First-principles study of the effects of selected interstitial atoms on the generalized stacking fault energies, strength, and ductility of Ni*

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We analyze the influences of interstitial atoms on the generalized stacking fault energy (GSFE), strength, and ductility of Ni by first-principles calculations. Surface energies and GSFE curves are calculated for the $\langle 11\bar{2}\rangle(111)$ and $\langle 10\bar{1}\rangle(111)$ systems. Because of the anisotropy of the single crystal, the addition of interstitials tends to promote the strength of Ni by slipping along the $\langle 10\bar{1}\rangle$ direction while facilitating plastic deformation by slipping along the $\langle 11\bar{2}\rangle$ direction. There is a different impact on the mechanical behavior of Ni when the interstitials are located in the slip plane. The evaluation of the Rice criterion reveals that the addition of the interstitials H and O increases the brittleness in Ni and promotes the probability of cleavage fracture, while the addition of S and N tends to increase the ductility. Besides, P, H, and S have a negligible effect on the deformation tendency in Ni, while the tendency of partial dislocation is more prominent with the addition of N and O. The addition of interstitial atoms tends to increase the high-energy barrier $\gamma_{\max}$, thereby the second partial resulting from the dislocation tends to reside and move on to the next layer.

Keywords: first principles, generalized stacking fault energy, Nickel based alloys, strength and ductility

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1. Introduction

Nickel (Ni)-based alloys are a unique class of high-temperature structural materials that are widely used in turbine engine vanes because of their outstanding mechanical properties.[1] The configuration and movement of dislocations play a key role in understanding the mechanical properties and plastic deformation, its existence leads to enhanced plasticity and high strength in Ni.[2] The contribution of some alloying elements to plastic deformation and mechanical properties in metal Ni has been reported.[3–7] It was found that impurities in ppm concentrations can result in a dramatic influence on the ductility and strength of metal materials.[8] Significant differences in mechanical properties of Ni-based alloys are caused by the relatively low concentration of impurities such as S, P, H, N, and O.[9,10] It has already been shown that impurities have strong effects on microstructure and hardness.[11,12] For example, as structural materials, the reliability of Ni-based alloys is limited by the brittleness induced by impurity S segregation to grain boundaries (GBs) during service at high temperatures and high thermal stresses because of its high-grain boundary enrichment ratio to Ni ($\sim 10^4$) and extremely low solid solubility ($< 10^{-4}$) to Ni. From the view of the atomic level, the segregation to GB is related to the diffusion behavior of the elements, due to more defects at the GB than that of the interior of the grain, especially at high temperatures and high thermal stresses. Despite decades of intense experimental and theoretical efforts, a direct and fundamental study focusing on the effect of impurities on the deformation mechanism and mechanical behavior in Ni is still lacking.

The quantum theory has served as an effective tool to understand and study the microstructure and deformation mechanism of metals at the atomic level. Crucial questions pertaining to the mechanism underlying this phenomenon can be explained by considering the generalized-stacking-fault energy (GSFE) (surface).[13,14] Tadmor and Bernstain[15] have shown that the tendency for partial dislocation emission and mechanical twinning in the face centered cubic (fcc) lattice strongly depends on the so-called unstable stacking fault energy ($\gamma_{\rm usf}$) and unstable twinning energy. Similarly, Rice[16,17] introduced the parameter $\gamma_{\rm usf}$ to evaluate the brittle versus ductile response in fcc and body centered cubic (bcc) metals in terms of the competition between dislocation nucleation and Griffith cleavage at a crack tip. Thus far, the GSFE has been computed for a number of fcc and hexagonal close-packed (hcp) metals and alloys, including Mg, Ti, Cu, Al, γ-Fe, and Ni.[3,18–23]

In fcc metal Ni and alloys, the $a/2\langle\bar{1}01\rangle\{111\}$ perfect dislocation will energetically dissociate into two favorable $a/6\langle\bar{1}\bar{1}2\rangle\{111\}$ Shockley partials dislocations connected by a

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SF ribbon. According to Frank's rule,[24,25] the dissociation process can be described by the following reaction:

$$\frac{1}{2}[10\bar{1}] \rightarrow \frac{1}{6}[11\bar{2}] + \mathrm{SF} + \frac{1}{6}[2\bar{1}\bar{1}]. \quad (1)$$

In this paper, we present the GSFE surfaces curve along the $\langle 10\bar{1}\rangle$ and the $\langle 11\bar{2}\rangle$ directions, and surface energies for the (111) plane in Ni by using the *ab initio* calculations. We have comprehensively discussed the influence of the interstitials S, P, H, N, and O on the GSFE surface, and the strength and ductility of Ni.

