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Analysis of the alloying system in Ni-base superalloys based on ab initio study of impurity segregation to Ni grain boundary.

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Abstract. A new approach to the design of Ni-based polycrystalline superalloys is proposed. It is based on a concept that under given structural conditions, the performance of superalloys is determined by the strength of interatomic bonding both in the bulk and at grain boundaries of material. We characterize the former by the cohesive energy of the bulk alloy, whereas for the latter we employ the work of separation of a representative high angle grain boundary. On the basis of our first principle calculations we suggest Hf and Zr as "minor alloying additions" to Ni-based alloys. Re, on the other hand, appears to be of little importance in polycrystalline alloys.

Introduction

Ni-base superalloys (NBS) are key materials for the manufacturing of aerospace engines. Sustainable growth of aerospace industry demands leads to a necessity of improvement of operational characteristics of NBS. Therefore, the leading laboratories in the world make a continuing intensive search for new chemical compositions and new technologies for the production of gas turbine engines.

The alloying elements which increase the bond strength in the bulk of the γ-matrix could be used to increase high temperature properties under given structural conditions [1,2]. The main elements for this purpose are transition metals, and the most important of them are W, Ta and Re. Some of these metals tend to segregate to the open surface of the crystals as well [3]. Taking into account the well known thermodynamic similarity between open and internal (grain boundary) interfaces in metals, we sought for the strengthening elements for polycrystalline NBS among transition metals that segregate to the surface above all.

The segregation energy itself is not sufficient to identify the elements that strengthen grain boundaries (GBs). Such elements should not only segregate to the grain boundary, but make it stronger as well. One can take the ideal *work of separation,* W_{sep}, as a fundamental thermodynamic quantity that controls the mechanical strength of an interface [4]. In essence, the work of separation characterizes the resistance of a grain boundary to decohesion and therefore is suitable for our analysis. Furthermore, that fact that the change of W_{sep} due to the segregation of impurity atoms is related to the segregation energies of impurity atoms to a grain boundary and to a free surface simplifies the analysis a great deal.

The main purpose of our study is to evaluate the segregation energies of some typical alloying elements (W, Ta, Re, Hf, Zr, B) and other impurities (S, Bi) to some representative GB and the respective free surface using first principles calculations. These are combined with (somewhat improved) previous calculations of the partial cohesive energies [1,2] which determine the contribution of each element into the bonding strength in the bulk, to arrive at some suggestion on impurities suitable for microalloying in NBS.

Details of calculation.

Calculations in this work were performed using the projector augmented wave potentials [5] as implemented in Vienna ab initio simulation package (VASP) [6] with generalized gradient approximation (GGA) [7]. The convergence accuracy of total energy was chosen as 10^{-5} eV and $9*10^{-3}$ eV/Å for forces. The ionic relaxations were included in the all types of calculations.

To represent a general high angle grain boundary in Ni we chose a symmetrical tilt Σ5 (210)[100] boundary. The boundary was modeled as a supercell containing 19 atomic layers of Ni (2 atoms per layer) separated with 8 Å of vacuum as shown in Fig. 1. In calculations with 0.5 ML impurity, a single impurity atom either replaces a Ni atom in the GB plane (substitutional site) or is inserted into a position marked I in the Fig. 1. The same strategy was used for the 0.25 ML calculations except that we doubled the cell along the [100] direction (76 atoms per cell). Same supercells, but with the grain boundary removed, were used for the calculations of free surfaces.

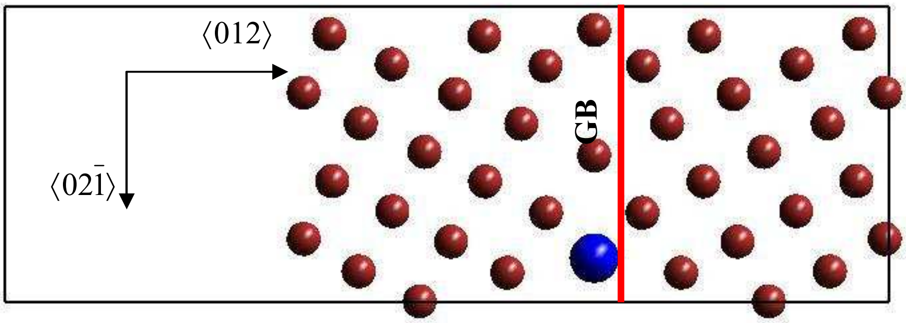

Fig. 1. Slab of the model system for 78 atoms containing Σ5 (210)[100] GB. The interstitial position is shown with a blue atom of larger size.

The $8\times4\times2$ and $4\times4\times2$ Monkhorst-Pack k-point meshes were used for single and double cell calculations, respectively, whereas the $6\times6\times6$ mesh was employed in our bulk calculations with 64 atom fcc supercells. The energy cutoff of 270 eV was used throughout our calculations.

The segregation energy in this work is defined as the difference between the total energy of a system with the impurity in the surface layer (or GB) and in the bulk and: ($E_{seg} = E_{surf} - E_{bulk}$). Hence, our sign convention is that the negative segregation energy corresponds to impurities that want to segregate.

