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Wettability of Femtosecond Laser Direct Fabrication of Micro and Nanostructures on Metal Surface

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ABSTRACT

In this article, we focused the femtosecond laser pulse on the nickel surface and scan with a pitch smaller than the size of focused beam size. After a homogeneous laser irradiation on the surface, a cylindrical two-scale micro/nano composite structure was prepared. We found that the wettability of micro-nanostructure surface does not spontaneously change from hydrophilicity to hydrophobicity in air, which is different from the result of micro/nanostructured surface prepared on steel, titanium alloy and pure coppersurfaces by femtosecond laser. The results ofthis article show that the contact angle of micro /nano structuredsurface can reach up to 148.28^{o} after silanization near to superhydrophobicity. This discovery is of significant importancefor the selection of the base materials for the preparation of metal wettability surface bymicro/nanostructures.

Key words: Femtosecond laser, Nickel Micro/Nanostructures, Hydrophobicity, Hydrophilicity

1. Introduction

In addition, the micro-nanostructures can also be written directly by laser, and the surface of the material can be melted and vaporized after absorbing laser energy, which will result in mass migration. The femtosecond lasers are a revolution in technology and have thrilling potential for numerous applications and have fetched about important progress in the studying of light-matter interaction [1]-[2]-[3]. The surface morphology of the material will change accordingly. The surface structure and size can be optimized by controlling the laser energy and scanning speed. Moreover, the superhydrophobic surface function can be realized without hydrophobic treatment because of the micro and nanostructures prepared by femtosecond laser on metal alloy surface. Superhydrophobic functional surfaces can also be obtained by chemical means, and Rubner's research group [4] alternately reacts the substrate in a solution of polyacrylamide (PAH) and polyacrylic acid (PAA) for one hundred cycles. Self-assembly, a rough surface with a type of honeycomb structure is obtained, resulting in a superhydrophobic surface with a static contact angle of up to 172°. Liu, Ziyuan, et al. [5] the surface of stainless steel with micro-nanostructure morphologies was prepared by femtosecond laser and the surface chemical modification method was used to obtain hydrophobicity.Various techniques already exists to produce large-area hydrophobic and superhydrophobic surfaces: transparent coatings have been developed for different kinds of window, as eyeglasses and automobile windows [6], or to increase the outstandingperformance of solar cells [7], bio-fouling [8] [9] [10], and to control bio-adhesion [11][12][13].

Alexandre et al. [14] obtained a rough microstructure on the surface of stainless steel by chemical etching. Camilo Florian et al. [15] obtained with the implemented laser structuring strategies show that by inducing controlled changes in the surface morphology of steel it is possible to tune the wetting behavior over a wide range of contact angles, obtaining superhydrophobic and hydrophobic surfaces with contact angles between 100^o and 150^o. Yuan et al. [16] imprinted the lotus leaf structure onto a polyvinyl chloride (PVC) film. Anne-marieKietzig et al. [17] used femtosecond lasers to fabricate different types of structures on different grades of steel. The wettability of the prepared samples gradually changed from initial superhydrophilic to hydrophobic (near superhydrophobic) over time.It is well known that the metal surface has medium wettability: it has neither good hydrophilic function nor hydrophobic ability, which makes the metal do not show good application value in this respect. In the past research work, various steel materials [18], pure copper [19] and aluminum materials [20] have been used to carry out experiments. The experimental results show that the wettability of the prepared samples will change spontaneously from hydrophilicity to hydrophobicity with the passage of time when they are placed in the air. In this paper, pure nickel samples by femtosecond laser to prepare the micro/nano structure on the surface. Different experimental phenomena were found: the wettability of nickel samples remained unchanged for a long time in the air.

