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ARTICLE

Effects of H, O, P, S and N Impurities on the Plasticity Deformation Mechanism of Ni by First-Principles Calculations

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Abstract: The relationships of H, O, P, S, and N impurities with the type of plasticity deformation displayed in Ni were studied using density functional theory. We found that different impurities have different segregation tendencies with regards to Ni. S, P, O, and H are most likely to occupy sites on the Ni surface, especially S and P impurity. S, P, H and O have little effect on the deformation mechanism of Ni when located in the grains of the Ni metal. Conversely, N prefers to occupy these grains, and lowers the generalized-stacking-fault energy for Ni, readily promoting the dissociation of dislocation into segments, and making cleavage fracture less likely to occur, which enhances dislocation nucleation. S, P and N cause a decrease in the plasticity of Ni, but H and O increase the probability of twinning for Ni. However, these impurities do not switch the deformation mechanism of Ni from dislocation-mediated slipping to twinning.

Key words: density functional theory; stacking fault; nickel; impurities; deformation mechanism

Nickel-based alloys are widely used in turbine engine vanes because of their outstanding mechanical properties [1]. Owing to their very high strength, the thermal behavior of Ni-based alloys produced by plastic deformation into ultra-high strains is of current interest; however, such materials also feature limited ductility. Optimization of their mechanical properties by thermal treatment following plastic deformation is therefore of immense technological interest. The plastic deformation of crystals could be mediated by ordinary dislocation gliding and mechanical twinning[2-5], and the latter is a competing process with dislocation slipping. Previous studies indicate that Ni has a greater tendency to form extended partial dislocations and twin faults[6]. In practice, at high stresses associated with low deformation temperatures and high strain rates, twinning is typically observed[7-9]. The contributions of various alloying elements to plastic deformation in Ni have also been reported[10-13], and such impurities have also demonstrated strong effects on the microstructure and hardness of these Ni materials[14,15]. Significant differences in the mechanical properties of Ni-based alloys can be caused by the presence of impurities such as S, P, H, N and O[16-18] even at relatively low concentrations. As structural materials, the reliability of Ni-based alloys is limited by the brittleness induced by segregation of S impurities to grain boundaries (GBs) during service at high temperatures and high thermal stresses, because of their high-grain boundary enrichment ratio ($\sim 10^4$) and extremely low solid solubility ($<10^{-4}$) to Ni [19]. Despite decades of intense experimental and theoretical efforts, a direct and fundamental study focusing on the effect of impurities on plasticity deformation mechanism in Ni has yet not been conducted.

At the atomic level, quantum theory has served as an effective tool to interpret the microstructures and deformation mechanisms of metals and metal-based materials. Crucial questions regarding these deformation mechanisms can be explained by the generalized-stacking-fault energy (GSFE) of the metal surface[20, 21]. This energy has been computed for all kinds of body-centered-cubic (bcc), face-centered-cubic (fcc), hexagonal close-packed (hcp) metals and alloys or nanowires[10,22-31]. This stacking fault can be produced by dissociation of perfect dislocations into more favorable $a/6[\bar{1}\bar{1}2]\{111\}$ Shockley partials dislocations for Ni. Our previous studies[18] analyzed the effects of impurities on the

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GSFE of Ni along different slipping directions, and the results showed that plastic deformation was facilitated along the $[11\bar{2}]$ direction, and the impurities had different effects on the mechanical behavior of Ni. These results also revealed that impurities can change the plasticity mechanism of this material from dislocation-mediated slipping to twinning, but the path by which this change occurs is not well known.

In the present work, a GSFE curve along the $[11\bar{2}]$ direction has been calculated to examine how H, O, P, S, and N impurities impact the plasticity deformation of Ni, using density functional theory (DFT). First, the segregating behavior of impurities within Ni is analyzed. The changes to dislocation nucleation barriers induced by impurities are also studied, as well as the tendency of the metal to undergo dislocation-mediated slipping instead of deformation twinning when these impurities are present.

