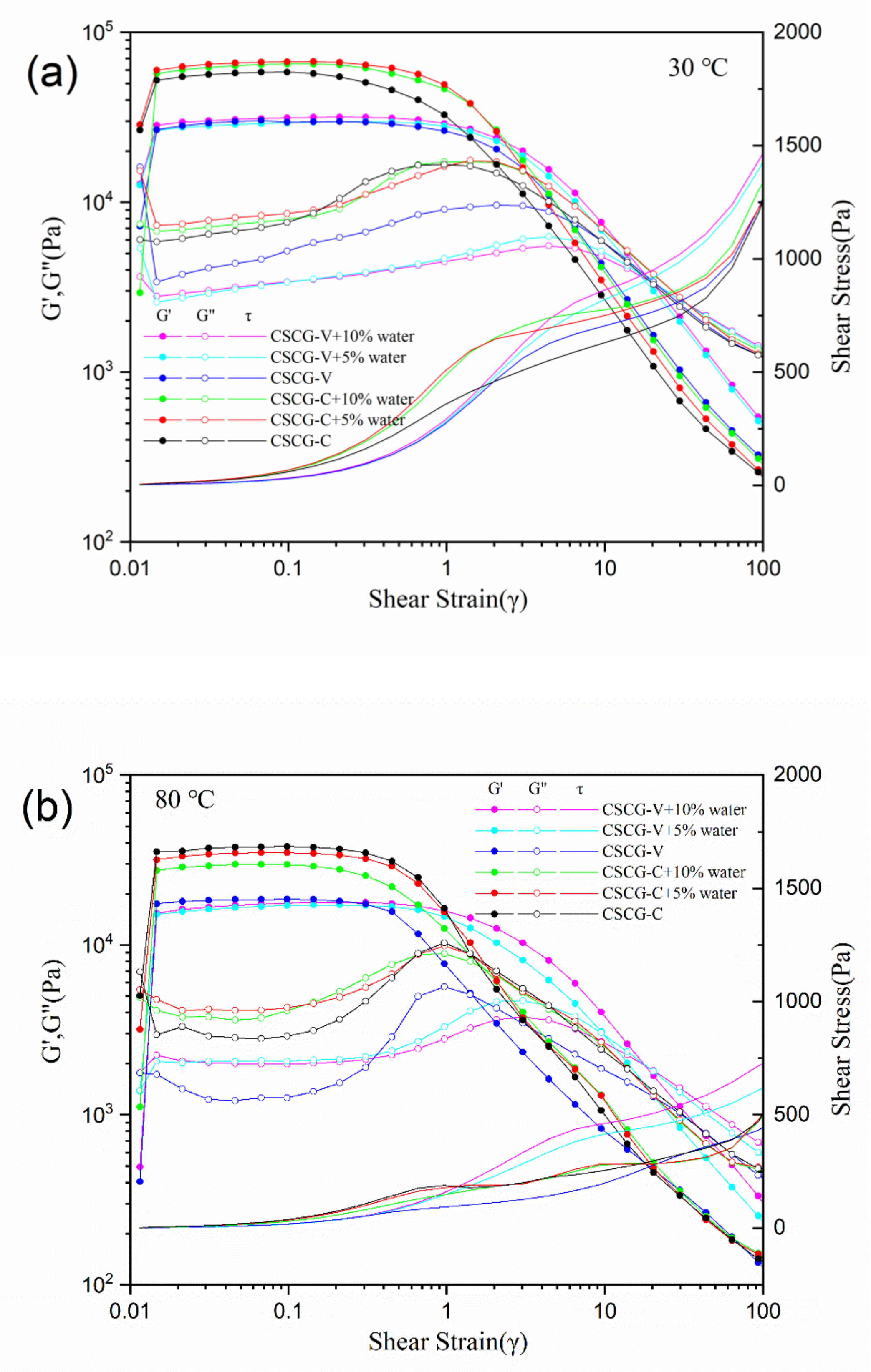

Figure 3. Storage modulus (G′), loss modulus (G″), and shear stress (τ) as a function of shear strain for CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water at (**a**) 30 °C and (**b**) 80 °C.