2. Calculation method and models

Atomistic calculations were conducted using the CASTEP code. We used the standard periodic boundary conditions with ultrasoft pseudopotentials for representing the core electrons and a plane-wave basis set for representing the valance electrons. The calculations were performed using a Gaussian smearing parameter of width 0.1 and a plane-wave cutoff of 500 eV. During geometry optimization, the K-point sampling was performed on a $5 \times 5 \times 1$ Monkhorst–Pack grid. The ultrasoft pseudopotentials were used with generalized gradient approximation (GGA) of electron correlation and exchange energy, within the scheme of the Perdew–Burke–Ernzerhof (PBE) functional. The energy relaxation was iterated until the forces acting on all the atoms were less than 0.05 eV/Å. Using these parameters, the lattice constant for pure Ni was calculated to be $a = 3.528$ Å, which was consistent with the experimental value of 3.524 Å.[26]

The GSFE was computed using a supercell comprising a 2×2 slab geometry with 12 (111) planes and 48 atoms. A vacuum region of 8 Å was included perpendicular to the slip plane. Due to the change in the geometry of the gaps localized in the slip plane, the doped structures were enriched with one interstitial atom placed in a stable octahedral position between the 5th and 6th atomic planes, in accordance with the methods reported in Refs. [27] and [28]. The solute concentration was 2.04 at.% in the fault planes. The atoms of the bottom layer were fixed during relaxation.

Figure 1 schematically illustrates the formation of fault structures during the shearing of the fcc lattice along the $\langle 11\bar{2}\rangle$ direction. The Burgers vector of the partial dislocation producing the shear is denoted by $\boldsymbol{b}_\mathrm{p} = a/6\langle 11\bar{2}\rangle$. The unstable fault structure can be formed by shifting the upper half of the surface structure relative to the lower half using a displacement of $0.5\boldsymbol{b}_\mathrm{p}$ along the $\langle 11\bar{2}\rangle$ direction. This corresponds to γ_usf. Here, the regular fcc stacking of planes is changed from $\cdots$ ABCABCAB$\cdots$ to $\cdots$ ABC|BCABC$\cdots$, where | indicates the position of the fault. Similarly, the stable fault structure can be formed by the shear displacement of $1\boldsymbol{b}_\mathrm{p}$ (Fig. 1(c)) corresponding to intrinsic stacking fault energy (γ_isf). Further shear along the $\langle 11\bar{2}\rangle$ direction would result in another unstable structure at the displacement of $2\boldsymbol{b}_\mathrm{p}$ (Fig. 1(d)).