1 Model and Computation Details

In this paper, calculations were performed based on standard periodic boundary conditions using the CASTEP code. The exchange-correlation energy was calculated under the generalized gradient approximation of the Per dew-Burke-Ernzerhof function. It was used for the Gaussian smearing parameter and a plane-wave cutoff with a width of 0.1 eV and 500 eV. *K*-point sampling was performed by applying a 5×5×1 Monkhorst-Pack grid. The energy relaxation was set to iterate until the forces acting on all the atoms were less than 0.5 eV·nm^{-1}. The lattice constant a=0.3528 nm obtained for bulk Ni with these parameters agrees with previously published experimental data[32], and it is over-estimated by only 0.1%. Because of this close agreement, the present parameter settings were determined to be reliable.

To calculate the GSFE, a crystal surface was created, comprising 48 atoms consisting of 12 atomic layers separated by a vacuum region of 0.8 nm. This has been verified to be large enough to avoid interactions between the surfaces of neighboring slabs. For a (111)/<112> slip system, GSFE calculations were performed with the following steps. First, layers 7 to 12 were shifted by (1/6)<112>, creating an ABCAB(C) BCABC stacking fault. Secondly, layers 8 to 12 were shifted to generate the deformed twin ABCAB (C) BABCAB. Impurities were placed in octahedral interstices between the 5th and 6th atomic layers at a concentration of 2.04at%, which agrees with previously published methods[33,34]. Fig.1 shows the schematics of the performed operations.

2 Results and Discussion

2.1 Preferred-site tendency of impurities in Ni

In order to determine the effects of impurities on the stability of the Ni structures, the binding energies of Ni doped with different elements were calculated as shown in Fig.2. The binding energy for H-, O-, P-, and S-doped Ni is greater than that of pure Ni (from lowest to highest), so these impurities lower the structural stability in Ni, particularly in the case of S. However, N-doped Ni has the lowest binding energy, lower than even pure Ni, meaning that N impurities actually enhance the structural stability of Ni.

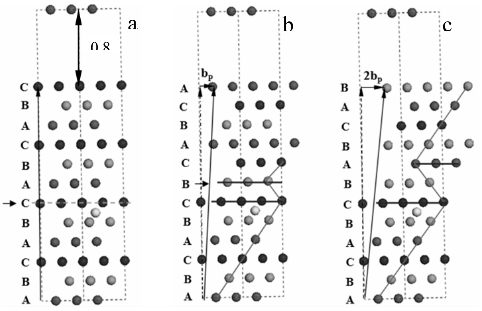

Fig.1 Selective schematic structures to explain the formation of the stacking fault and the twin: (a) initial structure, (b) stacking fault, and (c) two-layer twin

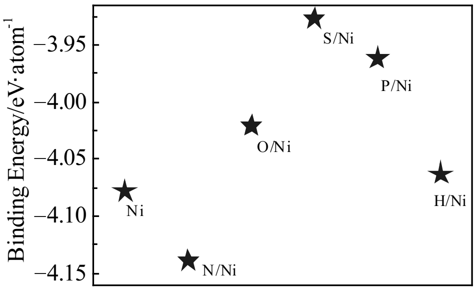

Fig.2 Binding energy of Ni and Ni with P, S, H, N, and O impurities

The segregation energy is defined as the difference between the binding energies of the doped and clean system, indicating the tendency of impurities to segregate the metal interface. Calculated segregation energies for Ni and doped Ni systems are shown in Fig.3. The positive segregation energies indicate that S, P, O, and H are more likely to occupy sites on the Ni surface, especially in the cases of S and P. However, the negative segregation energy implies that N prefers to locate in the grains of Ni.

