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Study on Heat Transfer Performance and Anti-Fouling Mechanism of Ternary Ni-W-P Coating

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Featured Application: After a long period of use, the solar collector has to be cleaned due to the serious blocking and efficiency decline. In this work, we prepared ternary Ni-W-P coating to inhibit the fouling deposition. Also, the thermal conductivity of ternary Ni-W-P coating and heat transfer coefficient of composite material were analyzed to make identification of the heat transfer performance of a matrix with and without the ternary Ni-W-P coating after flow fouling experiment. This work can provide a reference for using anti-fouling coating to prolong the life cycle and cleaning period of equipment.

Abstract: Since the formation of fouling reduces heat transfer efficiency and causes energy loss, anti-fouling is desirable and may be achieved by coating. In this work, a nickel-tungsten-phosphorus (Ni-W-P) coating was prepared on the mild steel (1015) substrate using electroless plating by varying sodium tungstate concentration to improve its anti-fouling property. Surface morphology, microstructure, fouling behavior, and heat transfer performance of coatings were further reported. Also, the reaction path, transition state, and energy gradient change of calcite, aragonite, and vaterite were also calculated. During the deposition process, as the W and P elements were solids dissolved in the Ni crystal cell, the content of Ni element was obviously higher than that of the other two elements. Globular morphology was evenly covered on the surface. Consequently, the thermal conductivity of ternary Ni-W-P coating decreases from 8.48 W/m·K to 8.19 W/m·K with the increase of W content. Additionally, it goes up to 8.93 W/m·K with the increase of heat source temperature 343 K. Oxidation products are always accompanied by deposits of calcite-phase CaCO_3 fouling. Due to the low surface energy of Ni-W-P coating, Ca^{2+} and $[\text{CO}_3]^{2-}$ are prone to cross the transition state with a low energy barrier of 0.10 eV, resulting in the more formation of aragonite-phase CaCO_3 fouling on ternary Ni-W-P coating. Nevertheless, because of the interaction of high surface energy and oxidation products on the bare matrix or Ni-W-P coating with superior W content, free Ca^{2+} and $[\text{CO}_3]^{2-}$ can be easy to nucleate into calcite. As time goes on, the heat transfer efficiency of material with Ni-W-P coating is superior to the bare surface.

Keywords: anti-fouling performance; first principle; heat-transfer characteristic; surface modification; thermal conductivity; transient state

1. Introduction

The fouling problem, which is regarded as “the main unresolved problem in heat transfer”, is mainly generated by the deposition of particulates, impurities, salts, and various organic species onto heat transfer surfaces [1–3]. It can be seen from Figure 1 that the fouling of calcium carbonate

and magnesium carbonate accumulate on the tube surface of solar-energy and water-inlet of solar collectors. Due to the corrosion caused by long-term use of water delivery pipes and valves, iron oxides and copper oxides accumulate on the outlet of insulating water tank. Furthermore, the influence of corrosion products on the heat exchanger surface results in further corrosion of metal. After long periods of use in the circumstance of hard water, the solar collector has to be cleaned due to the serious blocking and the reduced efficiency. Fouling inevitably increases the fouling resistance and reduces the heat transfer effectiveness, thus bringing about higher fuel consumption, maintenance costs.

Figure 1. Fouling on the pipes of solar collectors after long periods of use.

Since the 1980s, electroless plating has been treated as an operational technology of the surface modification, attracting widespread attention [4–8]. The results prove that electroless Ni-P-based coating is an advantageous method for fouling inhibition [9–13]. The mass gain method [10,11,14], the calcium ion loss method [12], and the fouling resistance method [15] were commonly used for measuring the deposition process of calcium carbonate fouling on materials surface. The surface is easy to be corroded and the oxidized surface is prone to form a “transition interface”, which works as a “bridge” to connect the matrix and fouling. The “transition interface” consists of corrosion or oxidation, and the lattice of the “transition interface” layer can be easily matched with the lattice of fouling. Therefore, the adhesion of fouling on the corrosion interface seems to be easier [13,16,17]. Simultaneously, compared with uncoated pipe, the tube with electroless coating can significantly improve the property of condensation heat transfer, showing the coexistence of dropwise and filmwise on most working conditions [18,19]. Calcium carbonate is the principal component of fouling in industry. It is easy to adhere to the surface of the heat transfer wall to form fouling, affecting the heat transfer efficiency. The compactness and adhesion strength of fouling on the surface of heat exchange wall depends on its crystal structure [20]. Meanwhile, the evidence demonstrates that the induction period of fouling can be effectively prolonged by the surface free energy of coating. Solubility of calcium carbonate reduces with the up of solution temperature, and the studies prove that the dissolved metal cation can further accelerate the deposition process of fouling [2,21,22]. From the preceding decades, the nucleation of CaCO_3 molecules have been studied theoretically based on molecular dynamics (MD) and density functional theory (DFT). Based on MD, the grain boundary energy was computed to investigate the change of energy in the aggregation process of Ca^{2+} and $[\text{CO}_3]^{2-}$. When the distance of interfaces between CaCO_3 particles came close to colliding, the dielectric constant of

