Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 82 (2015) 369–377

Acta MATERIALIA

www.elsevier.com/locate/actamat

# First-principles-aided design of a new Ni-base superalloy: Influence of transition metal alloying elements on grain boundary and bulk cohesion

V.I. Razumovskiy,[a,b,*] A.Y. Lozovoi[c,1] and I.M. Razumovskii[d]

[a] *Materials Center Leoben Forschung GmbH, Roseggerstraße 12, A-8700 Leoben, Austria*

[b] *Department of Materials Science and Engineering, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden*

[c] *Atomistic Simulation Centre, School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, UK*

[d] *Open Joint-Stock Company "Kompozit", 4 Pionerskaya Street, Korolev 141070, Moscow District, Russia*

Received 30 January 2014; revised 28 July 2014; accepted 21 August 2014
Available online 11 October 2014

**Abstract**—A new approach to the design of Ni-base polycrystalline superalloys is proposed. In this approach, we assume that the creep–rupture characteristics of a superalloy are mostly determined by the strength of interatomic bonding at grain boundaries (GBs) and in the bulk of $\gamma$ matrix. The ideal work of separation, $W_{sep}$, of a GB is used as a fundamental thermodynamic quantity that controls the mechanical strength of an interface, whereas the partial cohesive energy, $\chi$, of an alloy component serves to characterize its contribution into the strength of the bulk. Using the $\Sigma 5$ (210)[100] symmetric tilt GB as a representative high-angle GB in Ni, we calculate $W_{sep}$, $\chi$, and GB segregation energies, $E_{seg}$, for the complete set of 4*d* and 5*d* transition metal impurities, to which we add B (a typical microalloying addition), S and Bi (notoriously known as harmful impurities in Ni-base superalloys). The purpose of the analysis is to identify the elements that demonstrate a high tendency to segregate to GBs, have positive (preferably high) partial cohesive energies in the bulk, and have positive impact on $W_{sep}$ of GBs. We refer to these elements as low-alloying additions. Our study reveals Zr, Hf, Nb, Ta and B as the most promising low-alloying additions. Our next step is to introduce the elements found in the first step into a new powder metallurgy (P/M) Ni-base superalloy. The results of the subsequent testing confirm that the newly created P/M superalloy indeed demonstrates superior mechanical properties at high temperatures compared to the existing Russian P/M alloy EP741NP.


*Keywords:* Ab initio calculations; Grain boundaries; Cohesion; Ni-base superalloys; Mechanical testing

## 1. Introduction

Ni-base superalloys (NBS) are key materials used for the manufacturing of aerospace engines [1]. Some critical parts of gas turbines, e.g. turbine disks, are produced from polycrystalline NBS by means of powder metallurgy (P/M), which is one of the most efficient technologies for preparing "net–shape" turbine disks with fine polycrystalline structure and reduced macrosegregation [2].

In terms of creep resistance, grain boundaries (GBs) are the "weakest" elements of a polycrystalline alloy. Indeed, GBs are normally characterized by enhanced diffusivity [3], which favors creep under loads at high temperature (particularly in fine-grained NBS). It is well known that one of the most important factors affecting the properties of GBs is the chemical composition. The chemical composition of GBs differs from the average chemical composition of an alloy due to segregation of certain alloying elements and impurities to GBs. Several surfactant elements, referred to as "grain boundary elements" [2], can enrich GBs. GB elements, in turn, can be divided into "useful" microalloying additions and "harmful" impurities. It is considered that "useful" microalloying additions, such as boron, segregate to GBs and increase the work of GB separation [2]. "Harmful" impurities also segregate to GBs, but reduce the alloy's cohesive strength.

Thus, to assess the impact of the chemical elements on the state of GBs in alloys, one should, first, investigate their ability to segregate to a GB and, second, determine their effect on the cohesive strength of GBs. The second is a more difficult task. Indeed, the experimental determination of the cohesive strength of GBs is a complex problem that has rarely been the subject of an experimental study. A theoretical solution to this problem has been proposed by Rice, Thomson and Wang [4,5]. The Rice–Thomson–Wang approach is centered around the ideal work of separation (of a GB), $W_{sep}$, as a fundamental thermodynamic quantity

* Corresponding author at: Materials Center Leoben Forschung GmbH, Roseggerstraûe 12, A-8700 Leoben, Austria; e-mail: razvsevol@yahoo.com

[1] Present address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

http://dx.doi.org/10.1016/j.actamat.2014.08.047
1359-6462/

that controls the mechanical strength of an interface, and allows one to approach the problem from first principles.

Ab initio calculations based on the density functional theory (DFT) have been the most useful tool for investigation of GB segregation and embrittlement, especially during the last decade (see Ref. [6] for a recent review). Ni GBs are no exception. Perhaps the most theoretically studied element in this context is sulfur [7–12]. S is predicted to readily segregate to Ni GBs and cause the embrittlement of the latter, in perfect agreement with experiment [13,14]. Systematic studies of metal and non-metal *sp* impurities in Ni [9,12] suggest that most of them weaken Ni GBs, with the exception of Be, B and Si, which have a strengthening influence, whereas C, Al and P have little or no effect. Calculations of transition metals are scarcer. Sanyal et al. [11] predict that Hf has a strengthening effect, and according to Young et al. [8], Cr and Nb slightly strengthen GB, whereas Zr shows a small embrittling potency. The latter, however, disagrees with the prediction of a phenomenological model proposed by Geng et al. [15].