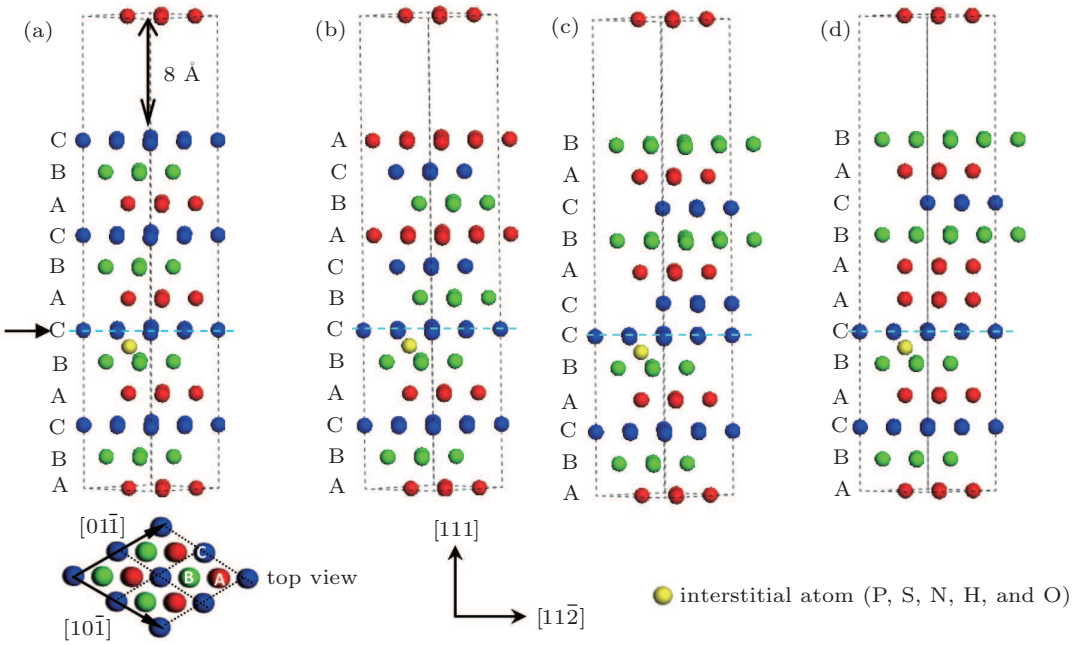


Fig. 1. (color online) A schematic illustration of the formation of GSFE along the (111) plane, and Burgers vector $\boldsymbol{b}_\mathrm{p}$; the different atomic layers are distinguished by different colors, i.e., red, green, and blue indicate A, B, and C, respectively. (a) Perfect structure, (b) slipping $0.5\boldsymbol{b}_\mathrm{p}$, (c) slipping $1\boldsymbol{b}_\mathrm{p}$, and (d) slipping $2\boldsymbol{b}_\mathrm{p}$ along the $\langle 11\bar{2}\rangle$ direction.

3. Results and discussion

3.1. Atomic configuration

Figure 2 shows the calculated interlayer distances for all segregates in the interstitial positions at the free surface model. As is seen, the interlayer distances of the Ni(111) surface are almost similar to those of bulk Ni. Except for H, the interlayer distances of the interstitials P, S, N, and O for the 6/7 layer in the Ni surface system are expanded by 0.034 Å, 0.038 Å, 0.023 Å, and 0.019 Å, respectively. Starting from the eighth layer, the interlayer distances slightly contract around the calculated bulk value of 2.035 Å. Furthermore, we could observe a damped oscillatory behavior with a slightly lower amplitude in the range of 0–0.05 Å. This indicates the adequate convergence with respect to the size, consisting of a 12 atomic-layers-thick slab and a vacuum gap of 8 Å.

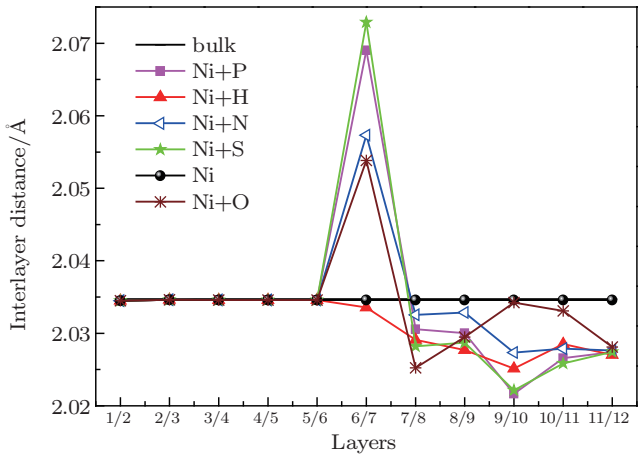


Fig. 2. (color online) Interlayer distances for different surface systems as a function of the layer number. For comparison, the corresponding results for unperturbed bulk Ni have also been included. In the figure, the numbering convention 1/2 indicates the interlayer distance between the first and second nickel layers, and so on.

