Temperature Effects of Water-Metallic Interface Energies and Their Influence on Contact Angle Test for Surface Cleanliness: A Combined Experimental and Molecular Simulation Study

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Abstract

To ensure the effectiveness of the high-power-laser facilities, the cleanliness of metal parts is of significance. In this paper, molecular modelings combined with contact angle tests were performed, in order to investigate the temperature effects of water-metallic interface energies and their influence on the tests for surface cleanliness. As results, the attractive forces were found between water and metallic surfaces, in which van der Waals forces contribute most, and the energies raised with elevated temperatures from 291 K to 303 K; meanwhile, the contact angle tests show both the Al and Fe components are hydrophilic, and the contact angle reduced with elevated temperatures; furthermore, correlations can be found between the energy change and the contact angle at varying temperatures. These conclusions are helpful in the accurate testing of surface cleanliness for optical scientific facilities.

Introduction

Surface cleanliness is a major challenge for optic scientific facilities, including high-power-laser facility which contains both expensive optics and large proportion of metal parts. In the laser devices, the metal parts often take more than 80 % of the whole device, and may directly contact with the optics, reducing the damage threshold of the optics if there is any contaminant on the surface. Thus the surface cleanliness of these metal parts is of great importance for the function and service-life of the whole facility [1].

The commonly-used metal parts in high-power-laser devices are made of the stainless steel 304 or aluminum alloy 6061, with main elements Fe or Al. The contact angle tests are used to determine the surface cleanliness of these metals [2, 3]. The surface cleanliness is related to the wetness degree of water on the surfaces, and the angle between the tangent line of gas-liquid interface and solid-liquid boundary, namely the contact angle, can determine the wetness [4–7]. For example, if the contact angle is less than 90°, the materials are hydrophilic and expected to be clean; otherwise they are hydrophobic materials which may be polluted by oil and other impurities [8]. The interface interactions are believed to cause the differences [9], which can be easily changed with thermodynamic temperatures. As results, temperature effects should be considered in order to investigate the interface interactions, as well as to obtain precise cleanliness test results [10].

In recent years, theoretical methods including molecular modelings show great ability in the investigation of solid-liquid interfaces, such as water-metallic interfaces, and the stable interface structures, as well as interface energies have been well represented using density functional theory [11] or molecular dynamics [12–15]. In this paper, a combined strategy of molecular modeling and surface experiment was carried out to find the temperature effects of water-metallic interface energies and their influence on the cleanliness tests. The results are helpful for ensuring the effectiveness and accuracy of the metal parts in high-power-laser facilities.

Methodology
Molecular simulations

In order to investigate the interface interaction energies for water on the metals at the temperatures 291–303 K, water-metallic interface models were constructed as shown in Fig. 4. The amorphous cells (AC) of water (H$_2$O) were established with a density of 1.0 g/cm$^3$, where the short lines between H and O atoms represent the chemical bonds in the water molecule; we use the crystalline structure of main element Al or Fe to represent the metallic samples, where Al crystal is in $f_{cc}$ stacking style, $f_{m-3m}$ space group, with cell parameters $a = b = c = 0.405$ nm, $\alpha = \beta = \gamma = 90^\circ$ [16]; and Fe crystal is in $b_{cc}$ stacking style, $i_{m-3m}$ space group, with cell parameters $a = b = c = 0.28664$ nm, $\alpha = \beta = \gamma = 90^\circ$ [17]. The neighbour atoms have metallic bonds are represented with the atomic interactions in the potential field, considering the existence of H$_2$O molecular system, the COMPASS force-field [18, 19] was applied, which can cover the interactions between H, O, Fe, and Al elements. Considering the anisotropy of the metallic crystals, the supercells of 5×5×5 Al and 10×10×10 Fe were cut along $(1\ 0\ 0)$, $(1\ 1\ 0)$, $(1\ 1\ 1)$, respectively. The amorphous cells containing 200 H$_2$O molecules were put onto each metallic surface to form water-metallic (liquid-solid) interface models, along with 2 nm vacuum layer on the top to overcome the influence of the upper interface. The interface models were optimized using molecular mechanics (MM) [20, 21], and then molecular dynamics (MD) simulations were carried out under COMPASS force-filed using NVT ensemble (constant particle number, volume and temperature), with varying temperatures 291 K, 296 K, 297 K, 298 K, 299 K, 300 K, 301 K, 302 K and 303 K. Nosé method was used to control the temperatures [22–24]. The van der Waals forces were summed by atom-based method, while the electrostatic forces were summed by Ewald method [25, 26]. For each system, three replica simulations are carried out to reduce random errors. Each MD simulation lasts 500 ps to ensure the equilibrium of both temperature and energy.

