

A STUDY OF THE REACTIONS BETWEEN WATER AND GRAPHITE IN TRIBOCHEMICAL SYSTEMS

Jean-Christophe Rietsch, Patrice Brender, Roger Gadiou, Joseph Dentzer, Cathie Vix-Guterl

Institut de Sciences des Matériaux de Mulhouse , 15 rue Jean Starcky
68057 Mulhouse

Introduction

The effect of water on the tribology of graphite is still not well understood. To explain the water effect, two models are proposed. The first one was established by Savage [1]. He proposed that water is physisorbed on the basal planes of graphite crystallites. This adsorption leads to a decrease of the surface energy of the particles, and thus to a decrease of the interparticular interaction. This phenomenon should explain the low friction coefficient values observed for friction in wet atmospheres. Later in the 90's, Zaïdi proposed another model in which the water acts as a stabilizer of the dandling bounds created during the friction [2]. Actually, during the friction, C-C bounds are broken and these resulting dandling bounds create adhesion between the two first bodies and induce a high friction coefficient. In a wet atmosphere, the water prevents the adhesion between the two counterfaces by dissociative chemisorption. This leads to a low friction coefficient. To the best of our knowledge, this last model has never been confirmed.

Brenlé proposed that a tribometer can be considered as a reactor where chemical reactions occur [3]. The graphite and the atmosphere are the reactants and the energy is brought to the system by the mechanical solicitation. A major drawback of tribometers is the fact that it is difficult to do a quantitative analysis of chemical reactions.

To overcome this, we used a planetary miller. In this kind of system, we also find the reactants (graphite and atmosphere) and mechanical energy. The greatest interest of grinders is that the atmosphere can be controlled and quantitative studies can be performed. Therefore the mechanisms linking chemical reactions and tribology can be better understood.

Experimental

3g of graphite were milled in a planetary ball miller with five balls and a jar in stainless steel. The atmosphere was composed of a mixture of argon and 10 μ l of water. The speed of rotation was fixed at 650rpm (rotation per minute). The atmosphere was controlled after each milling by mass spectrometry to ensure the lack of leaks (leak detected by the presence of a peak of $m/z=28$). To detect the occurrence of tribochemical reactions, D_2O and H_2O^{18} were used instead of H_2O . After ball milling, TPD-MS (Thermo-Programmed Desorption coupled with a Mass Spectrometer) experiments were carried out to observe if water decomposition occurred during the ball milling. The sound emitted during the milling

was also recorded during the milling to determine the milling mode in the set up [4] (see below).

Results and Discussion

There are two kinds of milling mode. The first one is a sliding mode in which the balls are in equilibrium along the jar. In this kind of ball milling, the material is not damaged very much. There is small increase in the surface area and a decrease of the structural ordering of the material. In the shock mode, the ball is thrown against the opposite face of the jar. This leads to a much damaged structure and therefore a strong increase of the surface area.

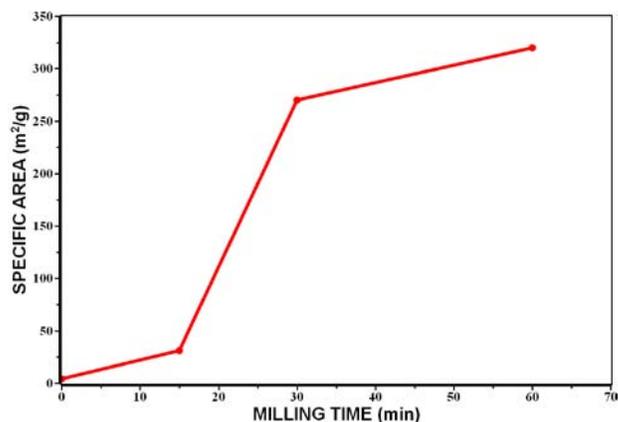


Fig. 1 Variation of Specific Area in terms of milling time

The milling mode is determined by the grinding atmosphere. If the dandling bounds created by milling can react with the atmosphere, there is no adhesion of graphite particles on the surface of the balls. The ball can slip along the jar and there is a sliding mode. If there is adhesion, the particles are stucked on the ball and the milling occurs in a shock mode.

A previous work has been done [4] in which we studied ball milling under oxygen atmosphere. We showed that when the gas pressure is sufficient, the milling was a sliding type one, whereas below a critical value of oxygen pressure, the grinding occurred on a shock type. This is due to the fact that during milling, oxygen is consumed by dandling bounds and below a certain value: the oxygen remaining is not sufficient to prevent the adhesion of graphite particles on the balls.

