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ARTICLE

Effect of Substrate Surface Morphology on Thermal Spraying and Bonding Strength of Ni/Fe via Atomistic Simulation

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Abstract: The molecular dynamics method was applied to simulate the effects of substrate surface morphology on nano-thermal spraying. The effects of columnar rough surface and smooth surface on cluster flattening, defect evolution of substrate, stress distribution, and the bonding strength between coating and substrate were investigated. The results show that the substrate surface morphology has a significant effect on the bonding strength of thermal spraying. The rough surface increases the actual contact area between the clusters and the matrix, improves the adhesion, causes the anchorage effect at the interface, and thereby enhances the bonding strength. In addition, the substrate surface morphology can change the stress distribution in the interface region. The columnar rough surface on the matrix weakens the stress concentration effect, decreases the critical stress, and reduces the damage to the substrate. Besides, the rough surface hinders the cluster slip and reduces the flattening ratio.

Key words: thermal spraying; rough surface; vacancy; bonding strength; molecular dynamics

With the improvement of thermal spraying technique, the surface strengthening and repair are widely used, and the demand of thermal spraying technique under complex working conditions is gradually increased, therefore requiring further enhanced bonding strength of thermal spraying.

In recent years, the bonding mechanism and bonding strength between the thermal spraying coating and the substrate attract much attention. Wang et al[1] found that two different types of microstructures can be formed when high temperature nano-Cu particles are sprayed on Cu substrate at room temperature. Jian et al[2] used numerical simulation to study the influence of droplets on solid substrates, observed two different splash mechanisms, and presented a phase diagram of droplet impact with gas viscosity and density. Chun et al[3] found that the bonding mechanism of cold spraying deposition of metal particles is the adiabatic shear instability caused by plastic deformation near the interface between metal particles and substrate at melting temperature. Meanwhile, Joshi et al[4] concluded that the bonding mechanism in the spraying process is attributed to adiabatic softening, adiabatic shear instability, and uniform coating caused by interfacial spraying of granular materials. However, Hassani-Gangaraj et al[5] proposed that when metal particles impact the substrate at a sufficiently high velocity, the interaction of strong pressure waves with the free surface at the particle edge can produce hydrodynamic plasticity to affect the bonding without the shear instability. Oyinbo et al[6] studied the interfacial deformation behavior and interatomic bonding mechanism of Pd-Cu composite metal film using molecular dynamics method and found that during the process of cold gas dynamic spraying, the Pd-Cu interface has asymmetry deformation. The higher bonding energy and higher interfacial shear strength at the interface of Pd-Cu composite metal film both reflect the improved bonding

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strength and compatibility between Pd and Cu.

The surface pretreatment of the substrate has an important effect on the bonding strength, including the purification and roughening. Purification can remove the oxides and impurities on the substrate surface. Roughening can roughen the purified surface and increase the bonding area to improve the mechanical bonding strength between the clusters and the substrate surface[7,8]. Currently, the effect of substrate surface coarsening on the bonding strength of heterogeneous interface between coating and substrate has been studied. Liu et al[9] studied the substrate surface from the aspect of in-situ element diffusion and post-remelting treatment, and concluded that the coarsening substrate surface can enhance the mechanical bonding strength. In addition, the rough surface morphology can increase the wetting degree between the droplet and the substrate surface and thereby reduce the interface crack and thermal stress. The main method of surface roughening is mechanical micro-engraving. Bobzin et al[10] processed a dovetail structure on the surface of AlSi substrate by polycrystalline diamond tool, and then deposited the coating with carbon of high content and low-alloy steel by thermal spraying. Compared with that of the coating treated by sandblasting, the bonding strength of the coating with dovetail structure is increased by 45%. In addition, Tahir et al[11] established a finite element model between surface roughness and bonding strength and studied the influence of surface roughness on bonding strength of WC-Co coating, providing a theoretical basis for optimizing the bonding parameters.