3.2. Surface energy

The surface energy (γ_s) is defined as the energy needed to create a free surface in a bulk, as indicated by the following expression:

$$\gamma_s = \frac{E^n_{\text{Slab}} - nE_{\text{Bulk}}}{2A}, \tag{2}$$

where E^n_{Slab} and E_{Bulk} are the total energies of the surface and bulk system, respectively, and n is the number of atoms, A is the area of the surface system in the supercell.

For pure Ni, the value of γ_s was calculated to be 1893 mJ/m^2, which is in reasonable agreement with the γ_s values of 1920 mJ/m^2, 1950 mJ/m^2, and 1450 mJ/m^2 reported in Refs. [3], [18], and [29], respectively. As can be seen from the results summarized in Table 1, the addition of S, N, and P tends to increase the γ_s value in Ni, thereby reducing the surface stability. On the other hand, the addition of H and O tends to decrease γ_s, thereby enhancing the surface stability. This implies that the elements S, N, and P are not suitable to segregate to the interior of the grain, while H and O prefer to locate in the interior of the grain in Ni. It has been previously reported[30] that the impurity S favors the surface and grain boundary rather than the inner grain. However, it is unfortunate that there are no experimental or theoretical studies to confirm this segregation tendency in the other impurity elements.

Table 1. Calculated surface energy (γ_s), unstable stacking fault (γ_{usf}), stacking fault energy (γ_{isf}), maximum of the GSFE curve (γ_{max}), and ductility parameters (D) for pure Ni and Ni with interstitial atoms.

		Ni	Ni+2.04 at.%P	Ni+2.04 at.%H	Ni+2.04 at.%S	Ni+2.04 at.%N	Ni+2.04 at.%O
Surface energy	γ_s/(mJ/m^2)	1893	2405	808	2952	2831	695
Slip system $a/2\langle 110\rangle(111)$	γ_{usf}/(mJ/m^2)	1031	1141	1118	1089	1092	1038
	γ_{isf}/(mJ/m^2)	68	78	82	105	98	83
	$D = 0.3\gamma_s/\gamma_{usf}$	0.55	0.63	0.22	0.81	0.78	0.20
Slip system $a/6\langle 112\rangle(111)$	γ_{usf}/(mJ/m^2)	278	293	277	277	180	212
	γ_{isf}/(mJ/m^2)	147	167	133	128	62	11
	γ_{max}/(mJ/m^2)	1696	1758	1713	1762	1714	1838
	$D = 0.3\gamma_s/\gamma_{usf}$	2.04	2.46	0.88	3.20	4.72	0.98
	$\gamma_{isf}/\gamma_{usf}$	0.53	0.57	0.48	0.46	0.34	0.05

3.3. Effects of P, H, N, S, and O on the generalized stacking fault energies surface in Ni

In theory, the GSFE surface is formed when one half of a crystal is translated relatively to the other through a fault vector $\boldsymbol{b}_p$. It is often determined by the energy difference per unit area between the structures with and without a stacking fault.[31,32]

Figure 3(a) shows the effects of the interstitial atoms on the GSFE surface in the $\langle 10\bar{1}\rangle(111)$ slip system. Table 1 summarizes the numerical values extracted from the extreme of the curves (γ_i) in each slip system. As evidenced from the results, if there is a dislocation slipping along the $\langle 10\bar{1}\rangle$ direction, then a potential barrier (γ_{usf}) of 1031 mJ/m^2 has to be overcome on the pathway. This value is four times larger than the potential

barrier along the $\langle 11\bar{2}\rangle$ direction. Thus, the perfect dislocation is likely to dissociate into partial dislocations due to the lower-energy barrier. Furthermore, the interstitial atoms remarkably increase the value of γ_{usf} in the $\langle 10\bar{1}\rangle(111)$ slip system of Ni. However, as observed from Fig. 3(b), the effect of the same elements on the GSFE in the $\langle 11\bar{2}\rangle(111)$ slip system is different from that in the $\langle 10\bar{1}\rangle(111)$ system. Here, interstitial atoms lower the value of γ_{usf}, the trend is: O < N < S < H < P. In terms of the minimum energy barriers for partial dislocation nucleation, the higher the value of γ_{usf} is, the greater the difficulty for emitting dislocation and occurrence of plastic deformation is. Therefore, it can be realized that the addition of the interstitials O, N, S, H, and P can facilitate plastic deformation or dislocation emission by slipping along the $\langle 11\bar{2}\rangle$ direction.