2. Experimental device and method

The experimental device for fabricating nanostructure of femtosecond laser is shown in Fig. 3.1, which includes femtosecond laser, electronic switch shutter, neutral absorption attenuator and focusing lens (f=200mm). The focusing lens is placed on a one-dimensional translation table (z-axis) which can move forward and backward along the direction of laser incidence to control the focusing position D (the distance between lens and target surface). The samples used in the experiment are titanium alloy (TC4). The edge length is 40 mm and the thickness is 27 mm. Before the start of the experiment, the surface was wiped with absolute ethanol to remove impurities such as dust, oil and dirt. The sample is fixed on a two-dimensional translation table perpendicular to the direction of laser incidence. The x-axis of the two-dimensional translation table is along the horizontal direction. Its velocity is defined as the scanning speed v, and the y-axis is along the vertical direction. The distance moved when the next scan is completed after each scan is called the scanning distance d. In the experiment, the femtosecond laser pulse is perpendicular to the surface of the titanium alloy target, and the (incidence angle is 0^o) to the target. The attenuator is used to control the output laser energy of femtosecond laser amplification system. The scanning speed v, y is adjusted by computer controlling x-axis translation table. The scanning distance d is controlled by y- axis platform, and the focusing position D is controlled by z-axis translation table. The whole experiment was carried out at a standard atmospheric pressure with relative humidity of 30% and indoor ambient temperature of 22^oC.

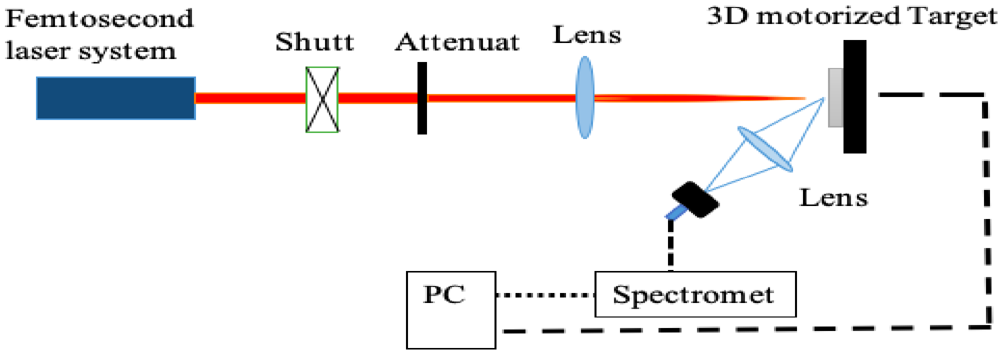

Fig (2.1) schematic diagram of the experimental device.

Fig. 2.2 (a) is a femtosecond laser system (Coherent Company Libra USA), which outputs pulsed laser space the mode is TEM, the spot diameter is 7m, the horizontal linear polarization (p polarization), the central wavelength is 800m, the repetition frequency is 1kHz, the pulse width is 50fs, the energy stability is less than 0.75% RMS, and the maximum power is 4W. Scanning electron microscopy (Fig. 2.2b) was used to measure and analyze the surface of processed samples. Wettability is measured by contact angle measuring instrument (Fig. 2.2 c).