Chen et al[12] used molecular dynamics to study the micro-jet process of metal surface containing grooved defects under impact load, and the results showed that the velocity of micro-jet body is increased and the number of particles is decreased with increasing the grooved half angle, and the jet causes the grooved defects. Hong et al[13] studied the surface roughness and the films by molecular dynamics method, and calculated the atomic horizontal stress before and after annealing process. The results show that the annealing process reduces the number of vacancies and holes of films, and the interfacial mixing of annealed films is better than that of deposited films. Feng et al[14] studied the influence of process parameters on thermal spraying by molecular dynamics method and found that the process parameters have a great influence on the bonding strength between the coating and substrate and on the cluster flattening. Zhang et al[15] studied the deposition of prefabricated columnar structure through molecular dynamics and found that the deformation behavior of the deposition template has a great influence on the morphology of the columnar structure. In addition, Oyinbo et al[16] studied the influence of surface configuration on multiple-impact plastic deformation of composite metal film during complex process and found that the surface morphology of substrate material has an important influence on the deposition and deformation process of spray clusters.

However, the continuum mechanics model cannot explain the spraying mechanism at microscopic scale. In order to explain the bonding mechanism and ameliorate the finite element analysis methods, the molecular dynamics method was used to study the influence of substrate surface morphology on atomic diffusion during thermal spraying, analyze the coarse columnar surface and plane matrix, and investigate the surface cluster flattening, the substrate atomic lattice transformation, the stress distribution, and the bond strength in this research.

1 Model Establishment

Fig. 1 shows the thermal spraying simulation calculation model, which is composed of Ni cluster and Fe substrate with the lattice constant of 0.352 and 0.285 nm, respectively. The substrate is divided into three parts: fixed layer, thermal layer, and Newtonian layer. In order to avoid the size effect, the periodic boundary conditions are applied along x and y directions, and non-periodic boundary conditions are applied along z direction. The size of smooth surface substrate is the same as that of columnar rough substrate, and the simulation parameters are shown in Table 1. In this research, the prefabricated columnar rough surface and the ideal plane surface were compared and analyzed. Roughness R could be expressed as the area ratio of rough surface to smooth surface. The relationship between roughness factor r and structural parameters of rough surface of square-column substrate is as follows[17]:

$$r=\frac{(b+c)l+4ah[l/(b+c)]}{(b+c)l}=1+\frac{4bh}{(b+c)^2} \quad (1)$$

where b, l, and h represent the length, width, and height of the square column on substrate surface, respectively; c represents the spacing between adjacent square columns (Fig.1).

In the simulation process, the interaction between atoms is

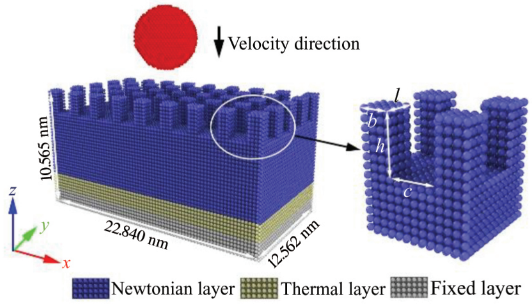

Fig.1 Thermal spray simulation calculation model

Table 1 Thermal spray simulation parameters

Parameter	Value
Ni cluster size/nm	5.28
Columnar Fe substrate size	22.840 nm×12.562 nm×10.565 nm
Smooth Fe substrate size	22.840 nm×12.562 nm×10.565 nm
Temperature of Ni clusters/K	1800
Temperature of Fe substrate/K	293
Spraying speed/m·s^{-1}	2000
Spray angle/(°)	90
Potential	Embedded atom model
Time step/fs	1

usually described by the empirical potential function which determines the accuracy of molecular dynamics simulation. In this research, the embedded atom model potential was used for calculation of the interatomic interaction potential of the Ni-Fe system[18], and the total energy E of the atoms could be expressed as follows:

$$E = \sum_{i} F_i(\rho_i) + \frac{1}{2} \sum_{i,j(i \neq j)} \varphi_{ij}(r_{ij}) \tag{2}$$

where $\sum_{i} F_i(\rho_i)$ represents the total energy of the entire system; φ_{ij} is the pair potential between atoms i and j; r_{ij} is the distance between atoms i and j; F_i is the electron cloud density embedded energy function between atoms; ρ_i is the extranuclear electron density of other atoms (in addition to atom i) in the case of the i-atom-combined electron clouds.