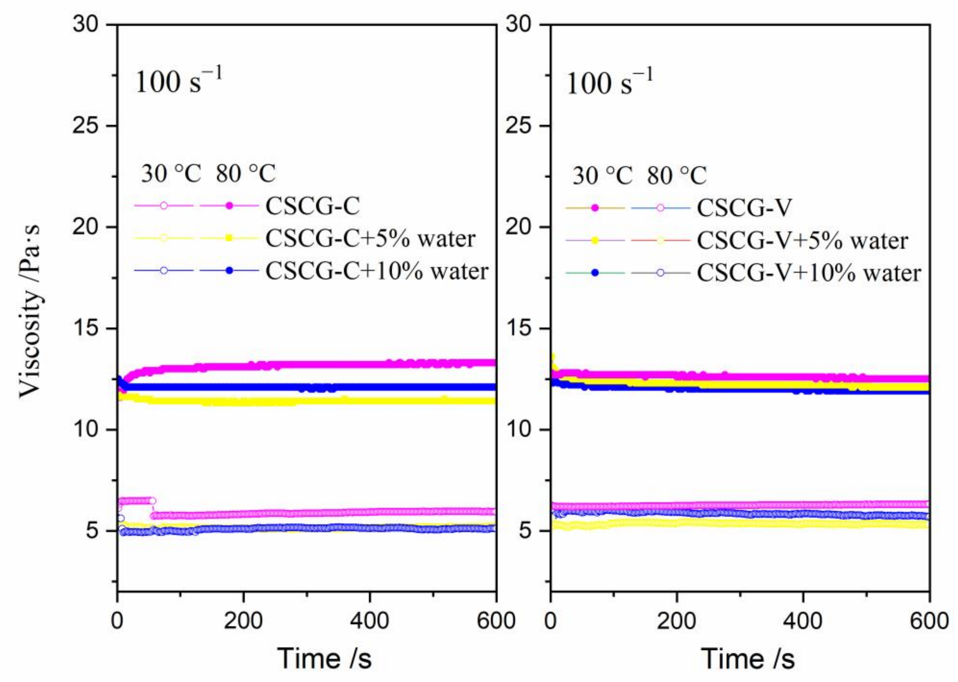

Figure 4. The evolution of shear viscosity for CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water at 30 °C and 80 °C.

3.3. Tribological Evaluation

The tribological performance of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water was evaluated by SRV tester at 30 °C and 80 °C. Firstly, the lubricating performance of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water was tested under 200 N at 30 °C. Figure 5a shows that the friction coefficient of CSCG-C was a slightly lower than that of CSCG-V at 30 °C. This was related to the better tribological properties of the calcium carbonate in calcite form. It is also seen that that the friction coefficients of CSCG-V with water are very large, and seizure even occurs in about 200 s ($\mu > 0.4$). In particular, the wear volumes of the steel surface lubricated by CSCG-V with water were very large, as shown in Figure 5b. This indicated that the calcium carbonate of vaterite with water could not form the effective protective film to decrease the friction coefficient and reduce the wear. The above results were in accordance with the Four-ball extreme pressure tests and previous reports [20,21]. Moreover, there is no obvious difference between CSCG-V with 5% water and CSCG-V with 10% water. However, the friction coefficients of CSCG-C with 5% water and CSCG-C with 10% water could be very smooth and noticeably even lower than that of CSCG-C. Moreover, the wear volumes of the steel surface lubricated by CSCG-C with 5% water and CSCG-C with 10% water showed almost same anti-wear performance with CSCG-C in Figure 5b. In the presence of water, the excellent tribological properties of CSCG-C with 5% or 10% water may be attributed to the fact that water not only hinders, but also promotes the formation of a boundary lubrication film. Calcium carbonate of calcite with water adsorbs on the friction surface and effectively reduces friction and wear.