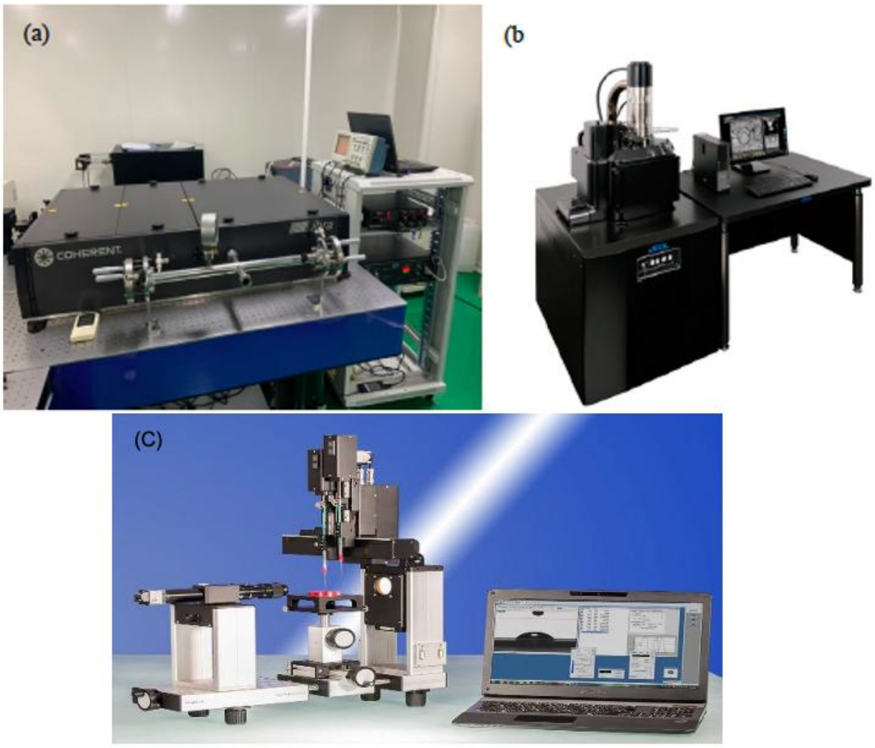

Fig.2.2 (a) Femtosecond Laser image, (b) The Scanning Electron Microscope (SEM) Image, (c) Contact angle measuring instrument for wetting characterizes testing.

3. Results and Discussion

At high energy density, the grooved micro-nanostructures can be written directly by femtosecond laser, while at relatively low laser energy density, the "columnar" micro-nanostructures can be formed by the accumulation of the number of irradiated pulses. The sample used in the experiment is pure nickel (30 mm in side length, 2 mm in thickness and 6 N in purity). Before the start of the experiment, the surface of nickel metal is wiped with absolute ethanol. After removing impurities such as dust and oil, the sample is fixed on the three-dimensional electric translation table. Femtosecond laser microstructures were fabricated using the devices and methods shown in section 2. The difference is that the scanning spacing is set in a range smaller than the size of the focusing spot, in order to obtain uniform irradiation to form self-assembled microstructures. The surface morphology of nickel was observed and analyzed by scanning electron microscopy (SEM) with incident laser energy E=0.94 mJ, scanning speed V=4 mm/s and scanning spacing d=0.05 mm femtosecond laser. As shown in Fig. 3.1, with the increase of focusing position, micron pit roughness appears randomly on the surface (Fig. 3.1 (a)), then micron bumps gradually forms and its size increases (Fig. 3.1 (b) - (e)). With the further increase of focusing position, micro bumps gradually disappears (Fig. 3.1 (f)).