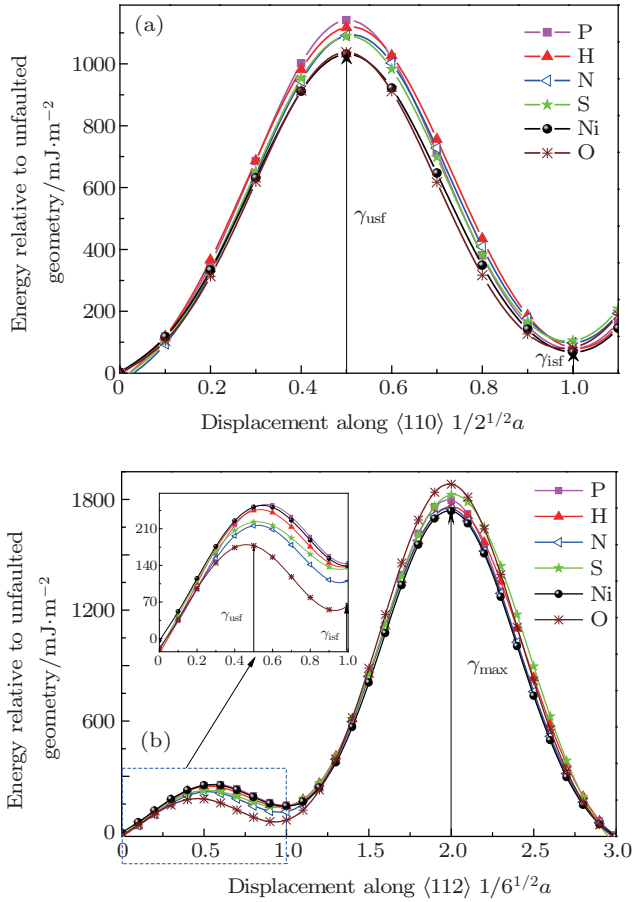


Fig. 3. (color online) The GSFE curves for stacking fault defects in Ni with interstitial atoms. (a) Slipping along $\langle 10\bar{1}\rangle$ direction; (b) slipping along $\langle 11\bar{2}\rangle$ direction. The displacements are in units of their Burgers vectors $\boldsymbol{b}_p$; a represents the lattice parameter of Ni.

As can be seen from Table 1, the γ_{isf} value calculated for the $\langle 11\bar{2}\rangle(111)$ slip system in Ni is 147 mJ/m^2 (experimental values are in the range of 125–128 mJ/m^2 [15,33]), which is in good agreement with the calculated result of 110 mJ/m^2 reported by Siegel.[3] With the addition of P, the value of γ_{isf} increases to 167 mJ/m^2, while it subsequently reduces to 11, 62, 128, and 133 mJ/m^2 with the addition of the interstitials O, N, S, and H, respectively. As is seen, γ_{isf} reduces significantly with the addition of O and N.

However, the γ_{isf} value is rather intermediate. The deformation mechanism cannot be explained solely with γ_{isf} alone, $\gamma_{isf}/\gamma_{usf}$ has to be introduced to represent the full dislocation tendency, as confirmed in Refs. [34] and [35]. The value of $\gamma_{isf}/\gamma_{usf}$ close to 1.0 implies that the deformation mechanism is dominated by full dislocation. On the other hand, when the parameter $\gamma_{isf}/\gamma_{usf}$ is < 1.0, the partial dislocations are observed. In the present study, the calculated $\gamma_{isf}/\gamma_{usf}$ for pure Ni is far less than 1. The parameter $\gamma_{isf}/\gamma_{usf}$ remains relatively unchanged with the addition of P, H, and S, while it reduces even further with the addition of N and O. Thus, the deformation mechanism in Ni is mainly in the form of partial dislocation, with the addition of P, H, and S exhibiting negligible effects on the deformation tendency. However, the tendency of partial dislocation is much more prominent with the addition of N and O.