Experimental tests

The contact angle tests were carried out on the metal parts, in order to validate the surface interactions and to determine the surface cleanliness of these components [27–30]. The portable contact angle tester (MobileDrop, KRÜSS GmbH) was used in all the test, which is accurate, portable and efficient. The tester has its own injector to drop liquid on the surface of the sample, with accuracy of 2 µl. The stainless steel 304 (with main element Fe) and aluminum alloy 6061 (with main element Al) are chosen as the samples of the tests to simulate the components of high power laser device, and both samples are in the same dimension of 100×100×10 mm. Before the surface tests, clean treatment process was carried out on each sample, firstly the sample was infiltrated in high-pressure water for 10 min, and in cleaning agent for another 10 min; then it was washed under high-pressure water for 3 times, dried under ethyl alcohol, and dried by heating for 4 hours. Finally, the surface test experiments are carried out on the treated samples under various temperatures as same as the molecular simulations from 291–303 K at a constant humidity of 40 % RH. As results, the contact angles at elevated temperatures were obtained [31, 32].

Results And Discussion

Anisotropy of interface interactions
The equilibrium trajectories were used to analyze the interaction energy \((E_{\text{inter}})\), which is the difference between the energy of the total system \((E_{\text{total}})\) and the divided systems including the metallic surface \((E_{\text{metal}})\) and the water AC \((E_{\text{water}})\), normalized by the contact surface area \((S)\) (Eq. 1), and the contributions of van der Waals force (vdW) and Electrostatic force (ES) were also calculated as shown in Fig. 2. From the results of three replica simulations for each system, it can be seen that the calculated energies remain the same for each system at specific temperature and pressure.

\[
E_{\text{inter}} = \frac{E_{\text{total}} - (E_{\text{metal}} + E_{\text{water}})}{S} \tag{1}
\]

It can be concluded from Fig. 2 that, the water molecules have attractive interactions with the metallic surfaces, in which the van der Waals forces contribute most [33–36], while the electrostatic forces also contribute mainly for \(\text{H}_2\text{O}\) molecular systems. For different metals, the interactions are different, in which water on Fe template are stronger, for Fe surfaces the absolute values of interaction energies are all lager than 60 kcal/mol per nm\(^2\), while that of the Al surfaces are all smaller than 50 kcal/mol per nm\(^2\). For the same metal, the interactions show anisotropy along different crystalline directions, for water on Al \((1\ 0\ 0)\\rightarrow(1\ 1\ 0)\rightarrow(1\ 1\ 1)\), while for water on Fe \((1\ 0\ 0)\\rightarrow(1\ 1\ 0)\rightarrow(1\ 1\ 1)\). Above all, the attractive forces between water and Al or Fe metallic surfaces are strong, making the samples a kind of hydrophilic materials, and the surface tension and contact angle between water and these materials are expected to be small [37].

**Temperature effects on interaction energies**

It should be noticed that, the absolute values of interaction energies raised with the temperature from 291 K to 303 K [10]. The energy gradients at elevated temperatures can be found by correlating interaction energies with temperatures (Fig. 3). The values of energy gradient for each system are summed in Table 1, from which it can be seen that the energy gradients for water on both Al and Fe show anisotropy.