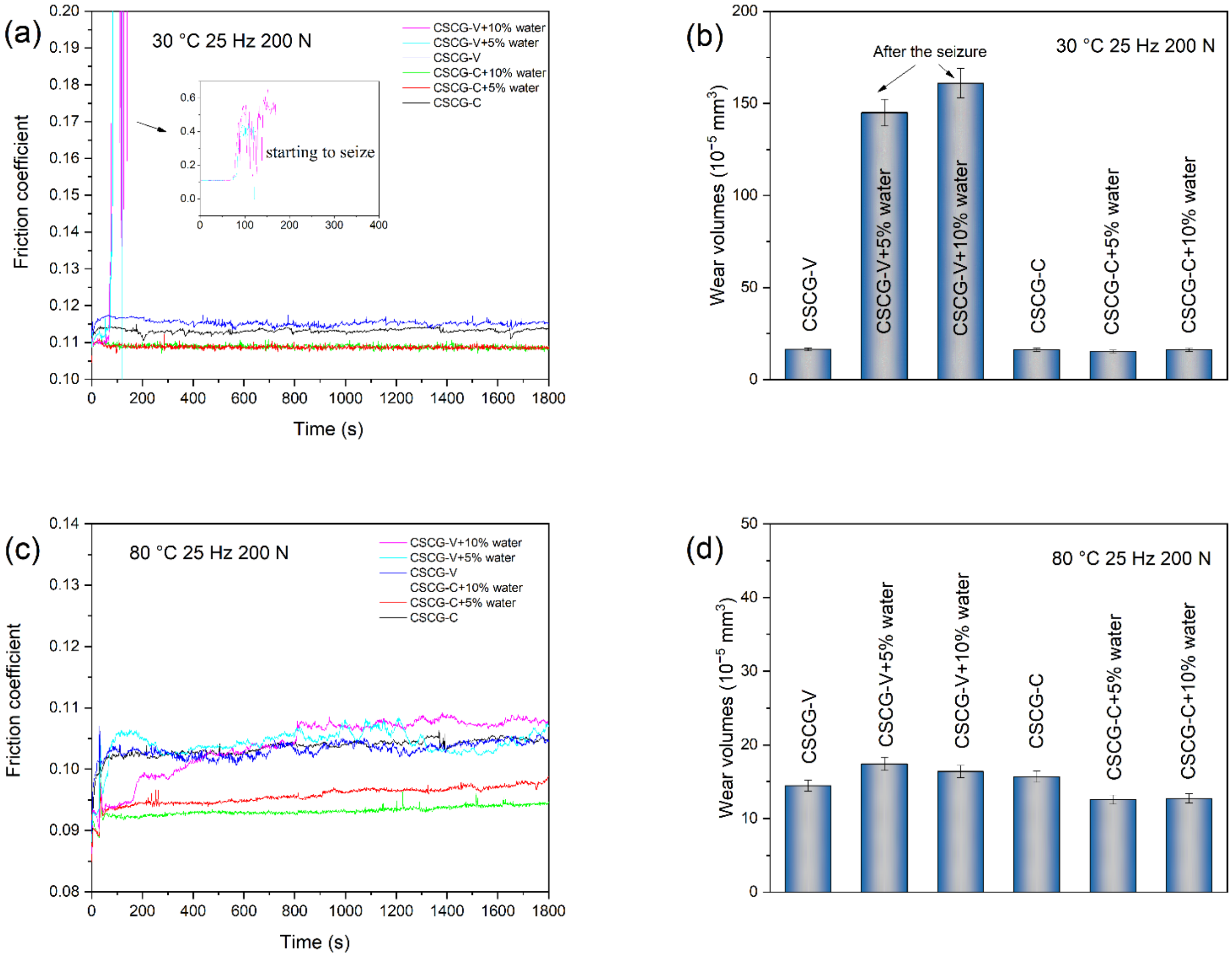

Figure 5. Friction curves at (**a**) 30 °C, (**c**) 80 °C and wear volumes at (**b**) 30 °C, (**d**) 80 °C of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water.