In this research, the large-scale atomic/molecular massively parallel simulator (LAMMPS) software was used for simulation, and open visualization tool (OVITO)[19] software was used to achieve the visualization. ORIGIN software was used to analyze and process the simulation results.

2 Results and Discussion

2.1 Effect of surface morphology on crystal structure transition

During the thermal spraying, the clusters impact the substrate at a high speed, which leads to the distortion and defects of the normal atoms in the substrate. In this research, the influence of substrate surface during thermal spraying on the lattice structure transformation of the substrate was analyzed by the number of atoms in close-packed hexagonal (hcp) structure. Fig. 2 shows the number of atoms in hcp structures of substrates with smooth surface and rough surface. The number of atoms in hcp structure of the smooth surface increases sharply during the thermal spraying process, and it gradually decreases to zero after the thermal spraying due to the elastic recovery of the substrate and the interatomic lattice reconstruction. In contrast, the number of hcp atoms of the substrate with the columnar rough surface barely changes during the thermal spraying process, because the protruding parts of the columnar rough surface prevent the cluster impact to a certain extent and absorb some of the kinetic energy, thereby reducing the impact force on the substrate. Less defective atoms are generated in the thermal spraying process, and only a small number of atoms participate in the transformation in the substrate lattice recovery process.

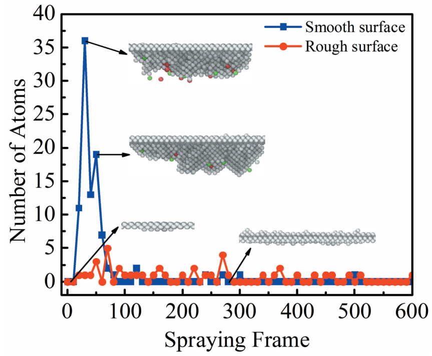

Fig.2 Number of atoms in hcp structure of substrates with different surfaces during thermal spraying

2.2 Effect of surface morphology on cluster flattening ratio

Cluster flattening ratio is widely used to describe the deformability of clusters in the spraying process, including the transverse flattening ratio (L/D) and longitudinal flattening ratio (H/D), which are the ratio of the maximum diameter of the cluster after spraying to the original diameter of the cluster and the ratio of the maximum height of the cluster after spraying to the original diameter of the cluster, respectively. During the thermal spraying, the surface morphology of the substrate can influence the cluster flattening. Fig.3 shows the cluster flattening ratios of substrates with different surfaces. It can be seen that both the surfaces have little influence on cluster flattening ratio during thermal spraying. The L/D value of the smooth surface is larger than that of the columnar rough surface, because the columnar rough interface hinders the flow of cluster atoms and reduces the spreading area after the cluster contacts with the substrate. The H/D value of the rough surface is smaller than that of the smooth surface, because the rough surface still acts as a buffer. Therefore, the cluster atoms have a larger influence on the substrate with a smooth surface, and the rough surface results in a small longitudinal flattening and a slightly better flattening effect. The larger the cluster flattening ratio, the denser the coating and the better the coating quality.