If the shearing is continued in the $\langle 11\bar{2}\rangle$ direction when arriving at an energy valley (γ_{isf}), we can observe a steep, huge energy barrier, γ_{max}, as shown in Fig. 3(b). Structurally, this would create an ABCABCAABCAB stacking, which is characterized by the on-top position of the two atomic planes across the fault plane. The energy of this configuration in Ni prohibits further slip after the formation of the intrinsic stacking fault. It is important to realize that such an energy profile is determined by the crystal structure, and not by a specific inter-atomic potential. Although the absolute magnitudes of the energies tend to change, the asymmetric shape of the energy landscape will remain unaffected. In this study, the calculated value of γ_{max} is about six times higher than γ_{usf} for Ni, as presented in Fig. 3(b). The addition of interstitial atoms results in a significant increase in the γ_{max} value. In the previous studies, not much attention has been paid to the high γ_{max} peak.[27,36] However, we speculate that this γ_{max} peak might play an important role in the observed twin nucleation or dislocation moving. Suppose a leading partial with exactly Burger vector as $\boldsymbol{b}_p$ is nucleated and propagates into the crystal, leaving behind a faulted region. Then it is difficult for a second partial with the same Burgers vector to glide on the same slip plane, because this high energy barrier γ_{max} makes the faulted region essentially a "forbidden region". As a result, the second partial resulting from the dislocation tends to reside and move on to the next layer.

Furthermore, to understand the effect of the interstitial atoms on the ductility of Ni, we used the model of the competition between dislocation emission from a crack tip and crack cleavage, as reported by Rice.[16] According to this model, a metal will be ductile if the ductility parameter satisfies $D = 0.3\gamma_s/\gamma_{usf} > 1$. The smaller the value of D is, the higher is the tendency of the metal to fail by cleavage frac-

ture rather than shearing by dislocation mediated slip. In the present study, due to the anisotropy of the single crystal, $D < 1$ for Ni in the $\langle 10\bar{1}\rangle(111)$ slip system, the addition of interstitial atoms does not seem to improve the condition (increasing the value of ductility D), while the addition of H or O atoms reduces the value of D further. These results imply that the slip along the $\langle 10\bar{1}\rangle$ direction tends to improve the yield strength, increase the brittleness of Ni, and promote the probability of cleavage fracture near the crack tip. In the $\langle 11\bar{2}\rangle(111)$ slip system, the value of D is 2.04, consistent with the reported D value of 2.14 in Ref. [3]. This reveals that Ni is an intrinsically ductile metal in this direction. In the two slip systems, H and O can effectively decrease the value of D (< 1), thereby improving the strength of Ni. The addition of other elements remarkably increases the value of ductility D. Especially in the $\langle 11\bar{2}\rangle(111)$ slip system, the addition of the elements in the interior grain increases the ductility of Ni in the following order: N>S > P.

4. Conclusions

In summary, we used first-principles calculation to study the influences of the interstitial atoms on the GSFE, strength, and ductility in Ni. The results of GSFE and surface energies calculated in this study are in good agreement with the theoretical and experimental results reported previously. This validates the accuracy of the method used in this study.

Because of the anisotropy of the single crystal, the addition of interstitial atoms slipping along the $\langle 10\bar{1}\rangle$ direction can increase the brittleness in Ni while facilitating plastic deformation by slipping along the $\langle 11\bar{2}\rangle(111)$ system. The addition of S, N, and P results in a surface energy higher than that in pure Ni, indicating that the interstitials S, N, and P are not apt to segregate to the slip plane. On the other hand, the addition of H and O results in a surface energy lower than that of pure Ni, implying that the interstitials H and O prefer to locate to the interior of the grain in Ni. Furthermore, the evaluation of the Rice criterion reveals that the interstitials H and O promote the probability of cleavage fracture in Ni, while the addition of S and N to the interior of the grain tends to increase the ductility. In addition, the interstitials P, H, and S tend to exhibit an almost negligible effect on the deformation tendency in Ni, while the tendency of partial dislocation is more prominent with the addition of N and O. The addition of interstitial atoms to Ni increases the high-energy barrier $\gamma_{\max}$, thereby the second partial resulting from the dislocation tends to reside and move on to the next layer.