Secondly, the lubricating performance of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water was tested under 200 N at 80 °C. As the temperature increases, the effect of water becomes relatively insignificant. As shown in Figure 5c, no seizure signals of the friction coefficient were recorded on CSCG-V with 5% water and CSCG-V with 10% water. On the contrary, the friction coefficient of CSCG-V with 5% water and CSCG-V with 10% water have slightly higher friction curves than CSCG-V. This shows that although the effect of water on the calcium carbonate of vaterite is basically relieved when the temperature increases, the tribological properties are still affected by water to some extent. The results also confirmed that when water gradually separated from the calcium sulfonate grease system, the calcium sulfonate returned to its initial state. However, CSCG-C with 5% water and CSCG-C with 10% water show a relatively lower friction coefficient ($\mu = 0.095$) than CSCG-C ($\mu = 0.105$). This phenomenon indicates that calcium carbonate of calcite with water still have a certain friction reducing effect when water has not completely separated from the calcium sulfonate grease system. As shown in Figure 5d, the wear volumes of the steel surface lubricated by CSCG-V with 5% water and CSCG-V with 10% water remain than CSCG-V. Similarly, the wear volumes of the steel surface lubricated by CSCG-C with 5% water and CSCG-C with 10% water remain less than CSCG-C. The anti-wear trend under the influence of water is consistent with that at 30 °C.

At last, the load-carrying capacity of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water was further tested at 30 °C and 80 °C. As shown in Figure 6a,b, the load-carrying capacity of CSCG-C with 5% water and CSCG-C with 10% water increased from 100N to 500 N with the increase in applied load at 30 °C and 80 °C, respectively. This phenomenon once again shows that a good lubricating film composed of calcium carbonate of calcite with water can be formed to reduce friction and wear.

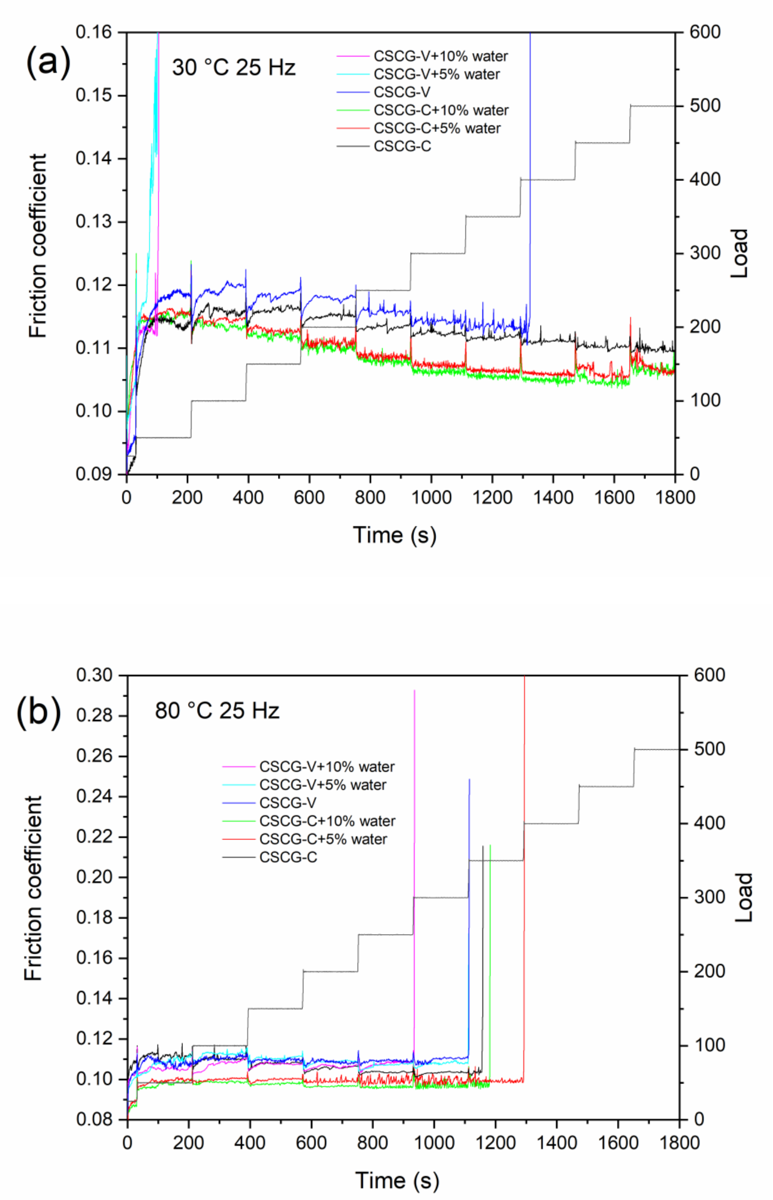

Figure 6. The variation of friction coefficient as a function of time during load ramp test from 50 to 500 N at (**a**) 30 °C, (**b**) 80 °C.