2.3 Thermal spraying stress distribution on different surfaces

The residual stresses can be divided into three categories according to the self-equilibrium range, namely the microscopic residual stress within the grain, the microscopic residual stress varying with the scale of a single grain, and the macro residual stress. The interaction between the substrate surfaces and clusters during the thermal spraying results in the change of interatomic stress, therefore affecting the thermal spraying effect and the substrate properties. The equivalent stresses between atoms in a simulated system were calculated by the virial stresses, i. e., by measuring the mechanical stresses at the atomic scale. The von Mises stress[20] was calculated for each atom i, which indicates the asymmetric

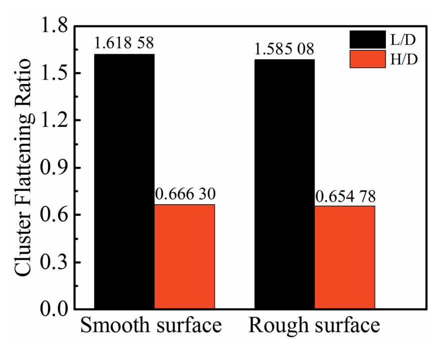

Fig.3 Cluster flattening ratios of substrates with different surfaces

local deformation, as follows:

$$\sigma_i^{\text{Mises}} = \sqrt{\sigma_{xy}^2 + \sigma_{xz}^2 + \sigma_{zy}^2 + \frac{(\sigma_{xx}^2 - \sigma_{yy}^2) + (\sigma_{xx}^2 - \sigma_{zz}^2) + (\sigma_{yy}^2 - \sigma_{zz}^2)}{6}} \quad (3)$$

where σ_{xy}, σ_{xz}, and σ_{zy} are the shear stress; σ_{xx}, σ_{yy} , and σ_{zz} are the normal stress.

The equivalent stress distribution on the substrates with columnar rough surface and the smooth surface during the spraying process is shown in Fig. 4. The substrate is sliced along the *y* axis and the stress distribution in the thermal spraying process can be observed along the *xz* plane. As shown in Fig. 4, a high stress concentration exists at the coating interface due to the plastic deformation on the substrate surface caused by the high spraying speed and pressure.

Therefore, the interface area is subjected to complex high stress. The clusters contact with the smooth interface at a single point, while they contact with the columnar rough surface with several convex parts which disperse the impact force of the clusters on the substrate. With further embedding the clusters, a higher local stress occurs on the substrate subsurface, which causes the plastic deformation on the substrate surface. When the cluster reaches the maximum impact state, the distribution of compressive stress on the substrate with smooth surface is significantly wider than that on the substrate with columnar rough surface, i. e., the distribution locates in the deeper position. After spraying and relaxation, the equivalent residual stress of the substrate with rough surface is higher, because the columnar rough surface can disperse the impact force and reduce the damage to the substrate. Thus, the equivalent residual stress of the substrate is larger.

2.4 Effect of surface morphology on bonding strength and mechanism

The bonding strength is an important index to evaluate the thermal spraying effect, which directly affects the service safety and service life of equipment components. The bonding strength mainly depends on the interface bonding force which refers to the force required for peeling off the coating from the substrate per unit area[21]. Currently, the tensile method, scratch method, and bending method are widely used to determine the bonding force[22]. Agrawal et al[23] proposed a tensile method based on the shear lag model for fiber-reinforced composites. Normal loads are applied to the bonding interface. When the load increases to a critical value, the coating and substrate will fracture. The instantaneous load at fracture is used as a reference for the bonding force. Because the tensile method is easy to operate and suitable for thermal spraying materials, it was used in this research for bonding force measurement. Fig. 5 shows the schematic diagram of bonding strength measurement and atomic scale model of Ni/Fe metal after thermal spraying with interface effect.

The combined part of the cluster and substrate after spraying was extracted and stretched under the load. The simulated temperature was 293 K and the strain rate was 10^{10} s^{-1}. Fig. 6a shows the tensile morphology of the interface model in thermal spraying under different strains until fracture. Fig. 6b shows the atomic positions under different strains, and correlation analysis was conducted. Fig. 6c shows the stress-strain curves of the ideal Ni/Fe interface model. The lattice distortion and defects caused by stretching can be visualized through observing the deformation process of the interface model.