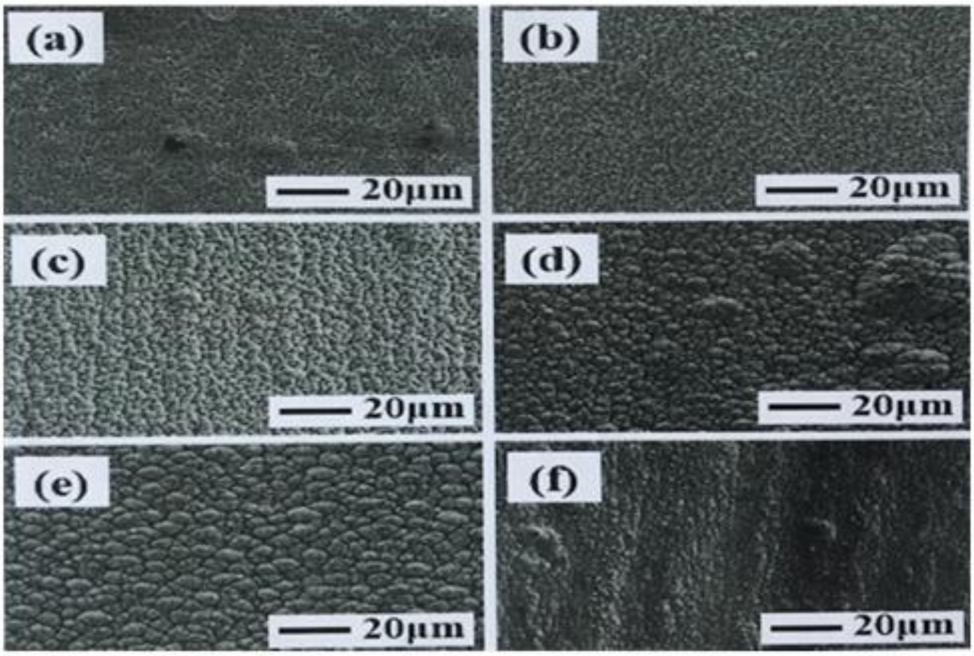

Fig. 3.1. SEM images of samples fabricated with laser energy of 0.94 mJ, scanning speed of 4 mm/s and scanning spacing of 0.05 mm at different focusing positions (a) D = 169.5 (b) D = 173.5 mm, (c) D = 177.5mm, (d) D = 181.5 mm, (e) D = 185.5 mm, (f) D = 189.5 mm and their corresponding contact angles.

The wettability of the surface was characterized by a contact angle measuring instrument (Fig. 3.2). The surface without femtosecond laser action was shown in Fig. 3.2 (a), and the contact angle was 93.45°. The typical results of femtosecond laser micro-nanostructure formation on the surface are as shown in 3.2 (b) - (c). Droplets fall behind and are absorbed rapidly by the surface of micro-nanostructure, showing hydrophilic characteristics.

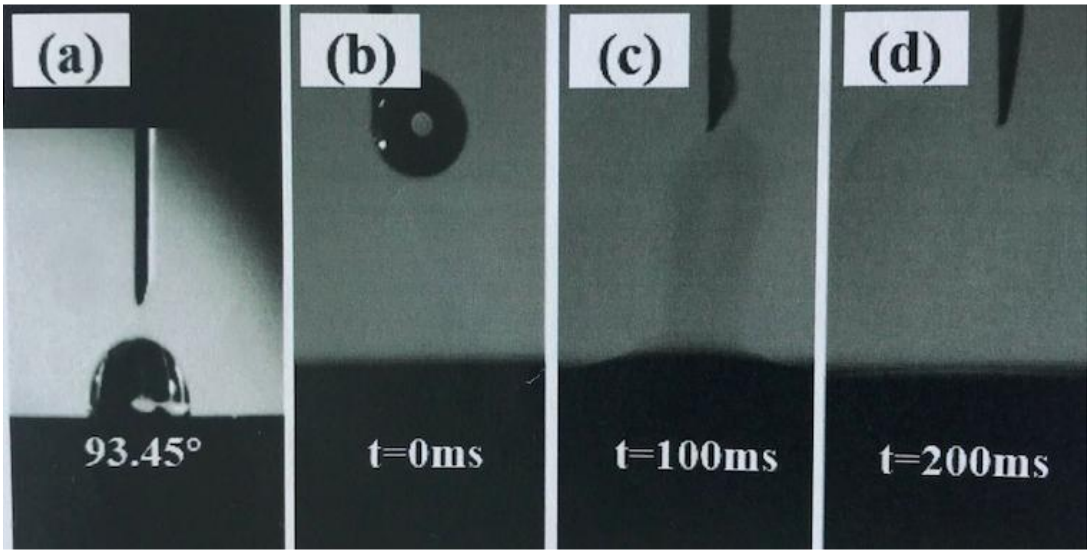

Fig.3.2 (a) is the test result of contact angle of sample before laser processing, (b) - (d) is the typical wetting characteristic test data (laser energy 0.94 mJ, scanning speed 4 mm/s, scanning distance 0.05 mm, focusing position 187mm).