water became small [23]. Jun, Kawano simulated calcium carbonate at high pressure and the phase transition between calcite and aragonite, and results show that in the 300–800 K temperature range, calcite transforms to aragonite at a pressure of around 8 GPa [24]. Additionally, when heated under high pressure, the first-order unsymmetric phase transition of calcite phase occurs first, and then the second-order transition of calcite and aragonite phases happens at a higher temperature [25]. Kazunori Kadota proved that the aggregation of primary particles led to the formation of calcite clusters. Because positive and negative charges attract each other, many particles form clusters in the same direction [26]. Due to the ions, Ca^{2+} and $[\text{CO}_3]^{2-}$ seem to be easily combined. In a real environment, dissolved metal cations in CaCO_3 solution also affect the growth of CaCO_3 , resulting in irregular nucleation during its crystal formation and inadequacy connecting of valence bonds. Thereupon, because of the unsaturation of valence bond, its electrostatic attraction, active centers and surface energy are all large, thus, it has a greater attraction to the surrounding ions. However, the nucleation energy of calcite, aragonite, and vaterite, which is a critical problem of industrial efficiency, remains elusive and is a field of intense research.

Based on this, we specially built a fouling environment. Ca^{2+} , as well as $[\text{CO}_3]^{2-}$, were induced to deposit on the surface of substrate and coating. The object of this project is to study the forming mechanism of calcium carbonate fouling and heat transfer performance on Ni-W-P electroless coating. Comparison between the heat transfer performance of a substrate with and without the Ni-W-P coating after fouling experiment was also investigated. Moreover, we give a theoretical simulation on the reaction path, transition state, and energy gradient change of calcite, aragonite, and vaterite to figure out that why calcite, aragonite, and vaterite deposit on the different surfaces.

2. Experimental Section

2.1. Materials and Preparation

Under the condition of stable heat transfer, the thermal conductivity of the material is measured with the plate method in the thermal conductivity meter. Thus, the sample must be the cylindrical form. At the same time, as the cylinder sample has a constant radial size, the relative error is small compared with the square sample in the fouling solution. So, the cylinder samples were used in this work. Firstly, we produced the substrate specimens with mild steel (Table 1) (diameter is equal to 30 mm, thickness is equal to 5 mm) by wire cutting, and then polished them with 320#, 600#, 800#, 1200# metallographic sandpaper, respectively. After that, the polished specimens, which are firstly stored in alcohol solution, were then ultrasonic cleaned. It is noted that the specimens should be degreased at 348 K (Table 2). The use of degreasing agent is utilized to remove grease on the specimen surface with the method of saponification and emulsification reaction. Polyxyethylene octylphosphonol ether is an anionic surfactant whose charged group is prone to be adsorbed on the surface of metal and solid dust. Thus, impurity and polyxyethylene octylphosphonol ether have the same charge and repels each, leading to the decrease of adhesion. At a higher temperature (above 343 K), polyxyethylene octylphosphonol ether has the excellent effect of degreasing and dewaxing. Before electroless plating preparation, electroless Ni-W-P baths must be adjusted by sodium hydroxide at $\text{pH } 7.8 \pm 0.2$. During the operation of pH adjusting, the bath should be vigorously stirred. When the specimens were put into the bath for preparation, the bath should be kept static and its temperature was maintained at 358 K (Table 3). The plating time goes 2 h in thermostat water bath. When finishing preparation, the specimens were ultrasonic cleaned again.

Table 1. Chemical composition of mild steel.

Name	Composition (Mass%)							
	C	Mn	Si	S	P	Cr	Ni	Fe
Mild Steel	0.16	0.6	0.3	0.05	0.05	0.031	0.012	Bal

Table 2. Formulation of alkali washing and degreasing.

Reagent	NaOH	Na ₂ CO ₃	Na ₃ PO ₄	Polyoxyethylene Octylphenol Ether
Concentration (g/L)	20~30	20~25	35~40	4~6

Table 3. Main components of electroless Ni-W-P plating solution.

Specimen Number	Nickel Sulfate (g/L)	Ammonium Acetate (g/L)	Sodium Citrate (g/L)	Lactic Acid (g/L)	Sodium Hypophosphite (g/L)	Sodium Tungstate (g/L)
1	18	12	35	20	20	25
2	18	12	35	20	20	30
3	18	12	35	20	20	35
4	18	12	35	20	20	40
5	18	12	35	20	20	45

2.2. Fouling Experiments and Heat Transfer Performance

Figure 2 displays the schematic of the flowing fouling experimental rig. The experimental system is primarily composed of a water heating system (red line), a fouling solution system, and a data acquisition system. First of all, the water in the water tank was heated to 343 K by the heating rod, and then was pumped in the inner tube of the heat exchanger through the transmission of the water pump. The flow and temperature of the hot water were adjusted by the two-way regulating valve and the water tank power controller, respectively. When the inlet and outlet water temperatures in the heat exchanger were kept constant, 0.1 g/L CaCl₂ solution and 0.1 g/L NaHCO₃ solution in pear-shaped separating funnel were mixed to 0.1 g/L supersaturated solution through magnetic stirring apparatuses. With the increase of temperature and the change of flow rate, the crystals of calcium carbon in the supersaturated solution precipitate, resulting in the fouling deposition. The use of CaCl₂ and NaHCO₃ can be hydrolyzed into Ca²⁺, Cl⁻, Na⁺, and HCO₃⁻ in fouling solution [27], and then further electrolysis can occur. The dynamic reaction is as follows,

Then, the mixed 0.1 g/L supersaturated solution of fouling is transported to the shell side of the heat exchanger with the function of peristaltic pump (Table 4).