Partial cohesive energies.

Partial cohesive energies of some elements in Ni-base alloys were reported in our previous work [1,2]. From the bond strengthening point of view, the "best" elements found were W, Ta and Re. However, this work did not include ionic relaxation and spin polarization energies of the pure atoms [8]. These are now taken into account in the present study.

Partial cohesive energies for chosen elements [3] in Ni alloys are shown in Fig. 2. Brooks and Johansson [8] considered only 3d, 4d, and some 5d and 5f elements in their work. Hence, the correction factors for S, B and Bi are unknown and have been ignored here. One can see in Fig. 2 that W, Re and Ta still have the leading position in terms of the bond strengthening in the bulk of fcc Ni alloys, as was the case in our previous work. B, Zr and Hf also increase the bond strength in the alloy, while S and Bi make bond weaker and should be treated as undesirable elements for the bulk alloying.

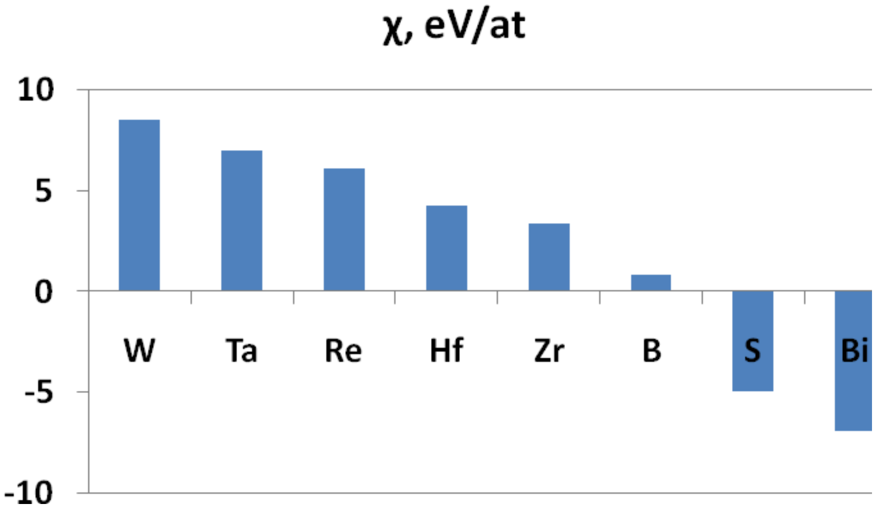

Fig. 2 Partial cohesive energies of bulk impurities in fcc Ni.

Surface and grain boundary energies of pure Ni.

The Σ5 (210)[100] tilted symmetric grain boundary was selected as a representative high angle grain boundary in NBS as its energy falls in the midrange of special GBs in pure Ni [9]. Equilibrium structure of this boundary used in the present work (Fig. 1) coincides with the structure used in other studies. Calculated grain boundary energy γ_{gb}^0, the energy of the respective (210) free surface γ_s^0, and the work of separation W_{sep}^0:

$$W_{sep}^0 = 2\gamma_s^0 - \gamma_{gb}^0 \qquad (1)$$

agree well with experiment [10-13] and previous theoretical calculations [14,15] (Table 1).

Segregation energies and the work of separation.

Segregation of impurity to a grain boundary changes its work of separation. The work of separation of the segregated boundary W_{sep} is related to the one of the pure boundary W_{sep}^0 as (see, e.g., [16]):

$$W_{sep} = W_{sep}^0 + \Gamma\left(E_{seg}^s - E_{seg}^{gb}\right), \qquad (2)$$

where Γ is the impurity excess at the grain boundary, E_{seg}^{gb} and E_{seg}^s are the segregation energies of impurity atom to the GB and to the free surface, respectively. A convenient parameter to characterize the effect of a particular impurity is the difference between works of separation of GB before and after the segregation per impurity atom. We refer to this parameter as η. From Eq. (2) one finds:

$$\eta = (W_{sep}^0 - W_{sep}) / \Gamma = E_{seg}^{gb} - E_{seg}^s \qquad (3)$$

which is exactly the parameter that we shall be using for our analysis.

Table 1. The energies of $\Sigma5(210)[100]$ grain boundary (γ_{gb}^{0}) and (210) free surface (γ_{s}^{0}) in pure Ni in eV/at.

	present	[14]	[15]	Exp. (polycryst)	
γ_{gb}^{0}	0.97	1.13	1.08	1.24	[11]
		1.17		0.77	[12]
				0.94	[13]
γ_{s}^{0}	1.83	2.18	2.03	1.97	[14]
		2.19		2.02	[11]
				2.07	[12]
W_{sep}^{0}	2.69	3.23	2.98	2.80	[11]
		3.21		3.37	[12]

In our calculations we proceed as follows. Firstly, at a given impurity excess (0.5 ML or 0.25 ML) we insert the impurity atom at either the interstitial or substitutional position at the GB. Comparing respective E_{seg}^{gb}, we select for Eq. (3) the smallest one, as this would represent a system with the lower Gibbs free energy (which is just the total energy in our zero temperature calculations). According to Table 2, only S and B prefer interstitial positions. The rest of considered elements prefer to replace the host atom at the grain boundary.