The extension of the interface model starts from the elastic deformation in the initial stage until it reaches the initial yield strain at point A of ε=0.009. In this stage, the tensile stress and strain present a proportional relationship, and there is no lattice change or dislocation. When the strain at the interface exceeds 0.009, the stress suddenly drops, indicating the plastic deformation stage caused by the sudden outbreak of dislocations along the sliding plane as the lattice structure of some atoms begins to change. Subsequently, the crystal region of the interface model returns to its initial stage. Similar dislocation evolution in Au nanowires was reported in Ref. [24]. With increasing the strain, the stress is gradually increased, the slip bands appear obviously in the substrate, and the bearing capacity of the material is recovered. When the strain ε

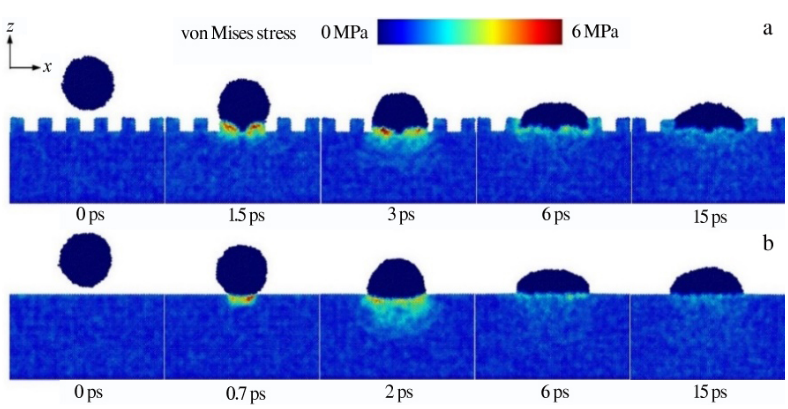

Fig.4 Equivalent stress distributions on substrates with rough surface (a) and smooth surface (b)

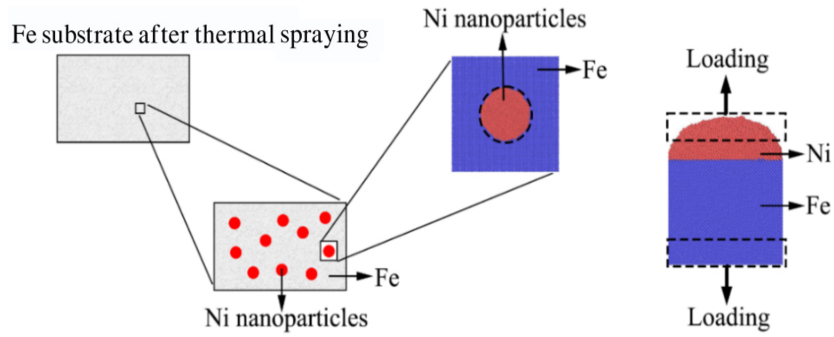

Fig.5 Schematic diagram of bonding strength measurement and atomic scale model of Ni/Fe substrate after thermal spraying