Table 4. Experimental parameters of flow fouling.

Item	Water Temperature/K	Water and Solution Velocity/m·s ⁻¹	Concentration of CaCO ₃ Solution/g·L ⁻¹	Recording Interval/s	Experimental Time/h
Parameter	343	0.15	1.0	120	72

In Figure 3, the experimental heat exchange device is similar to a double-pipe (heat) exchanger. The inner tube of the heat exchanger is connected with the heating circulating water of 343 K, which is to keep the temperature constant in fouling solution system. Meanwhile, the outer tube is filled with the fouling solution and heated by the water temperature of the inner tube. Before the experiment, the specimens of the fouling test are embedded into the foam board and placed in the detachable lids of the measurable anti-fouling heat exchanger. So, the working surfaces of the specimens are parallel to the pipe centerline, which can reduce the effect of obstruction of the specimen surfaces on the water

flow in the pipe and ensure that the specimens do not have galvanic effect with other metal surfaces. At the same time, the screw in the inner tube was used to fix the chip thermocouple in the nearby area of each specimen and the temperature of the fouling solution can be measured continually.

Figure 2. Schematic diagram of flow fouling experimental rig.

Figure 3. Measurable anti-fouling heat exchanger.

To avoid the fouling solution deposited on the inner surfaces of pipeline, reduce errors in the experiment, maintain the heat transfer effect of the inner tube, this heat exchanger is made of stainless steel in this experiment [28].

It should be noted that the trend of fouling deposition, which is on the heat exchanger surfaces formed of different materials, was recorded. When the experiment is done, mass gain method was

adopted to measure the rate of fouling. Besides, the surface morphology of specimens and crystal form were observed. The fouling deposition rate S is defined as

$$S = (m_1 - m_0) / a \quad (6)$$

where m_0 and m_1 are the mass of the specimen before and after flow fouling experiment, g. a is the surface area, m^2 .

After being weighed, the thermal resistance and thermal conductivity of specimens were tested by thermal conductivity meter (DRL-III, Xiangtan instrument Co Ltd., Xiangtan, China) and the changes of coated surface with fouling layer and the bare surface with fouling layer were further analyzed [29,30]. Firstly, the thermal conductivity of bare substrate was tested and the equation was given by Goldstein, R.J. [31].

$$\lambda_1 = \Phi_1 \delta_1 / [A(T_1 - T_2)] \quad (7)$$

where Φ_1 is the heat exchange amount of substrate, W. δ_1 is the thickness of substrate, m. A is the area of heat transfer, m^2 . T_1 and T_2 are the hot side and cool side temperature of substrate, respectively, K.

The thermal conductivity λ_1 of the substrate is measured under the set temperature. As the thickness of ternary Ni-W-P coating is thinner than that of fouling layer and substrate. The steady state method is employed to calculate thermal conductivity of coating. The characterization of thermal physical parameters of micro-scale Ni-W-P coating will be further carried out in our subsequent research. Now, take the thermal conductivity of Ni-W-P coating into the equation

$$\Phi_2 = A(T_1 - T_3) / (\delta_1 / \lambda_1 + \delta_2 / \lambda_2) \quad (8)$$

where Φ_2 is the heat exchange amount of substrate with Ni-W-P coating, W. δ_2 is the thickness of Ni-W-P coating, m. λ_2 is the thermal conductivity of Ni-W-P coating, W/(m·K). T_3 is the cool side temperature of Ni-W-P coating, K.

We can obtain the thermal conductivity of Ni-W-P coating from Equation (8). Then, the change of it with the variety of ambient temperature, as well as differences of W element content at constant temperature can be analyzed. Put λ_1 and λ_2 into the equation

$$\Phi_3 = A(T_1 - T_4) / (\delta_1 / \lambda_1 + \delta_2 / \lambda_2 + \delta_3 / \lambda_3) \quad (9)$$

where Φ_3 is the heat exchange amount of substrate with Ni-W-P coating after flow fouling experiment, W. δ_3 is the thickness of fouling layer, m. λ_3 is the thermal conductivity of fouling layer, W/(m·K). T_4 is the cool side temperature of fouling layer, K. Thus, the fouling resistance can be calculated by

$$R = A \Delta t / \Phi \quad (10)$$

Substantially, the change process of fouling resistance R is further calculated with Equation (10). Compare the changes of fouling resistance of the specimen with or without Ni-W-P coating after fouling, the heat transfer coefficient K [32] can be obtained from

$$K = d / R \quad (11)$$

After that, crystal shape and thermal resistance of fouling layer were analyzed.