| System         | Energy gradient \([\text{kcal/}(\text{mol}\cdot\text{nm}^2\cdot\text{K})]\) | System       | Energy gradient \([\text{kcal/}(\text{mol}\cdot\text{nm}^2\cdot\text{K})]\) |
|----------------|----------------------------------|--------------|----------------------------------|
| \(\text{H}_2\text{O}-\text{Al} \ (1\ 0\ 0)\) | 0.4824                           | \(\text{H}_2\text{O}-\text{Fe} \ (1\ 0\ 0)\) | 0.1880                           |
| \(\text{H}_2\text{O}-\text{Al} \ (1\ 1\ 0)\) | 0.2355                           | \(\text{H}_2\text{O}-\text{Fe} \ (1\ 1\ 0)\) | 0.2813                           |
| \(\text{H}_2\text{O}-\text{Al} \ (1\ 1\ 1)\) | 0.2216                           | \(\text{H}_2\text{O}-\text{Fe} \ (1\ 1\ 1)\) | 0.1643                           |

**Correlation interface interactions to contact angles**

From the results of the contact angle tests at various temperatures from 291 K to 303 K and a constant humidity 40 % RH, it can be seen that, for each sample, two different test points on the surface were
chosen to do *in situ* tests; for each point, 10 parallel tests of contact angle were performed to reduce the random error, and the average value of the results were calculated as shown in Fig. 4.

As results, for both Al and Fe samples, the contact angles are all small (< 60°), in the range for hydrophilic materials, which match with the calculation results of strong surface energies. In addition, for both samples, the contact angles reduce with elevated temperatures from 291 K to 303 K. Linear relationship can be found for each test with correlation coefficients all larger than 0.90, and the slope values which represent the contact angle gradient at elevated temperatures are as shown in Table 2. It can be seen that the contact angle gradients for Al sample and Fe sample are all around the value of -2.4 °/K, with slight changes caused by the different test points. The changes of contact angle also match with the surface energy gradients, proving that with elevated temperature, the atomic and molecular movements exacerbated, and surface energy rose, causing the reducing of surface tension and contact angle [38]. It can be concluded that, the experiments consisted with the computations.

| System     | Contact angle gradient [°/K] | System     | Contact angle gradient [°/K] |
|------------|-------------------------------|------------|-------------------------------|
| Al sample 1 | -2.3737                       | Fe sample 1 | -2.4020                       |
| Al sample 2 | -2.4187                       | Fe sample 2 | -2.3819                       |
| average    | -2.3962                       | average    | -2.3920                       |

**Table 2**  
Contact angle gradient at elevated temperatures from 291 – 303 K

**Conclusions**

Combined methods of experimental tests and molecular simulations were carried out to investigate the temperature effects of interface interactions for water on metallic surfaces. Conclusions can be found as follows:

Firstly, there are strong attractive forces between water molecules and the metallic surfaces; for different metals, the interactions are different, where the interaction energies between water and Fe are stronger than that of Al; for the same metal, the interactions show anisotropy along different crystalline directions.

Moreover, the absolute values of interaction energies raised with temperatures, and the energy gradient at elevated temperatures are anisotropic.

Meanwhile, the experimental tests show that the contact angle are relatively small, proving the metallic surfaces to be hydrophilic; what’s more, the contact angle reduce with elevated temperatures, and the contact angle gradient versus temperatures can also be calculated and related to the energy gradient.
The above show the temperatures have positive effects on water-metallic interface energies, which should be considered in accurate contact angle tests for cleanliness of high-power-laser facilities.

Declarations

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The authors have no conflicts of interest to be declared.

Availability of data and material

All raw data are available from the authors upon reasonable request.

Code availability

The calculations were performed using Materials Studio Release 6.1. provided by Accelrys Software Inc.

Author contributions

All authors designed the project; Y.J., L.N., H.L., G.Z. and C.Y. did the surface cleanliness tests; W.Q., Y.J. and X.M. did the calculations, data collections and analysis; W.Q. and Y.J. contributed to the writing of the manuscript.

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Figures
Figure 1

Atomic model for water-metallic interface [H2O-Fe(1 0 0) is taken for an example, and Fe, H, O atoms are represent using purple, white, and red respectively]
Figure 2

Interaction energies for water on different metallic surfaces
Figure 3

The interaction energies as functions of temperatures for different surfaces
Figure 4

The experimental contact angle as functions of test temperatures

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