2.2 Effects of impurities on plasticity deformation in Ni

Fig.4 shows GSFE curves for various impurity configurations, and values of the characteristic parameters of the GSFE

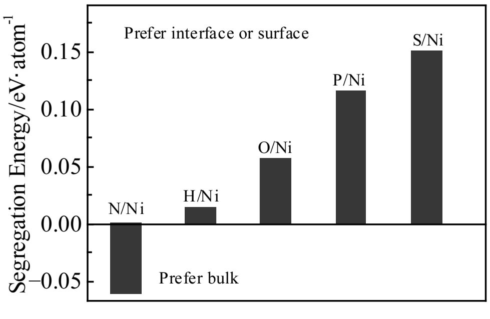

Fig.3 Segregation energy of Ni and Ni with P, S, H, N, O impurity

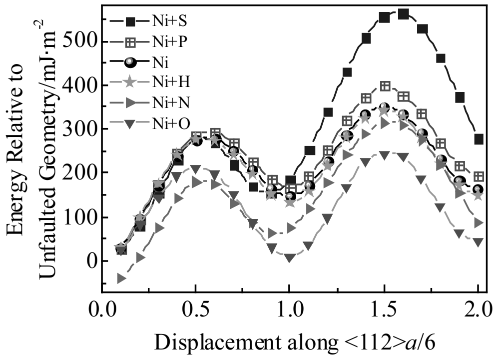

Fig.4 GSFE of Ni and doped Ni slipping along (111)/<112> system

Table 1 Calculated GSFE (in mJ·m^{-2}) for Ni and Ni doped systems

System	γ_{isf}	γ_{us}	γ_{ut}	γ_{isf}/γ_{us}	γ_s	D	δ_{us}^{ut}	τ_a
Ni	147	278	351	0.53	1893	2.04	73	0.94
P-doped Ni	167	293	400	0.57	2405	2.46	107	0.90
H-doped Ni	133	277	342	0.48	808	0.88	65	0.96
S-doped Ni	128	277	555	0.46	2952	3.20	278	0.73
N-doped Ni	62	180	314	0.34	2831	4.72	134	0.82
O-doped Ni	11	212	244	0.05	695	0.98	32	1.05

are shown in Table 1. The intrinsic stacking fault energy (γ_{isf}) corresponds to the first minimum in this curve, for pure Ni, γ_{isf} is equal to 147 mJ·m^{-2}, which is in general agreement with previously calculated values[10] and experimental data[35,36]. γ_{isf} increases to 167 mJ·m^{-2} with the addition of P and decrease to 11, 62, 128, and 133 mJ·m^{-2} with the additions of O, N, S, and H, respectively.

Two energy values that correspond to the first and second maxima in the GSFE curves (Fig.4), namely, the unstable stacking energy (γ_{us}) and the unstable twinning energy (γ_{ut}), represent minimum energy barriers for partial dislocation and micro-twin nucleation. Rice et al.[37] showed that γ_{us} is proportional to the energy release rate required for the nucleation of dislocation, leading to the ductility parameter D ($0.3\gamma_s/\gamma_{us}$), where γ_s is the (111) surface energy. Dislocation-mediated deformation occurs when $D>1$, whereas the metal will tend to fail by cleavage fracture rather than shearing by dislocation mediated slipping when $D<1$. Calculated D values are also listed in Table 1. For Ni, γ_s= 1893 mJ·m^{-2} and yields D=2.04, which implies Ni deformation along the <112> direction by way of dislocation-mediated slipping, as reported previously [10]. With the addition of H or O, $D<1$ and Ni will fail by cleavage fracture because of the resulting low γ_s and high γ_{us}. However, P and S have a tendency to segregate extensively on the interface, so these impurities have little effect on the deformation mechanism for Ni even though the addition of P or S increases the value of D. By contrast, the presence of N increases the value of D for Ni, thereby rendering cleavage fracturing less likely to occur and enhancing the activity of dislocation nucleation.

Swygenhoven et al.[2] posited that the deformation mechanisms of metals are expected to depend on the value of γ_{isf}/γ_{us}; if γ_{isf}/γ_{us} is close to 1.0, deformation by full dislocation is preferred, while a decrease in γ_{isf}/γ_{us} indicates deformation by partial dislocation. All calculated γ_{isf}/γ_{us} values are listed in Table 1. The low γ_{isf}/γ_{us} value of pure Ni suggests that deformation by partial dislocation is preferred, and the addition of P, H, or S has a negligible effect on the deformation tendencies. However, the addition of N and O is beneficial in promoting the dissociation of dislocation into fragments more easily.