3.4. Surface Analysis

Figure 7 displays SEM and 3D analysis of the wear surface lubricated by CSCG-V (a1–a3), CSCG-V with 5% water (b1–b3), CSCG-V with 10% water (c1–c3), CSCG-C (d1–d3), CSCG-C with 5% water (e1–e3), and CSCG-C with 10% water (f1–f3) at 30 °C. Obviously, the worn surfaces lubricated by CSCG-V with 5% water and CSCG-V with 10% water display more serious flaking and scratching than others, as marked in the red lines in Figure 7(b2,c2). This indicated that abrasive wear and adhesive wear had taken place on the worn surface, ascribed to the poor film forming capacity under the lubrication of CSCG-V with 5% or 10% water. However, this is consistent with the friction test data in Figure 5, that the worn surfaces lubricated by CSCG-C with 5% water and CSCG-C with 10% water are regular and smoother, especially in the existence of a dense lubricating film on the surface. This observation further suggested that water could worsen the lubrication capacity of CSCG-V, whereas water could provide assistance to the lubrication capacity of CSCG-C.

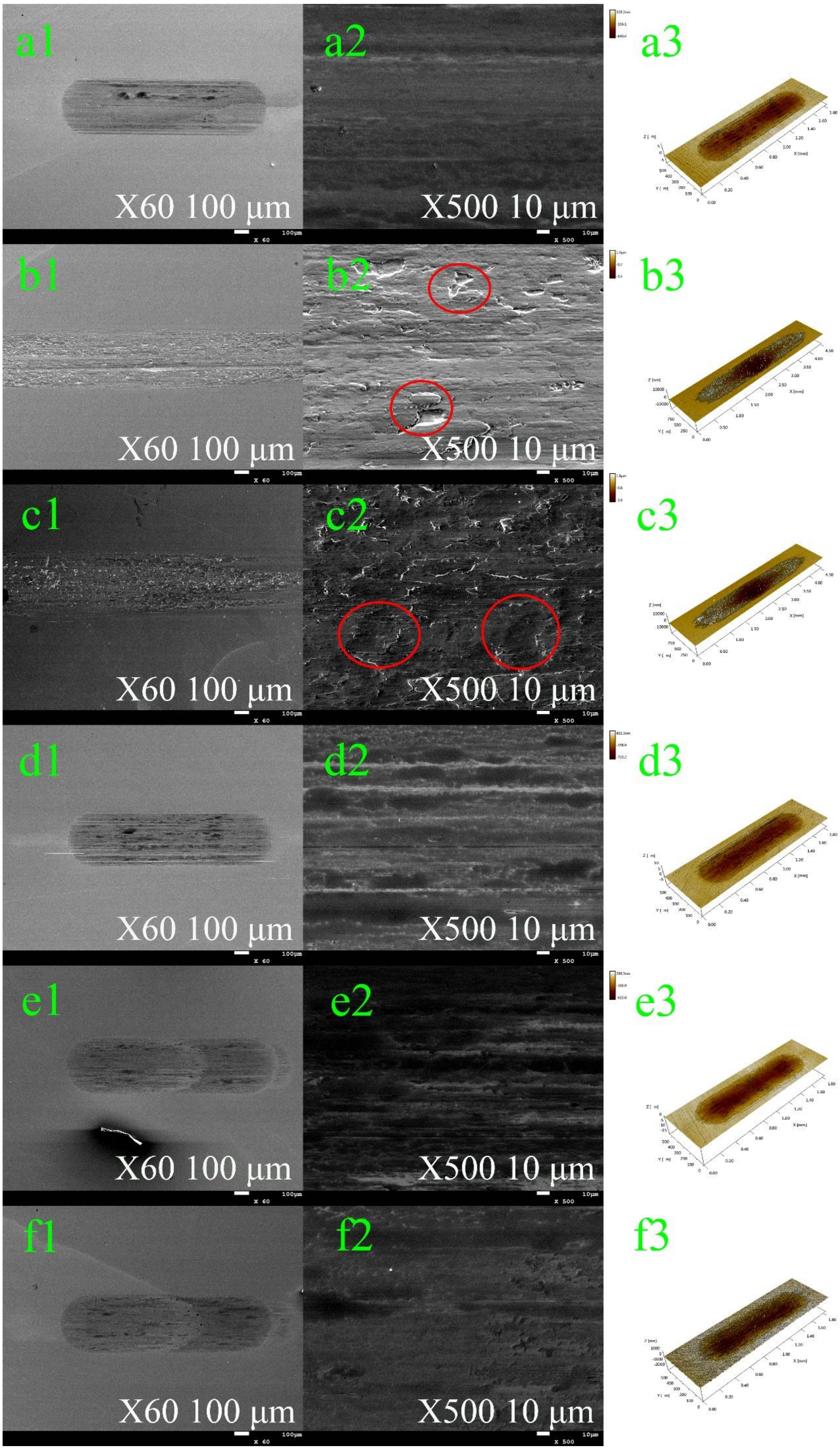

Figure 7. SEM and 3D of wear surface lubricated by CSCG-V (**a1**–**a3**), CSCG-V with 5% water (**b1**–**b3**), CSCG-V with 10% water (**c1**–**c3**), CSCG-C (**d1**–**d3**), CSCG-C with 5% water (**e1**–**e3**) and CSCG-C with 10% water (**f1**–**f3**) at 30 °C.