After the samples were placed in the air for one week, the samples were tested for wettability, and it was found that the wettability did not change significantly, after one month, there was still no significant change. Subsequently, the sample was washed with absolute ethanol in a similar literature [27], and naturally dried at room temperature, and the hydrophilic properties of the surface of the sample were not changed, and the phenomenon of transition from wettability to hydrophobic properties as described in the literature was not observed.

3.1 Surface wettability of micro-nanostructure after silanization

3.1.1 Surface silanization process

Rinse the sample with absolute ethanol, and then wash it with ultrasonics to wash away the impurities inhaled during air. Mix the perfluorodecyltriethoxysilane with absolute ethanol and shake it in a beaker for one hour to make a mass fraction. It is a 1% solution of perfluorodecyltriethoxysilane in ethanol, followed by silanization of the sample to reduce the surface energy of the sample. The sample is placed in the prepared solution for four hours, and finally the soaked sample is placed. Bake in an oven at 100^{o}C for 1 hour and cool in the oven.

3.1.2 Characterization of Surface Wettability after Silanization

The wettability of the samples without laser processing before and after silanization to reduce the surface energy is shown in Fig. 3.3. The contact angle before silanization is 93.45^{o}, and after silanization the contact angle increases to 97.27^{o}. Obviously, the wettability of nickel surface has not changed significantly due to silanization treatment.

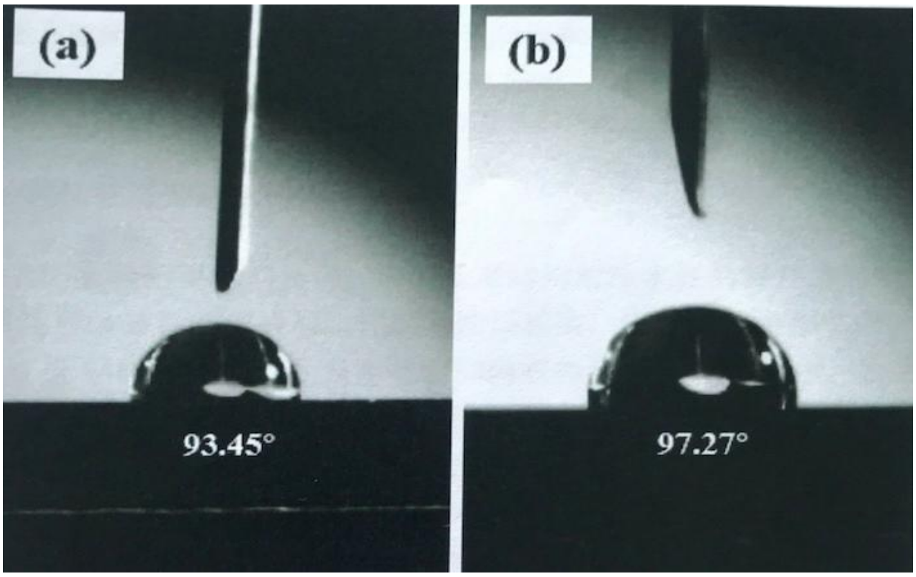

Fig. 3.3: Change of contact angle before (a) and after silanization (b) of the original surface of nickel metal.

Figure 3.4 shows the SEM images of bulk samples fabricated at different focusing positions. The illustration at the upper right corner shows the contact angles measured after their silanization reduces the surface energy. With the increase of the focusing position, the contact angles have different degrees, when D = 185.5mm, the increase is the best. After silanization, the surface of microstructures fabricated in femtosecond laser changed from hydrophilic to hydrophobic. This shows that after surface energy is repaired, femtosecond laser fabricated micro and nanostructures make the surface hydrophobic.