In this paper we undertake a systematic investigation of the effect of transition metal impurities on a representative GB in Ni. Thus, our study is complementary to those of *sp* impurities in Ni by Yamaguchi et al. [9] and by Všianská and Šob [12] as it considers the complete set of 4*d* (Y–Ag) and 5*d* metals (La–Au), to which we add Cr, B, S and Bi. We further show how these data can be used to select the most efficient alloying elements in terms of GB resistance to decohesion ("low-alloying additions" concept). Finally, the proposed "low-alloying additions" concept is tested in an experimental study of a new P/M NBS.

## 2. Theory

We would like to ascertain a few physical quantities that are unambiguously defined and can be employed to characterize the individual contributions of each alloy component to the overall strength of the polycrystalline material. It would be also beneficial if these quantities are straightforward and reasonably quick to calculate ab initio.

Recently it was suggested [16] that the partial molar cohesive energy of impurity atoms could be used to characterize the cohesion in the bulk. Indeed, an excellent correlation between impurity cohesive energies and high-temperature properties of single-crystal NBS was found (see Section 2.2). Encouraged by this finding, in the present study we shall also use the partial contribution of alloying elements to the ideal work of GB separation as a suitable quantity to characterize cohesion at the GB of polycrystals. To these, we add a third quantity, namely the energy of impurity segregation to GB, as it is important that the impurity in question is present at GBs in thermodynamic equilibrium (see Section 2.1).

### 2.1. Segregation energies and the work of GB separation

The ideal work of separation, $W_{sep}$, is a fundamental thermodynamic quantity that controls the mechanical strength of an interface [4,5]. In essence, the work of separation characterizes the resistance of a GB to decohesion and therefore is relevant to our analysis.

In the interface thermodynamics, there are two similar quantities responsible for the interface decohesion: the work of adhesion, $W_{ad}$, and the work of separation, $W_{sep}$ [17]. The former is defined as the reversible work required to cleave a GB into two free surfaces (FSs) and assumes that full thermodynamic equilibrium is maintained during the decohesion:

$$W_{ad} = 2\gamma_{fs} - \gamma_{gb}, \tag{1}$$

where $\gamma_{gb}$ and $\gamma_{fs}$ are the energies of GB and the respective FSs per unit area. In particular, it is $W_{ad}$ that is responsible for the existence of a contact angle at a droplet of liquid on a solid surface.

The work of separation is also defined as the reversible work of decohesion, except that any diffusion exchange between the interface and the underlying bulk is suppressed during the decohesion (the fast separation limit). In this case, the "local" equilibrium is maintained between impurity atoms and the surface layer of the host. This equilibrium corresponds to the impurity chemical potential $\mu'$ different from the one in the bulk $\mu$, and the expression for $W_{sep}$ reads [18]:

$$W_{sep}(\Gamma_{gb}) = 2\gamma_{fs}(\Gamma_{gb}/2) - \gamma_{gb} + (\mu' - \mu)\Gamma_{gb}, \tag{2}$$

where $\Gamma_{gb}$ is the surface excess of the impurity, and it is assumed that the impurity distributes evenly between two newly created surfaces.

In this study we shall also assume the fast separation limit, i.e. assume that the notional cleavage of GBs occurs too rapidly for any impurity to diffuse into or out of the bulk during the process. Hence it suffices for our purposes to consider the ideal work of separation $W_{sep}$ rather than the work of adhesion $W_{ad}$.

Secondly, we shall be working in the dilute limit for bulk alloys, in which the surface impurity excess is just the number of impurity atoms per unit surface area $A$:

$$\Gamma_{gb} = N_{gb}/A, \tag{3}$$

where $N_{gb}$ is the number of impurity atoms at GB and $A$ is the area of GB.

Thirdly, we neglect all temperature effects since our ab initio calculations refer to zero temperature. What is neglected here are the temperature dependence of internal energy of the system (through, for instance, lattice expansion) and the entropic contribution to the Gibbs free energy. At high temperatures these contributions are of course not negligible, but still are not large enough to reverse the effect found at $T = 0$. On the other hand, taking the temperature properly into account would enormously complicate the computations. Thus, it is a common practice to leave these effects aside.

The three simplifications outlined above allow one to relate $W_{sep}$ to the segregation energies of impurity to an FS, $E^{fs}_{seg}$, and to a GB, $E^{gb}_{seg}$, defined as the change in the total energy corresponding to impurity being taken out of the bulk region of the system and distributed over the FS or over the GB, respectively.

Expression (2) for $W_{sep}$ then becomes [19]:

$$W_{sep} = W^0_{sep} + \Gamma_{gb}\left(E^{fs}_{seg} - E^{gb}_{seg}\right), \tag{4}$$

where $W^0_{sep}$ is the work of separation of the pure GB:

$$W^0_{sep} = 2\gamma^0_{fs} - \gamma^0_{gb}, \tag{5}$$

and $\gamma^0_{fs}$ and $\gamma^0_{gb}$ are the energies of the pure FS and GB.

More details on the thermodynamics of decohesion and the Rice–Thomson–Wang approach can be found in Refs. [19,20] and references therein. The important fact for our