References

[1] Pollock T and Argon A 1994 *Acta Metallurgica et Materialia* **42** 1859
[2] Datta A, Waghmare U V and Ramamurty U 2009 *Scripta Mater.* **60** 124
[3] Siegel D J 2005 *Appl. Phys. Lett.* **87** 121901
[4] Yu X X and Wang C Y 2009 *Acta Mater.* **57** 5914
[5] Zhao Y, Zhu Y, Liao X, Horita Z and Langdon T 2006 *Appl. Phys. Lett.* **89** 121906
[6] Cong W and Chong Yu W 2009 *Chin. Phys. B* **18** 3928
[7] Ma S C, Xuan H C, Zhang C L, Wang L Y, Cao Q Q, Wang D H and Du Y W 2010 *Chin. Phys. B* **19** 117503
[8] Holt R and Wallace W 1976 *Int. Met. Rev.* **21** 1
[9] Wei Y and Anand L 2004 *J. Mech. Phys. Solids* **52** 2587
[10] Kobayashi S, Tsurekawa S, Watanabe T and Palumbo G 2010 *Scripta Mater.* **62** 294
[11] Gianola D, van Petegem S, Legros M, Brandstetter S, van Swygenhoven H and Hemker K 2006 *Acta Mater.* **54** 2253
[12] Richter V and Ruthendorf M 1999 *Int. J. Refract. Met. Hard Mater.* **17** 141
[13] Vitek V 1968 *Philos. Mag.* **18** 773
[14] Vitek V 1974 *Cryst. Lattice Defects* **5** 1
[15] Tadmor E and Bernstein N 2004 *J. Mech. Phys. Solids* **52** 2507
[16] Rice J R 1992 *J. Mech. Phys. Solids* **40** 239
[17] Rice J R and Beltz G E 1994 *J. Mech. Phys. Solids* **42** 333
[18] Wu X Z, Wang R, Wang S F and Wei Q Y 2010 *Appl. Surf. Sci.* **256** 6345
[19] Brandl C, Derlet P and van Swygenhoven H 2007 *Phys. Rev. B* **76** 054124
[20] Branicio P, Zhang J and Srolovitz D 2013 *Phys. Rev. B* **88** 064104
[21] Muzyk M, Pakiela Z and Kurzydlowski K 2011 *Scripta Mater.* **64** 916
[22] Chandran M and Sondhi S 2011 *J. Appl. Phys.* **109** 103525
[23] Liao M, Li B and Horstemeyer M F 2013 *Scripta Mater.* **69** 246
[24] Wu X, Wang R and Wang S 2010 *Appl. Surf. Sci.* **256** 3409
[25] Klamecki B E 1982 *Wear* **77** 115
[26] Kohlhaas R, Dunner P and Schmitz P Z 1967 *Z Angew Physik* **23**
[27] Kibey S, Liu J, Curtis M, Johnson D and Sehitoglu H 2006 *Acta Mater.* **54** 2991
[28] Kwasniak P, Muzyk M, Garbacz H and Kurzydlowski K J 2013 *Mater. Lett.* **94** 92
[29] Foiles S, Baskes M and Daw M 1986 *Phys. Rev. B* **33** 7983
[30] Schusteritsch G and Kaxiras E 2012 *Modell. Simul. Mater. Sci. Eng.* **20** 065007
[31] Acet M, Zähres H, Wassermann E and Pepperhoff W 1994 *Phys. Rev. B* **49** 6012
[32] Nie X, Wang R, Ye Y, Zhou Y and Wang D 1995 *Solid State Commun.* **96** 729
[33] Bernstein N and Tadmor E 2004 *Phys. Rev. B* **69** 094116
[34] van Swygenhoven H, Derlet P and Frøseth A 2004 *Nat. Mater.* **3** 399
[35] Frøseth A, Derlet P and van Swygenhoven H 2004 *Acta Mater.* **52** 5863
[36] Li B, Cao B Y, Ramesh K T and Ma E 2009 *Acta Mater.* **57** 4500