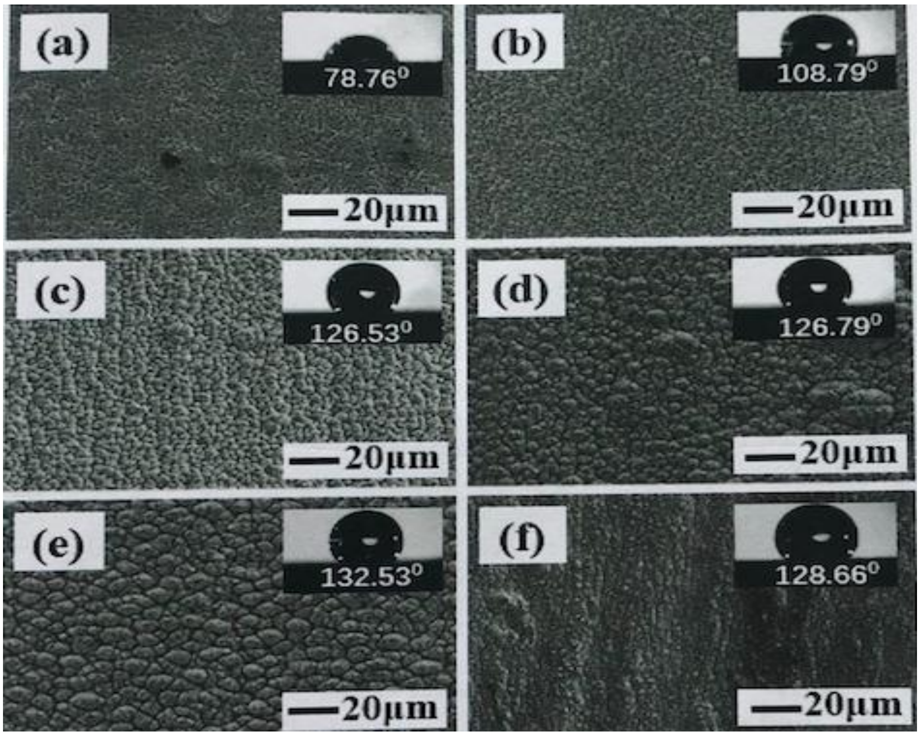

Fig. 3.4 SEM images of samples fabricated and their corresponding contact angles, laser energy 0.94mJ, scanning speed 4mm/s, scanning distance 0.05mm, at different focus positions (a) D=169.5mm (b) D=173.5mm, (c) D=177.5mm, (d) D=181.5mm , (e) D = 185.5 mm, (f) D = 189.5 mm.

3.1.3 Micro and Nanostructure optimization to enhance hydrophobicity properties

Through the above experimental results, we found that the columnar microstructure has the most obvious improvement in hydrophobicity (Figure 3.4 (e)). The formation of the columnar microstructure is closely related to the laser irradiation. Therefore, in this section, the scanning speed of the experimental parameters is reduced to V = 1 mm/s, in order to obtain more irradiation pulses per unit time. As shown in Figure 3.5, we can clearly see that there is a big difference between the morphology of the surface formed microstructures and that in the previous one. As the focus position increases, a more ideal columnar structure is formed at the positions of D=187.5 mm and D=191.5 mm.