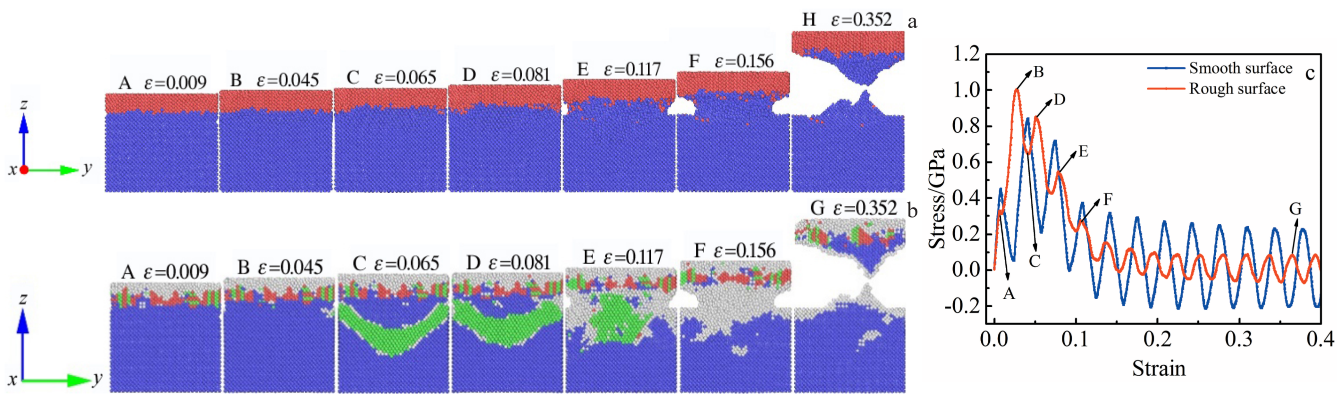

Fig.6 Tensile morphology of interface model in thermal spraying under different strains (a); interface deformation under different strains (b); stress-strain curves of substrates with different surfaces (c)

=0.045, the maximum yield stress is obtained and lattice distortion occurs in the substrate. In Fig. 6b, the first and second yield states are presented by the morphologies at point A and B. The atomic arrangement changes significantly at the second yield stress. The strength of the interface model continues to decline after reaching the maximum value. When the strain is 0.065, the completely distorted lattice penetrates the interface model at the angle of 45°, which is consistent with the tensile fracture results of Fe[25]. When the strain is 0.117, the amorphous crystallization region can be observed near the interface due to the high strain rate deformation in molecular dynamics simulation, and the fracture is formed at the outer edge of the Ni/Fe metal junction. As shown in Fig.6c, the stress-strain curves fluctuate slightly after ε=0.156 and tend to be flat, and therefore the interface crack continues to increase. Finally, when the strain is 0.352, the fracture is completely fractured at the angle of 45°. The boundary between thermal spraying cluster and substrate is weak, where the fracture forms easily.

Meanwhile, the stress-strain curves in Fig. 6c can also be used to evaluate and analyze the mechanical properties and bonding strength between clusters and substrate. The higher the maximum yield strength in the stress-strain curve, the better the interfacial bonding strength and the better the bonding strength of the material. It is clear that the maximum yield strength of the substrate with the columnar rough surface is higher than that with the smooth surface, indicating that the rough surface can improve the bonding strength between the coating and substrate.

The thermal spraying coating is mainly ascribed to the mechanical bonding, and the bonding types mainly include bite type, anchoring type, mating type, and spreading type, as shown in Fig. 7a[26]. In the simulation, the joint of the smooth surface belongs to spreading type, while that of the columnar rough surface belongs to bite type and mating type. As shown in Fig. 7b[27], the clusters are tiled on the smooth surface, and no obvious deformation occurs in the substrate. Only a few cluster atoms are embedded into the substrate, and the non-gap surfaces are completely connected, forming a continuous bonding interface. The clusters into the columnar coarse surface, clusters sedimentary deformation, and columnar rough surface of substrate all have obvious plastic deformation, thereby increasing the contact area of the clusters and substrate, improving the metal particle deposition efficiency, and enhancing the mechanical interlock through the substrate surface roughness, i. e., the anchor effect occurs, therefore improving the bonding strength. The simulated results are similar to the experiment results, as shown in Fig.7c and 7d[28], indicating that the surface morphology of the substrate has a great influence on the bonding strength during the thermal spraying process.