2.3. Surface Morphology, Microstructure, and Phase Composition

After the specimens were fouled for a set time, specimens with fouling were taken out. After the process of fouling adhesion, surface morphology of fouled sample and Ni-W-P coating were characterized by means of a scanning electron microscopy (SEM, Model QuantaTM250, FEI, USA). Elementary changes of Ni-W-P coating were analyzed with energy dispersive spectroscopy (EDS,

Model QuantaTM250, FEI, USA). Crystal forms of fouling on the surface of Ni-W-P coating and bare mild steel were studied with the method of X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany). Through the results of scanning electron microscopy and X-ray diffraction on different surfaces, different phase calcium carbonate can be determined.

2.4. First Principle on Transformation of Calcite, Aragonite, and Vaterite

Calcium carbonate is a salt that heat transmits via the vibration of atoms. Atoms in calcium carbonate crystals are bound together by interatomic forces. The interaction force between atoms can be obtained by derivation of atomic potential energy [33].

$$F = -d\phi/dx \quad (12)$$

where dx is the interatomic distance, Å.

While the distance between atoms is far, the nucleus of one atom is attracted by the electrons of the other atom. Whereas, when the atoms are close to each other, the electron orbits of different atoms will overlap. Atoms will always vibrate near their equilibrium positions. The motion of each atom is limited by the potential energy of its neighbors, while the differences of binding energy of the calcite, aragonite, and vaterite crystals in calcium carbonate fouling deposited on the heat transfer surface was seldom reported. Therefore, the interaction force between atoms and the density of states of them were studied respectively in this work.

Material Studio 8.0 software was utilized for the simulation. Firstly, three models of calcite, aragonite, and vaterite were established and the numbers of atoms per cell were all 120. The primary growth surface (0 0 1) was utilized to build super-cell [34]. The geometry optimization in Dmol³ module serves to minimize the energy of super-cell. Also, electronic exchange was disposed with the Perdew-Burke-Ernzerhof (PBE) [35,36] functions of Generalized Gradient Approximation (GGA) when minimizing the energy between electrons. In the Brillouin area, the k-space grid points are chosen with Monkhorst-Pack [37]. This is because the lower the coverage of the surface is, the stronger the interaction between the adsorbed material and the substrate surface is [38]. Linear synchronous transit (LST) and quadratic synchronous transit method (QST) in TS search module is utilized to calculate the intermediate state. Firstly, initial states (calcite, aragonite, vaterite) were established and the geometry optimization in Dmol³ serves the relaxed geometry of them. Then LST/QST method in TS search was used to get the vibrational modes of the TS. Specifically, initial structure started from the low-energy reactants and guided by the tangent of the ST path at the current position. Then the structure marched along the response path (climbing step) hypothesized by LST/QST. The purpose is to make the structure of reactants reach the highest energy point of the hypothetical path (near the secondary region of the real transition state). When a certain criterion is satisfied, the exact transition state was calculated subsequently. When the transition state has only one imaginary frequency, the calculation of the corresponding transition state is completed as it has only one imaginary frequency [39]. Also, its vibration mode should be used to check whether the direction of vibration connects the reactant with the terminal state.

After that, the frequency analysis and calculation of intermediate and transition states are carried out at the same level to verify the correctness and interconnection of them. Furthermore, the reaction path, transition state, and energy gradient change rule of calcite, aragonite, and vaterite are further studied. Transition state structures of calcium carbonate and their analysis will be researched in later articles.

3. Results

3.1. Surface Morphology and Microstructure

As shown in Figure 4a,b, fouling were deposited on the surfaces of the specimens. Compared with the fouling on the surface of the coated specimen, red products on the uncoated specimen were caused

by the corrosion products generated on the bare substrate surface after the flow fouling experiment. Therefore, there are not only calcium carbonate fouling but also iron rust formed on the substrate surface. The result conforms to our previous studies [10,13] and proves that Ni-W-P has an admirable effect on anti-fouling performance. After calculating the mass change of the fouled specimens, it was found that there is no obvious rule between the mass change and the W content in the coating, while the certainty is that the mass gain of fouling on all the coated specimen is less than that of the bare substrate surface in the same period. Due to the difference of fouling adhesion, the deposit growth rate is the most significant parameter during the process [40], the thickness of fouling layer changes. As a result, the thermal resistance of the fouling layer also increases notably. In other words, the heat transfer coefficient of the untreated material has been affected partly due to the existence of Ni-W-P coating. As shown in Figure 4, the result reveals that the fouling on the surface of the specimen did not change significantly with the increase of W content. Because of the scouring effect of water flow and the influence of Van der Waals force in the molecules, the deposited fouling could fall off on the surface of the specimens and the mass change shows irregularly. Thus, the phenomenon of mass gain of fouling is inconsistent with our previous study in static fouled solution [10,16]. Whereas, it is certain that the existence of Ni-W-P coating, the surface tension decreases, which makes it more difficult for fouling to adhere and the deposition of fouling has been inhibited.

Figure 4. Mass change of coated specimens after 72 h fouling (a) macro appearance of specimen with Ni-W-P coating after flow fouling; (b) macro appearance of bare specimen after flow fouling.