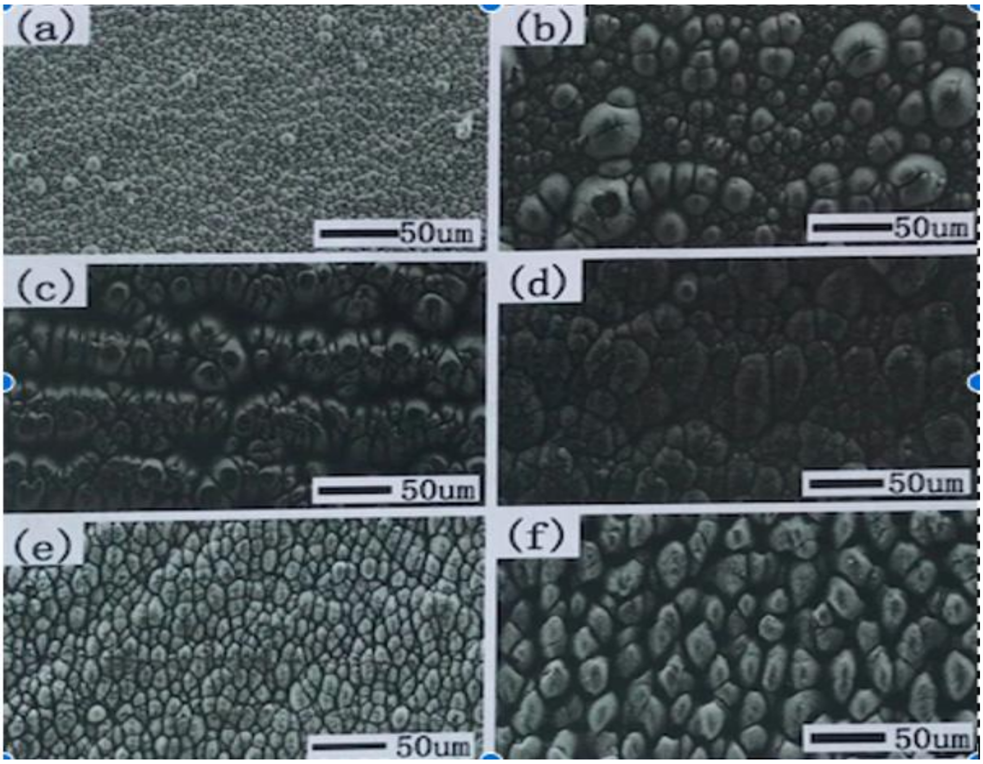

Fig. 3.5 The SEM images of nickel surface at different focusing positions (a) D = 171.5mm, (b) 174.5mm, (c) 179.5mm, (d) D = 182.5mm, (e) D = 187.5mm (f) D = 191.5mm when the laser energy is 0.99mJ, the scanning speed V = 1mm/s and the scanning distance d = 0.05mm.

The laser energy of 0.99 mJ, the scanning speed of 1 mm/s, the scanning distance of 0.05 mm, and the focusing position D of prepared at a spacing of 187 mm to 190.5 mm at intervals of 0.5 mm, respectively. A total of 8 samples (30 mm *30 mm) were prepared and silylated. The experimental results are shown in Fig. 3.6. When the focusing position D = 187 mm, there are more elliptical "columnar" structures, when the focusing position D = 189.5 mm, D = 190 mm and D = 190.5 mm, the gap between the "columnar" structures increases slightly (as shown in Fig. 3.6 (f), (g), (h). In terms of hydrophobic properties, the 8 samples showed better contact angles, about 148.28^{o}, approaching superhydrophobic properties. It also shows that the optimized columnar surface morphology is more conducive to the improvement of hydrophobicity.