Figure 8 displays C 1s, Fe 2p, O 1s, Ca 2p of worn surfaces lubricated by CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water. It can be seen that CSCG-C and CSCG-V could form the protective films on the worn surfaces whether there is water in them or not. The C 1s peaks at about 284.8 eV in Figure 8a can be attributed to C in air, while the weak peaks at about 289.4 are attributed to carbonate [31]. The Fe2p peaks at 710.1 eV and 723.1 eV in Figure 8b can be attributed to iron oxides while the O1s wide peak at about 529.5–531.4 eV in Figure 8c refers to the iron oxide, calcium oxide, and calcium carbonate [32–34]. It is worth noting that due to the thick film of calcium carbonate, the peaks of iron oxide in CSCG-C with 0%, 5%, 10% water were so weak. In addition, CSCG-V was also very weak than CSCG-V with 5%, 10% water. Meanwhile, the peaks of Ca2p at about 347.3 and 350.9 eV in Figure 8d were attributed to calcium carbonate and calcium oxide [35,36]. However, the peaks of Ca2p on the worn surfaces lubricated by CSCG-V with 5%, 10% water were not obvious. This phenomenon further explains that water could worsen the lubrication capacity of CSCG-V so as not to form the effective protective film to decrease the friction coefficient and reduce the wear. The above results clearly show that all greases have similar lubrication mechanisms. Calcium carbonate in grease could form a protective film on the friction surface to reduce friction and wear. The boundary friction film composed of $CaCO_3$ and CaO may be the key factor to protect the steel surface. Therefore, the ability of $CaCO_3$ polymorphs to interact with the surface to form boundary films is critical to tribological behavior.