To study the thickness and structure of the fouling deposited on the coated surface, scanning electron microscopy with energy dispersive spectroscopy was employed to test the structure of the deposited Ni-W-P coating. In Figure 5a, we can obviously observe that the surface of Ni-W-P coating is well-organized with cell body lines. The appearance of the globular morphology, which is in the form of the salient of the cell body, can be explained as the uneven deposition of P element. Without P element, Ni would grow orderly in accordance with the structure of face-centered cubic. The P element can densify the cell body of the coating and co-deposit the Ni on the substrate surface. During this process, P atoms will hold the positions of several Ni atoms, thus forming Ni-P supersaturated solid solution. When it increases to a certain stage, the Ni-W-P coating cannot array orderly in accordance with the structure of crystal Ni. Consequently, the Ni-W-P coating shows an amorphous structure, which can be proved by the XRD result.

Figure 5. (a) Surface morphology of specimen 1 after electroless plating; (b) Surface morphology of nickel accumulation; (c) Cross-sectional morphology of nickel accumulation; (d) Back scattered-electron cross-sectional image of Ni-W-P coating of specimen 1; (e) Scattered-electron cross-sectional image of Ni-W-P coating of specimen 1.

As can be seen in Figure 5b,c, the color of the tissue changes distinctly. It turns out that the globular morphology is filled with Ni[W,P] structure. The thickness of globular morphology is larger than that of the coating in Figure 5c. The possible explanation for this is the local inhomogeneity of the bare substrate surface that leads the excessive deposition of Ni[W,P] in the hole. Meanwhile, we cut the cross sections of several areas in order to calculate the heat transfer behavior of Ni-W-P coating. It was found that the thickness distribution of Ni-W-P coating after 2 h plating is $20\ \mu\text{m} \pm 2\ \mu\text{m}$. According to the Figure 6, there are apparent peaks of Ni, W, and P at the cross section. As the W and P elements were solid dissolved in the Ni crystal cell, the content of Ni element is obviously higher than that of the other two elements. Here, we calculate the heat transfer of the Ni-W-P coating uniformly without local distinction.

As shown in Figure 7, SEM tests were performed on specimens after 72 h of fouling. Figure 7a,b exhibit the surface morphology of the uncoated mild steel. It is notable that there are a large number of fouling deposits on the surface in the form of massive and columnar particles, as well as agglomerates. Columnar fouling is also surrounded by loose-cotton-flocculent fouling. Based on the previous results, uncoated mild steel is primary composed of massive calcite and columnar aragonite, while calcite-phase CaCO_3 fouling takes up a high proportion. A considerable amount of fouling indicates that the induction stage of the fouling deposition process on the bare substrate was ended and the heat transfer of the specimen surface could be severely affected by the rapid growth of calcite-phase and aragonite-phase fouling. The deposited products on the surface of Figure 7c are principal acicular aragonite mixed with a small amount of massive calcite and oxide [41,42]. The grain sizes of aragonite were estimated to be significantly smaller than calcite grains [43]. In the vicinity of calcite-phase CaCO_3 fouling (Figure 7e), oxidation products also deposit nearby. However, no oxidation products were found near the aragonite-phase CaCO_3 fouling (Figure 7d). At the same time, we also carried out a typical observation at the edge of the specimens. It can be found that the edge of the specimen is covered by the calcite and oxide. No aragonite deposited on their margins. On the one hand, the fouling solution will periodically form the double-line vortices arranged regularly in opposite rotation

direction when passing through the edge of the specimens. The formation of Kármán vortex street after the non-linear effect, leading to the increase of the pressure of fouling deposition on the edge of the specimen, as well as the difference of nucleation energy of the fouling lattice [44]. On the other hand, when the vortex appears, the fluid will produce a periodic alternating transverse force on the edge of specimens. The natural frequencies of similar phase of CaCO_3 fouling nuclei keep close to each other, leading to resonance of the crystal nucleus and then the selective deposition of the corresponding phase fouling, as well as the nucleus growth. Further study on nucleation energy barriers and bonding changes of different crystal-phase CaCO_3 fouling will be reported in Section 3.3 See Figure 8, the XRD patterns of fouling of coating and bare substrate show different. There is an amorphous peak due to the penetration of X-ray in thin fouling layer, which is according with the results of Figure 8. It also can be noticed that there are both diffraction peaks of calcium carbonate and amorphous peaks of Ni-W-P coating showing on the coated sample. However, as the fouling layer on the surface of the bare substrate is relatively thick, the X-ray is reflected when it reaches the surface of the fouling layer. Compared with the sole crystal form of CaCO_3 on the bare surface, it indicates that more aragonite deposit on the surface of ternary Ni-W-P coating.

Figure 6. (a,b) Energy dispersive spectroscopy results of Figure 5e.

Figure 7. Surface morphology of the specimen after being fouled (a,b) uncoated specimen (c–f) specimen 1.

Figure 8. X-ray diffraction pattern of the fouling on specimen surfaces.