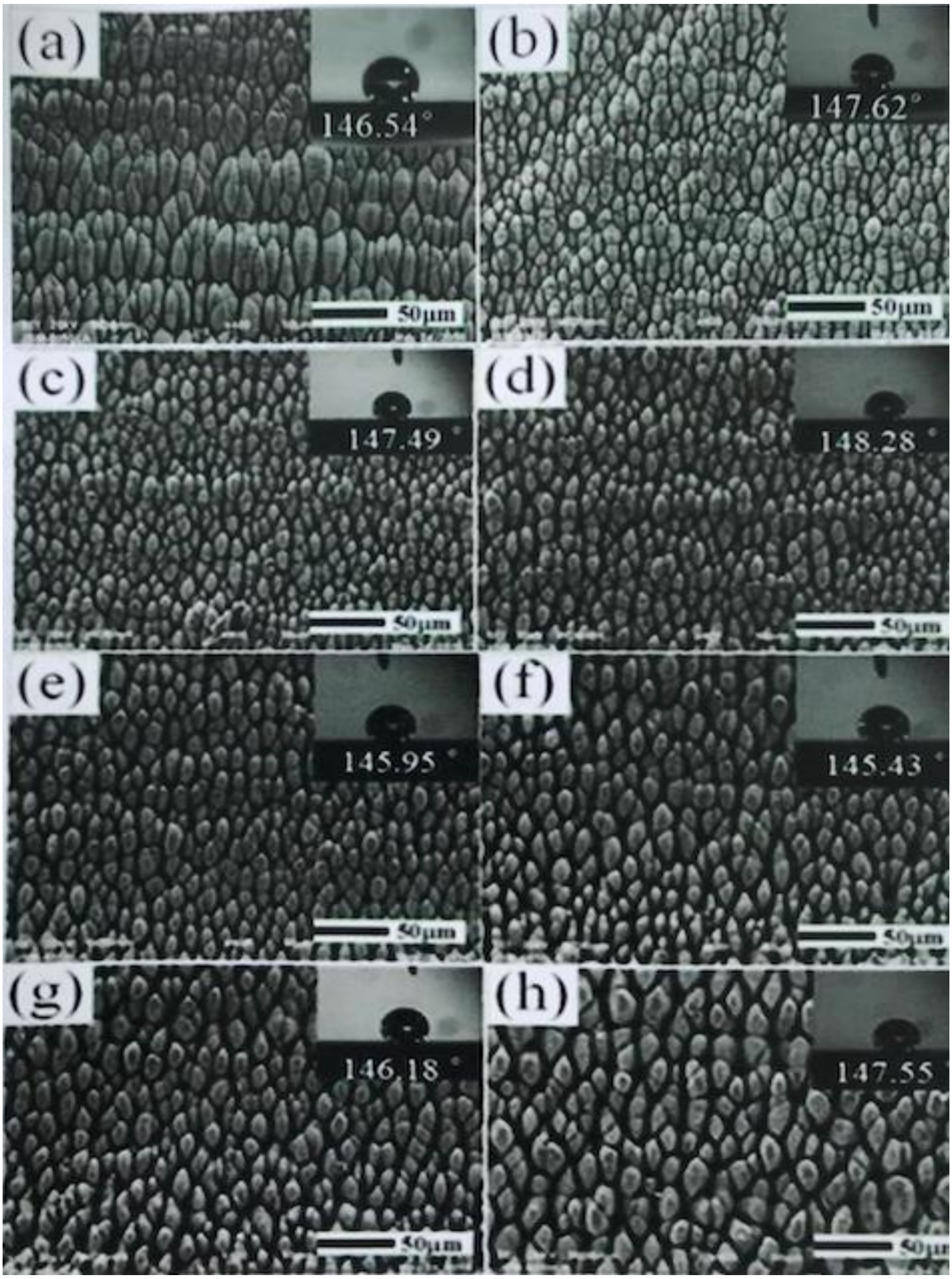

Fig. 3.6 SEM image of micro-nanostructure fabricated by nickel (purity 6N) at different focus positions and their contact angle after silanization at a laser energy of 0.99 mJ, a scan speed of 1 mm/s, and a scan pitch of 0.05 mm.

4. Conclusions

1) Femtosecond laser microstructures were fabricated on nickel surface. The contact angle measurements show that the prepared nickel microstructures have hydrophilic properties. However, the results are different from those reported previously: the hydrophilic properties of the prepared

nickel microstructures did not change to hydrophobic properties when they were placed in air for a long time (7-30 days). The results are useful for the selection of substrate materials for superhydrophobic micro and nanostructures fabricated by femtosecond laser.

2) By silanization the surface of the prepared micro and nanostructures, the hydrophobic function of the surface was obtained, and the contact angle of the columnar micro and nanostructures surface was found to be the best, up to 148.28^{o}. Interpretation of two-scale air interlayer the reason of hydrophobicity formation was discussed.

5. References

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