When graphite is ball milled under a mixture of argon and D_2O or argon and H_2O^{18} during one hour at a speed of 650 rpm, we observed that for short milling times, the structure is only slightly damaged. The surface area increases from 4 m^2/g (for pristine material) to about 30 m^2/g during the first 15 minutes. That means that the particular size doesn't decrease so much (figure 1). We observed then a strong increase of the surface area between 15 and 30 minutes of milling, meaning that the particle size decrease significantly. This is due to the

fact that the milling mode is a sliding one at the beginning and changes to a shock mode after a period of 15 to 30 minutes.

If we look on the molar balance (figure 2) of deuterium quantified by TPD-MS, we observe that during the sliding period the total amount of D injected in the jar is not consumed. Whereas after the transition to the shock type milling, the total amount of D injected is consumed. That means that the milling transition is due to the consumption of all the D₂O injected. If we compare this to the ball-milling under oxygen, we have the same kind of transition: under a certain amount of oxygen/water, we have a sliding type milling and below this value, the milling changes to a shock type one.

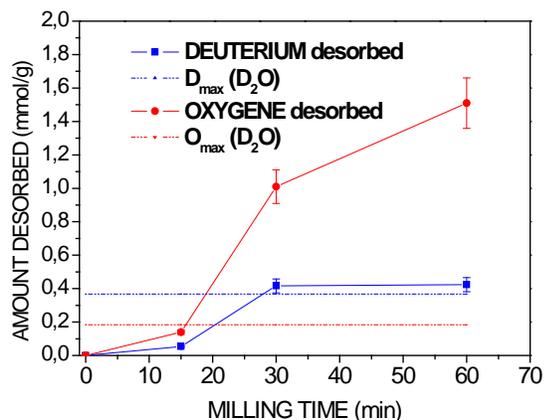


Fig. 2 Molar balance of deuterium and oxygen released in function of milling time for a milling in D₂O

The TPD-MS profiles of the graphite ball-milled under a mixture of argon and D₂O are presented in figure 3. We observe that HD and D₂ desorptions occur after 750°C. These desorptions are due to the decomposition of C-D and C-OD functions when the sample is heat-treated. These functions can only come from the dissociation and chemisorption during the ball milling, showing that the water can also act as Zaïdi predicted.

The same trend is observed for the material ball-milled under the mixture Ar/H₂O¹⁸: a desorption of CO¹⁸ (m/z=30) occurs when the sample is heat treated during the TPD-MS experiment. This desorption is due to the decomposition of O¹⁸ groups on the carbon surface. These O¹⁸ functions come from the dissociation-chemisorption process during the ball-milling. This is also a proof that water lubrication is also due to chemisorption reactions.

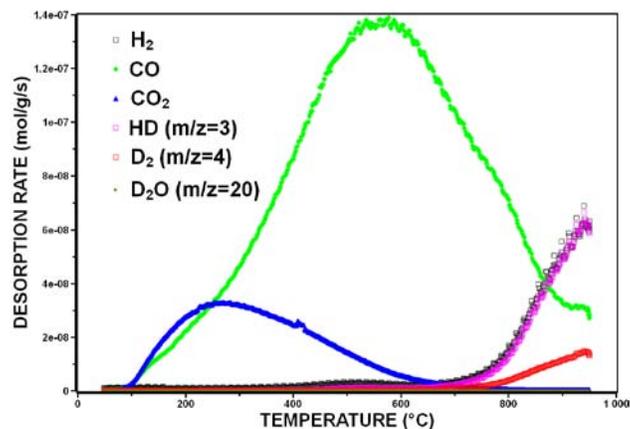


Fig. 3 Thermo-Programmed Desorption spectrum of graphite after ball-milling under Ar/D₂O during 1h at 650rpm

Conclusions

By using a ball-miller instead of a tribometer, we showed that the active sites are created by mechanical energy. Water could be dissociated and chemisorbed by the dangling bonds created when C-C bonds are broken. This was confirmed by the fact that desorptions of HD and D₂ occur after 750°C during a TPD-MS measurement of graphite milled under a mixture of argon and D₂O. This confirms the hypothesis proposed by Zaïdi in the 90's supposing that water acts not only by physisorption but also by chemisorption to lubricate sliding graphite contacts.

References

- [1] Savage R.H. Graphite Lubrication J. of Appl. Phys. 1948; 19 (1) 1-10
- [2] Zaïdi H., Néry H., Paulmier D. Stability of lubricating properties of graphite by orientation of the crystallites in the presence of water vapour Appl. Surf. Sci. 1993; 70/71 180-185
- [3] Brendlé M., Stempflié P. Triboreactions of graphite with moisture-a new model for integrating friction and wear Wear 2003; 254 818-826
- [4] Rietsch J.-C., Gadiou R., Vix-Guterl C., Dentzer J. The influence of atmosphere on the mechanisms of degradation of graphite in planetary ball-millers J. of Alloys and Comp. 2010; 491 L15-L19