3.2. Heat Transfer Behavior

Figure 9a shows the test data obtained from the flow fouling experiment. Water heating tank is used for the heating of flowing water. CaCO_3 solution is heated after until temperature range of fouling deposition is 328 ± 1 K through the heat transfer of the wall of the inner tube in the measurable anti-fouling heat exchanger temperature. Logarithmic mean temperature difference (LMTD) of measurable anti-fouling heat exchanger is calculated according to the Equation [2].

$$\Delta t_m = (\Delta t_{\max} - \Delta t_{\min}) / \ln(\Delta t_{\max} / \Delta t_{\min}) \quad (13)$$

where $\Delta t_{\max}$ and $\Delta t_{\min}$ represent the maximum and minimum temperature difference of the inlet and outlet in the process of re-fluent heat transfer, K. Equation (14) is then used for determining the heat load of CaCO_3 solution and heated water.

$$\Phi_4 = q_{m1}c_1(t'_1 - t''_1) = q_{m2}c_2(t'_2 - t''_2) \quad (14)$$

where q_{m1} and q_{m2} are mass flow rate of water and CaCO_3 solution, respectively, kg/h. c_1 and c_2 are specific heat capacity of water and CaCO_3 solution, respectively, J/(kg·K). t'_1 and t''_1 are the hot side and cool side temperature of water, respectively, K. t'_2 and t''_2 are the hot side and cool side temperature of water, respectively, K.

Figure 9. (a) Test data of experimental rig; (b) Heat transfer of measurable anti-fouling heat exchanger.

After that, the heat transfers coefficient of the measurable anti-fouling heat exchanger can be calculated by

$$k = \Phi_4 / A' \Delta t_m \quad (15)$$

where A' is the heat transfer area of inner tube of measurable anti-fouling heat exchanger, m².

Figure 9b displays the heat transfers coefficient change of the measurable anti-fouling heat exchanger. It can be known that the heat transfer coefficient of the designed heat exchanger is stable at about 2500 W/m²·K after 1 h.

The worst problem caused by fouling and oxide deposition is the terrible effect on the heat transfer performance of the material surface. In Figure 7, the uncoated specimen has obvious fouling deposition. Besides, thermal resistance of the Ni-W-P coating itself has contributed to the decrease of the overall heat transfer coefficient of the coated material. Therefore, we specially compare and analyze the heat transfer coefficients of different specimens after fouling at the same time. Meanwhile, the thermal conductivity of ternary Ni-W-P coating was measured to determine the process of thermal conductivity changing with W content, which is utilized to ascertain the optimum coating parameters.

Figure 10a shows the heat transfer coefficient curves of ternary Ni-W-P coatings with different W contents. Notwithstanding the W content has changed, there is un-conspicuous law of corresponding

heat transfer coefficient. Whereas, the decreasing rate of heat transfer efficiency of the specimen coated with ternary Ni-W-P coating has decreased significantly after 72 h, which proves that the heat transfer performance is better than that of the uncoated mild steel. Although there is still some fouling deposited on the surface of ternary Ni-W-P coating, the thickness of ternary Ni-W-P coating is merely 20 μm . Compared with the influence of fouling layer, the effect of the coating thickness on the heat transfer of coating can be ignored. As shown in Figure 10a, we can easily know that the heat transfer efficiency of specimen 5 increases with the up of the temperature of the heating source. The up of temperature can improve the heat transfer efficiency of coating while it can also accelerate the deposition rate of CaCO_3 fouling, resulting in the further increase of fouling layer thickness. However, the temperature of the heat source should not be reduced unilaterally just in terms of deposition of CaCO_3 fouling. How to effectively balance the needs of the economy and efficiency should be in conformity with the actual heat transfer conditions of industrial requirements.

Figure 10. (a) Heat transfer coefficient of specimens after being fouled; (b) Thermal conductivity of specimens varied with the temperature; (c) Thermal conductivity of specimens varied with tungsten content.

To avoid the measurement deviation of heat transfer coefficient caused by uneven local fouling deposition, we multi-measured the heat transfer coefficient of the specimen coated with ternary Ni-W-P coating before flow fouling experiment. As shown in Figure 10b, it is noticeable that the thermal conductivity of the specimen coated with ternary Ni-W-P coating decreases from 8.48 W/m·K to 8.19 W/m·K with the up of W content. Specifically, excessive W element deposited on the surface of the substrate with the concentration of sodium tungstate in the plating solution increases, leading to more W element solid dissolved in amorphous Ni unit cell. The phonon vibration was suppressed and the average kinetic energy of heat transport of electrons as hot carriers decreased during thermal conduction simultaneously [32,45,46]. The heat transfer process of the coated specimen thus is inhibited as well. In Figure 10c, the thermal conductivity of the coating increases from 8.38 W/m·K to 8.93 W/m·K with the up of the heat source temperature, which is also consistent with the heat transport mechanism [31,32]. With the increase of temperature, the average velocity of thermal carriers in amorphous Ni[W,P] solid solution increases accordingly. Since the collision process of energy exchange between thermal carriers is more intense and frequent, the heat transfer rate is accelerated and the thermal conductivity of the coating mounts. During this process, the thermal resistance of the un-fouled specimen with ternary Ni-W-P coating decreases from 191,500 Km^2/W to 179,800 Km^2/W . This is compatible with the conclusion we analyzed before in Figure 10a.