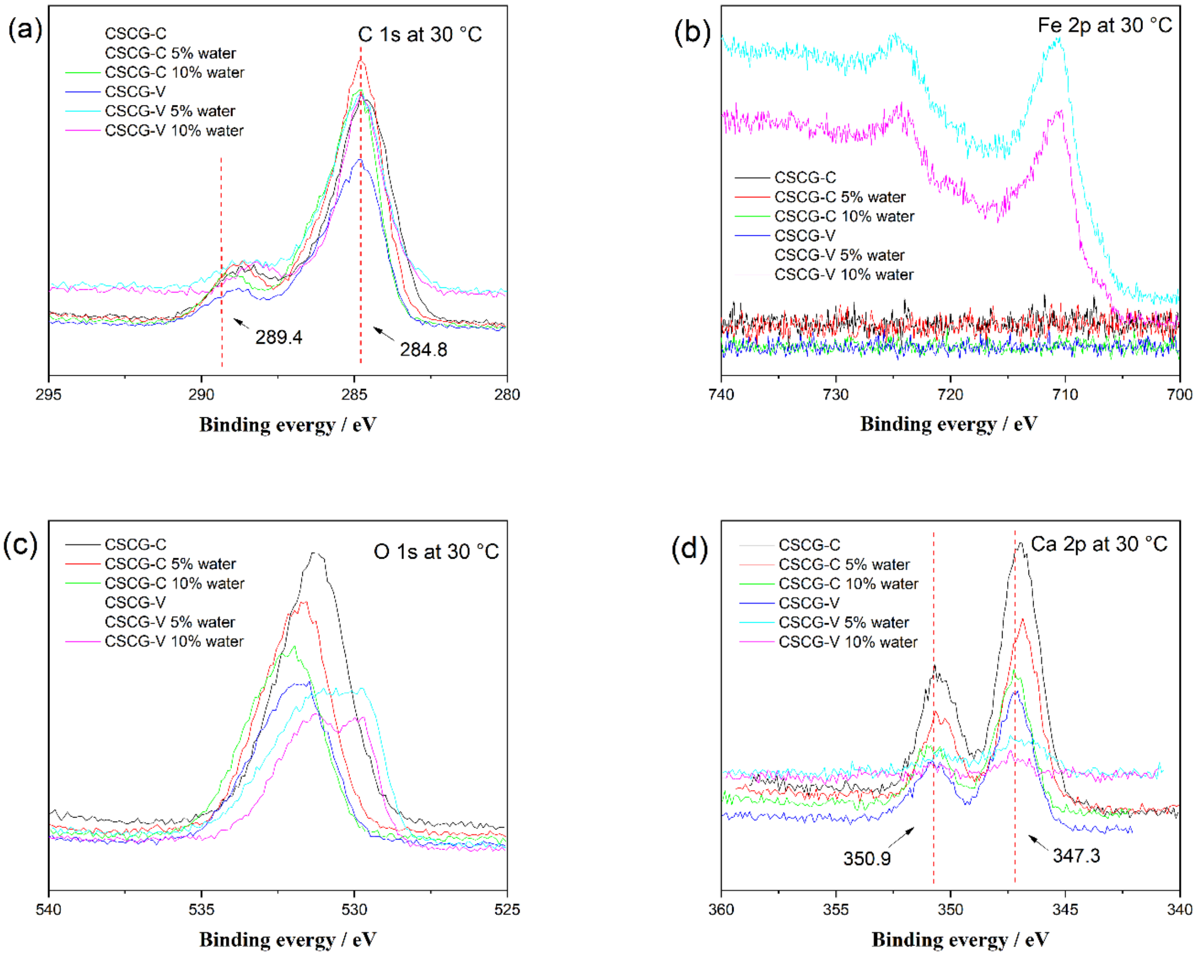

Figure 8. XPS spectra of C 1s (**a**), Fe 2p (**b**), O 1s (**c**), Ca 2p (**d**) on the worn surfaces lubricated by CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water.

3.5. Possible Mechanism Discussion

The lubricating properties of CSCG mainly rely on calcium carbonate instead of others additives [21,22]. As studied before, the calcium carbonate of calcite in CSCG shows better tribological properties than the calcium carbonate of vaterite under harsh conditions. In addition, the calcium carbonate of calcite also shows better tribological properties than amorphous calcium carbonate as additives in grease. Different calcium carbonate crystal forms show different surface film-forming ability. Under the boundary lubrication, the absorbed calcium sulphonate thickener with calcium carbonate formed a physical adsorption film to avoid the direct surface contact at the very start. Then, calcium carbonate absorbed on the surface reacts with the surface to form a protective film when the physically adsorbed films could not withstand continuous shear and load. These chemical boundary films bring a significant reduction in friction and wear. Thus, the film forming capacity of calcium carbonate polymorphs is the key to the lubricating performance of calcium sulfonate grease. However, when water exists in grease, the film-forming ability will be more or less affected. Therefore, the influence of water on the film forming capacity of calcium carbonate on the surface is crucial for CSCG under the conditions of a water environment [37–39].