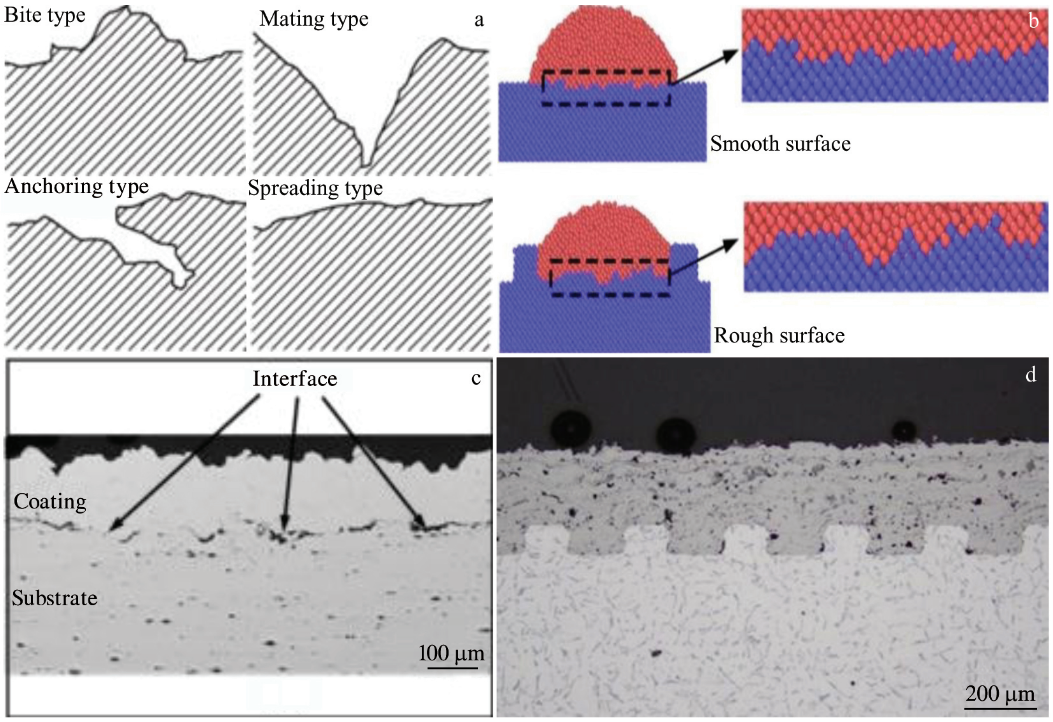

Fig.7 Schematic diagrams of interface combination types[26] (a) and interfacial bonding mechanisms[27] (b); morphologies of coating/interface (c) and square groove face (d)[28]

3 Conclusions

1) Compared with the smooth substrate surface, the rough interface at the atomic scale can inhibit the cluster slip and reduce the flattening effect. The substrate surface morphology can change the stress distribution, and the columnar rough surface can decrease the critical stress and reduce the damage of the substrate subsurface.

2) The substrate surface morphology has a significant effect on the bonding strength after thermal spraying. The rough surface not only increases the contact area between the coating and the substrate, but also improves the adhesion. The mechanical interlock is enhanced by the substrate with rough surface, forming the anchor effect, which leads to improved bonding strength.

3) The larger the cluster flattening ratio, the denser the coating and the better the coating quality. The boundary between thermal spraying cluster and substrate is weak, where the fracture forms easily. The fracture surface expands at the angle of 45°, which is consistent with the experiment results.

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基体表面形貌对Ni/Fe热喷涂及结合强度影响的原子模拟

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摘　要：通过分子动力学方法模拟了基体表面形貌对热喷涂的影响。研究了柱状粗糙表面和光滑表面对团簇展平、基体缺陷演化、应力分布、涂层与基体结合强度的影响。结果表明，基体表面形貌对热喷涂结合强度影响显著，粗糙表面不仅增加了团簇与基体的实际接触面积，提高了附着力，而且在界面结合处形成锚固效应，从而提高了界面结合强度。同时，基体表面形貌改变了界面区域的应力分布，柱状粗糙表面可以减小应力集中效应，降低临界应力，减轻对基体的损伤。此外，粗糙表面会阻碍团簇的滑移，减小了展平比。

关键词：热喷涂；粗糙表面；空位；结合强度；分子动力学

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