3.3. Transient States of Calcite, Aragonite, and Vaterite

In order to explore the nucleation selectivity of CaCO_3 fouling on the different surface of specimens, three different-crystal forms of CaCO_3 (calcite, aragonite, and vaterite) were investigated. As shown in Figure 11a, the plane triangle of $[\text{CO}_3]$ is perpendicular to the threefold axis and arranged as layer-structure. The direction of $[\text{CO}_3]$ triangle in the identical layer is the same while the direction of them in the adjacent layer is the opposite. Ca, distributed alternately with $[\text{CO}_3]$, perpendicular to

the threefold axis is also arranged as layer-structure and in the form of cubic closest packing (CCP). Its coordination number is 6 and the Ca constitute $[\text{CaO}_6]$ octahedral with 8 $[\text{CO}_3]$. The structure of aragonite is isomorphic with calcite. Ca in aragonite is organized in the structure of hexagonal closest packing (HCP) (Figure 11b). Ca, as well as $[\text{CO}_3]$ triangles, are well arranged in layer-structure parallel to the aragonite (001). Both of them are arranged alternately along the c axis and $[\text{CO}_3]$ layers [47]. There are six $[\text{CO}_3]$ around each Ca and 9 angular top oxides of them are connected to the Ca, forming the nine-fold coordination. In Figure 11c, a hexagonal lattice $[\text{CO}_3]$ groups formed by Ca is distributed along the hexagonal axis. The number of coordination per cell is at least 12 [48].

Figure 11d1 shows the PDOS of calcite. It can be viewed that the peaks of 3p orbit of calcite are at -19 , -18 , -8 eV and the peaks of 4s orbit is at -38 eV. On the bonding of Ca- $[\text{CO}_3]$, 3p orbit of Ca and the 2s orbit of O have obvious resonance at -18 eV. Additionally, resonances are established by the 2p orbit of C and the 3p orbit of Ca at -18 eV, indicating that they are likewise bonded. Comparing with the PDOS in Figure 11d1,d2, we can find that the orbit peaks of the two phases are virtually similar, which manifest that the bond strength and type of them are near-identical [49]. In Figure 11d2, the resonance peaks of the 2s orbit of O and the 3p orbit of Ca at -18 eV are sharper than that of the calcite. This is because the difference of the coordination number of Ca with $[\text{CO}_3]$ in the two different-crystal structures. Their coordination number is 6 and 9, respectively. From the PDOS of vaterite in Figure 11d3, it is clearly observed that the resonance region shifts to the negative direction obviously and 2s orbit of C resonates with the 4s orbit of Ca at -42 eV. Meantime, 2p orbit of C contributes to 3p orbit of Ca at -24 and -22 eV, which proves that Ca have a stronger effect on C in the vaterite phase structure and leads to multi-orbit bonding of Ca- $[\text{CO}_3]$. Antibonding orbits in vaterite move to the negative direction as a whole compared with calcite and aragonite, showing that the bonding effect in vaterite decreases.

Figure 11. Cont.

Figure 11. Structure of three crystal calcium carbonate (a1–3) calcite; (b1–3) aragonite; (c1–2) vaterite; (d1–3) density of state of calcite, aragonite, and vaterite.

The geometry optimization in Dmol³ module was used to minimize the energy of super-cell. Meantime, electronic exchange was disposed with the Perdew-Burke-Ernzerhof (PBE) [35,36] function of Generalized Gradient Approximation (GGA) when minimizing the energy. The total energy of different-crystal nucleation of Ca²⁺ and [CO₃]^{2−} was computed in Table 5. As shown in Figure 12b, it displays an energetic profile for potential energy surface of calcite, vaterite, and aragonite by relative energy *E*. The energy of nucleation of calcite, aragonite, and vaterite formed by the Ca²⁺ and [CO₃]^{2−} decreases. The corresponding decreased energy of a single molecule are 2.13 eV, 2.68 eV, and 2.43 eV, respectively. The energy barriers of the transition state TS1a, TS1b, and TS1c between free-state ions and their crystal phase are 0.66, 0.18, and 0.10 eV, respectively. During the banding process, the distance between Ca²⁺ and [CO₃]^{2−} reduces. In addition, it is found that Ca²⁺ attacked [CO₃]^{2−} and formed the multi-intermediate under different attacking sites when computing the TS1a. Similarly, the calculations of the transition state for the intermediate of vaterite and aragonite show multi-intermediates. The frequency analysis and calculation of the reaction intermediates, as well as transition states were conducted to optimize structures. After the consequence shows only one imaginary frequency, the only one structure in the transition state of TS1a, TS1b, TS1c, TS2, TS3, and TS4 were ascertained authentically and accurately. Meanwhile, during the process of crystal transition of calcite, aragonite, and vaterite, the crystal type of CaCO₃ will also change due to different pressure and temperature [50–54]. According to Figure 12b, it is a need to cross the corresponding energy barrier in the process of mutual transformation under the experimental conditions (328.15 K, 0.1 MPa). Additionally, the relative stretch length of the intermediate of Ca²⁺ and [CO₃]^{2−} is 0.220 Å, 0.027 Å, and 0.095 Å, respectively. In the previous research, the ternary Ni-W-P coating has the lower surface free energy based on the experimental results of contact angle Figure 12a [9,10,16]. With the decrease of W content, the surface free energy of Ni-W-P coating was also lower. Take the consequence of Figure 12b into consideration, as the free Ca²⁺ and [CO₃]^{2−} are easy to transfer to the transition state TS1c with low energy barrier on the surface of Ni-W-P coatings with low surface energy, CaCO₃ is prone to nucleate into structure of aragonite-phase [55,56]. Besides, because of the influence of high surface free energy on the surface of bare substrate and Ni-W-P coating with high W content, Ca²⁺ and [CO₃]^{2−} in free state can cross high energy barrier and form calcite-phase CaCO₃.