When water enters the structure of CSCG, there are two main forms: one is the restricted water adsorbed around calcium carbonate, and the other is the unrestricted water free between soap molecule [40]. As shown in Figure 9, calcium carbonate of vaterite adsorbed more restricted water since it has higher surface energy than calcium carbonate of calcite. This characteristic explains why the rheological behavior of CSCG-V with water shows better structural stability than others. Although the structural strength of CSCG-V with water is higher, this characteristic affects its tribological behavior. Too much restricted water makes it difficult for calcium carbonate of vaterite to support a tribo-chemical reaction on the surface, which has also been well confirmed in tribological tests. On the contrary, calcium carbonate of calcite adsorbed less restricted water based on its stable crystalline state. The polarity of water makes it easy for calcium carbonate of calcite to adsorb on the surface, thus increasing the tribological properties of CSCG-C with water. Meanwhile, when the temperature rises from 30 °C to 80 °C, the influence of water becomes weak. Even so, CSCG-C with water still have better film forming capacity than CSCG-V with water. In addition, since the vaterite is more hygroscopic than the calcite forming hydrated calcium carbonate, the partial structural changes in the CSCG-V seem to be another possible factor affecting its film-forming ability.

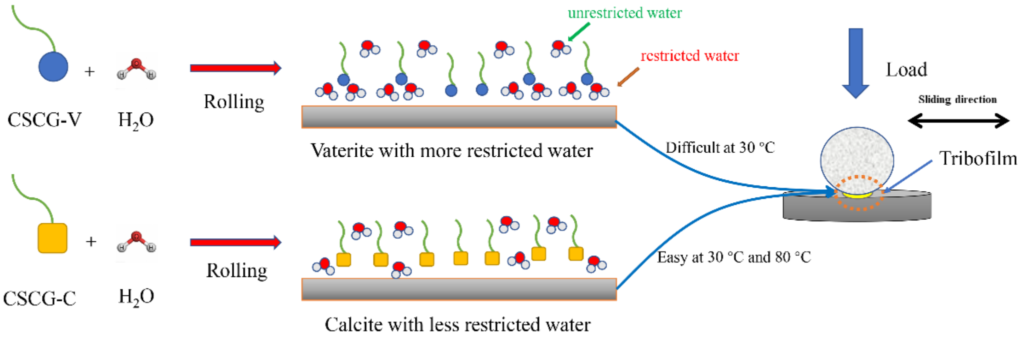

Figure 9. Possible tribological mechanism for CSCG-V with water and CSCG-C with water under boundary lubrication condition.

Based on the above discussion, the tribological performance of CSCG with water are more complex than pure CSCG. The calcium carbonate polymorphs affected by water could return distinct results. In the present work, CSCG-C with water could easily absorb on the steel surface to form stable films to protect the surface.

4. Conclusions

CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water were prepared and characterized, and the rheological and tribological performance of CSCG-V with 0%, 5%, 10% water and CSCG-C with 0%, 5%, 10% water was investigated at 30 °C and 80 °C. FTIR results showed that calcium carbonate polymorph in CSCG-V was vaterite, while CSCG-C was calcite. Rheological analysis demonstrates that water could affect the microstructure and properties of CSCG-V more than CSCG-C, and CSCG-V could combine with water to form a stronger microstructure. Tribological results clearly show that CSCG-C with water shows better tribological properties than CSCG-V with water under harsh conditions. XPS analysis indicated that boundary tribofilms consisting of $CaCO_3$ and CaO were formed on the rubbing surfaces. There was no significant difference in the components of the films regardless of grease within or without water. However, the influence of water on the film forming capacity of calcium carbonate on the surface is crucial for CSCG under the conditions of a water environment. Therefore, stable calcite in CSCG-C is beneficial to improve the tribological performance of grease under the conditions of a water environment. The completed conversion of calcium carbonate polymorphs for preparing the CSCG in industrial application is the key to improving the tribological performance. Future studies should concentrate on the effect of calcium carbonate polymorphs with solid additives on the tribological properties.

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