Secondly, we compare surface segregation energies, now for 0.5 ML and 0.25 ML, and again select the smallest one. This corresponds to how impurity atoms distribute themselves between two free surfaces formed after the cleavage of the grain boundary. The data in Table 2 suggest that most impurities distribute evenly between the created surfaces, sulphur being the only exception.

Overall, according to parameter η in Table 2 W, Zr, Hf, B, Ta, and Re should all improve the GB resistance to decohesion, with W and Re having higher impact, whereas Bi and S should lead to the deterioration of GB strength. Dependence of η on impurity concentration appears to be a second order effect.

Concept of minor alloying additions.

All three parameters χ, E_{seg}^{gb} and η can be combined together to evaluate the effect of alloying. In single crystal alloys only χ parameter has the crucial influence on the alloy properties as no grain boundaries are present. The situation changes in polycrystalline alloys, such as wrought Ni-base superalloys. The bond strength in the bulk of γ-matrix (parameter χ) is still important, but grain boundaries might also be essential for the alloy performance. Therefore, in addition to χ one should consider the ability of alloying elements to segregate to grain boundary (E_{seg}^{gb}) and their influence on the GB resistance to decohesion (parameter η).

"Good" elements are those with positive values of χ and negative values of η and E_{seg}^{gb} parameters (these elements strengthen both bulk and GB), "bad" elements have negative values of χ and positive values of η (these elements weaken bulk and GB), whereas elements with positive E_{seg}^{gb} simply have no effect on GBs. According to this classification, S and Bi are definitely "bad" elements, whereas the rest of the analyzed elements (except Re) fall into the "good" category. Re does not segregate much to the GB, therefore its strengthening effect is limited to the grain interior. W and Ta are already well recognized as "good" alloying additions. The outcome of our study are therefore Zr, Hf, and B. Compared to W and Ta, these elements should have less pronounced but yet sizable effect on GBs. Situation with boron is particularly interesting. Since B prefers the interstitial segregation, its positive effect might *combine* with the effect of substitutional segregants such as W, Ta, Zr, and Hf.

Table 2. Segregation energies of impurity atoms to the free surface (E^{s}_{seg}), to the grain boundary in substitutional (E^{gb}_{seg}) and interstitional ($E^{gb}_{seg,i}$) positions, and the work of separation of the grain boundary with impurity atoms in substitutional (W_{sep}) and interstitial ($W_{sep,i}$) positions. All data are presented in eV/atom for 0.5 monolayer and 0.25 monolayer concentrations of impurity atoms. In pure Ni, W^{0}_{sep} = 2.69 eV/at (see Table 1). Values in parenthesis are taken from Ref. [15].

		W	Zr	Hf	Bi	S	B	Ta	Re
E^{gb}_{seg}	0.5 ML	-0.39	-1.91	-1.62	-2.31	-0.26	0.54	-0.91	-0.01
	0.25 ML	-0.45	-1.94	-1.65	-2.31	-0.32	0.65	-0.93	-0.12
E^{s}_{seg}	0.5 ML	1.11	-1.46	-0.93	-4.15	-2.71	-0.87	0.33	1.45
	0.25 ML	0.87	-1.77	-1.16	-4.33	-2.65	-0.95	0.13	1.21
$E^{gb}_{seg,i}$	0.5 ML	0.70	-0.95	-0.50	-1.75	-1.60	-1.65	0.21	0.53
	0.25 ML	0.63	0.17	0.34	-0.36	-1.56	-1.65	0.53	0.64
W_{sep}	0.5 ML	3.45	2.93	3.05	1.78	1.47	1.99	3.32	3.43
	0.25 ML	3.03	2.74	2.82	2.20	2.12	2.30	2.96	3.03
				(3.35)		(2.70)			
$W_{sep,i}$	0.5 ML	2.91	2.45	2.49	1.50	2.14	3.09	2.76	3.16
	0.25 ML	2.76	2.22	2.32	1.71	2.43	2.87	2.60	2.84
				(2.69)		(2.65)	(3.17)		
η	0.5 ML	-1.26	-0.14	-0.46	2.02	1.12	-0.70	-1.04	-1.21
	0.25 ML	-1.32	-0.17	-0.49	2.02	1.15	-0.70	-1.05	-1.33

Conclusion.

On the basis of first principles calculations we analyze partial cohesive energies, grain boundary segregation energies and the work of GB separation in Ni-X alloys, where X is a typical alloying (W, Re, Ta, Zr, Hf) or microalloying (B) addition or impurity (S, Bi) in Ni-base superalloys. We classify Hf and Zr as “minor alloying additions” to Ni-base superalloys. According to our approach, “minor alloying additions” are the elements with high tendency to segregate to grain boundaries, positive (preferably high) partial molar cohesive energies in the bulk, and positive impact on the grain boundary work of separation (elements that increase the resistance of a grain boundary to cleavage).

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