fouling [43], which is consistent with our previous mesoscopic results of the fouling crystal types on the surface of Ni-W-P coating. Refer to Figure 11, we can know that the crystal configuration of both calcite-phase and aragonite-phase is more stable than that of vaterite. In this case, vaterite belongs to the structure of unsteady state [43]. Thereupon, the vaterite transformed to calcite and aragonite can be regarded as the process of transforming the stable phase or the metastable phase to the unsteady state [48] and vaterite undoubtedly is the dissipative structure. The thermodynamic performance of vaterite is unstable [49], and it will be transformed into a more stable structure of aragonite or calcite phase in the subsequent reaction.

Table 5. Energy and frequency of reaction of Ca^{2+} and $[\text{CO}_3]^{2-}$.

Species	Energy (eV)	Vibrational Frequency (cm^{-1})
Ion state	−22.05315	−
Calcite	−23.79033	−
Vaterite	−24.09105	−
Aragonite	−24.34573	−
TS1a	−21.38945	1425.5
TS1b	−21.86688	1405.0
TS1c	−21.94878	1412.9
TS2	−23.69758	1411.9
TS3	−23.71231	1487.0
TS4	−23.77383	1474.2

Figure 12. (a) Contact angle and surface energy of uncoated specimen and the Ni-W-P coatings; (b) Energetic profile for potential energy surface of calcite, vaterite, and aragonite.

4. Discussion

Via the aforementioned studies, we evidenced that the deposition of CaCO_3 fouling can be effectively inhibited by ternary Ni-W-P coating after fouling in a certain period of time. This can reduce the decreasing rate of the heat transfer efficiency of the substrate surface caused by fouling. Because of the different energy barriers of transition state during the nucleation process of different lattice types of CaCO_3 fouling, the nucleation process on surface with different free energy was induced distinguishingly [54,55], resulting in different types of calcite-phase, aragonite-phase, and vaterite-phase CaCO_3 fouling deposited on surfaces. Moreover, the changes in the thermal conductivity of ternary Ni-W-P coating were principally caused by the difference of the hot carriers of the different phase structure in the energy transfer process.

Although ternary Ni-W-P coating can obviously inhibit the deposition process of CaCO_3 fouling and oxide, it should also be conditional in its application because of the thermal resistance of ternary Ni-W-P coating itself. Fortunately, we found that after 72 h of depositing in high concentration supersaturated fouling solution, the thermal resistance of the coating has been offset by the influence of a thicker fouling layer. Nevertheless, the Ni-W-P coating with low W content should be used as the anti-fouling interface firstly in the field of industrial heat. One reason is that it can ensure a good heat transfer efficiency. The other reason is that it can more effectively inhibit the excessive deposition of hard-to-remove calcite-phase CaCO_3 fouling on the surface.

5. Conclusions

In this work, specimens with Ni-W-P coating were prepared for the purpose of flow anti-fouling. Consequently, the oxidation products are always accompanied by deposits of calcite-phase CaCO_3 fouling. Due to the low surface energy of ternary Ni-W-P coating, Ca^{2+} and $[\text{CO}_3]^{2-}$ are prone to cross the transition state with a low energy barrier, resulting in the more formation of aragonite-phase CaCO_3 fouling on ternary Ni-W-P coating. Nevertheless, because of the interaction of high surface energy and oxidation products on the bare substrate or Ni-W-P coating with superior W content, free Ca^{2+} and $[\text{CO}_3]^{2-}$ can climb over TS1a of high energy barrier and eventually nucleate into calcite. The thermal conductivity of ternary Ni-W-P coating decreases with the increase of W content. Additionally, it goes up with the increase of heat source temperature. As time goes on, the heat transfer efficiency of coated surface after fouling is superior to the bare substrate with fouling layer.

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Abbreviations

DFT	Density Functional Theory
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
LMTD	Logarithmic Mean Temperature Difference
CCP	Cubic Closest Packing
HCP	Hexagonal Closest Packing
GGA	Generalized Gradient Approximation
PBE	Perdew-Burke-Ernzerhof Function
LST	Linear Synchronous Transit

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