Furthermore, we also have analyzed the effects of impurities on the plastic deformation of Ni. According to criteria developed by Tadmor and Hai [38], the relative sizes of γ_{us} and γ_{ut} in a given Ni sample provide a qualitative gauge of whether the preferred deformation mechanism will be dislocation-mediated slipping or deformation twinning. Once a leading partial dislocation has been nucleated, whether or not a subsequent nucleation event will occur with a trailing partial or from micro-twinning on an adjacent slip plane is be influenced by the relationship $\gamma_{ut}-\gamma_{us}\equiv\delta_{us}^{ut}$. For doped Ni systems, it can be seen from the data listed in Table 1 that γ_{us} is less than γ_{ut} in all cases ($\delta_{us}^{ut}>0$), suggesting that the dominant deformation mechanism would not be switched from dislocation-mediated slipping to micro-twinning by the presence of impurities. In addition, the presence of S, P or N increases the value of δ_{us}^{ut} for Ni, which leads to an increase in partial dislocation deformation and a decrease in plasticity. However, H and O reduce the value of δ_{us}^{ut}, increasing the probability of twinning for Ni.

Bernstein and Tadmor[35,36] derived an extensive treatment of the balance between dislocation-mediated slipping and deformation twinning in the form of the twin-ability measure (τ_a) shown in Equ. (1):

$$\tau_a=[1.136-0.151\frac{\gamma_{isf}}{\gamma_{us}}]\sqrt{\frac{\gamma_{us}}{\gamma_{ut}}} \tag{1}$$

τ_a is a relative measure of the tendency of a polycrystalline metal to undergo deformation twinning, with larger τ_a indicating greater propensity for twinning. For pure Ni the computed values of τ_a is 0.94, which agrees with previous calculations and experimental data[36,39]. H or O increase the value of τ_a for Ni, implying that these impurities increase the probability of twin-ability, while P, S or N decrease the value of τ_a for Ni, and once again decrease the plasticity.

3 Conclusions

1) For H-, O-, P-, and S-doped Ni, the binding energy is greater than that of pure Ni, so they lower the structural stability in Ni, particularly in the case of S. The positive segregation energy indicates that S, P, O, and H are most likely to occupy sites on the Ni surface, especially for S and P. In addition, S, P, H or O has little effect on the deformation

mechanism of Ni when located in the grains of Ni.

2) N enhanced the structure stability for Ni, and preferentially moving into the grains of Ni. Meanwhile, N lowered the generalized-stacking-fault energy for Ni, which encourages the dissociation of dislocation into fragments, renders cleavage fracture less likely to occur, and enhances the activity of dislocation nucleation.

3) S, P or N impurities cause a decrease in the plasticity for Ni, while H or O increases the probability of twinning for Ni. However, these impurities are not found to switch the deformation mechanism from dislocation-mediated slipping to twinning in Ni.

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杂质 H，O，S，P，N 对金属 Ni 塑形形变机制影响的第一性原理研究

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摘　要：基于密度泛函理论研究了 H、O、P、S 和 N 杂质以间隙式固溶于 Ni(111)后对其变形能力的影响。发现：S、P 在晶粒内部不稳定，不易存在于 Ni(111)的间隙位置，而易向界面和表面扩散，H、O 和 N 可在晶内分布，且 N 在 Ni 晶内分布的倾向性较大。对于 Ni (111)<112>滑移系，P 使得 Ni 层错能增大，而 H、N、O、S 降低了 Ni 的层错能，即 H、N、O、S 固溶于 Ni 使其沿(111)<112>滑移更为容易。总体来看，当外部环境介质 H、N、O 侵入到 Ni 基体时，由于使得体系的层错能降低，除产生的氧化、腐蚀等作用外，还使得该区域抵抗变形的能力下降，增大了蠕变变形的可能性。

关键词：密度泛函理论；层错能；金属 Ni；杂质；塑形形变机制

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