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The role of thermal expansion and composition changes in the temperature dependence of the lattice misfit in two-phase γ/γ' superalloys

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The relative role of thermal expansion and composition changes in the temperature dependence of the lattice misfit in γ/γ' alloys was investigated on the basis of ab initio calculations. We show that over a wide temperature range, up to approximately $0.6T_{\text{melt}}$, the lattice misfit is determined by the difference in thermal expansion of γ and γ' phases and exhibits only a slight variation. For higher temperatures, the redistribution of the major alloy components between the phases becomes a leading contribution to the lattice misfit.

Keywords: Ab initio electron theory; Nickel alloys; Platinum group metals; Thermally activated processes; Lattice misfit

Single-crystal nickel-based superalloys are widely used in turbine blades for power generation and aircraft engines [1]. Their success as high-temperature materials is attributed to the two-phase γ/γ' structure, which combines the ductility of the Ni-base matrix (γ phase, with face-centered cubic (fcc) structure) with the strength of the coherent ordered Ni_3Al precipitate (γ' phase, with $L1_2$ structure). This microstructure is being mimicked in the development of "refractory superalloys", a new class of alloys based on platinum group metals, most notably Pt [2], Ir [3] and Rh [4]. These superalloys are targeted at applications at the ultra-high-temperatures which Ni-base superalloys cannot reach. One of the most promising among them is the Ir–Nb system, which reportedly [3,5] maintains high strength even at 2100 K, while showing superior oxidation resistance.

It is well established [6,7] that the high-temperature mechanical behavior of two-phase superalloys is very sensitive to the value and sign of the lattice misfit, δ, between the γ and γ' phases. If the misfit has an optimum value at a given temperature, a so-called rafted microstructure forms under tensile stress conditions, which results in the remarkable creep strength of superalloys. Experimentally, the lattice misfit in Ir-based alloys exhibits an almost linear, but slightly decreasing dependence on the temperature, $\delta(T)$, up to 1600 K [8] – in sharp contrast with Ni-based alloys where $\delta(T)$ falls rapidly above 900 K [9]. The reasons for the latter behavior are still unclear and are the subject of debate; two contributions to the $\delta(T)$ dependence are considered: (i) the difference in thermal expansion of the conjugated phases [10], and (ii) the changes in alloy composition due to redistribution with temperature of the alloying component between the γ and γ' phases [7,9]. Since the lattice parameters of the phases can change by up to several per cent due to the thermal expansion alone in the temperature range considered, its contribution to $\delta(T)$ could become significant. On the other hand, the few per cent variation in the composition can result in up to 1% changes of δ if the difference in ionic radii of the alloy components is little as 10%.

In this work, the role of both thermal expansion and composition changes in the temperature dependence of

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the lattice misfit $\delta(T)$ for the Ni–Al and Ir–Nb γ/γ' alloys are explored on the basis of ab initio electronic calculations. We demonstrate that over a wide temperature range, up to approximately $0.6T_{\mathrm{melt}}$, the lattice misfit is controlled by the difference in thermal expansion of the γ and γ' phases, and shows only a slight variation with temperature. For both alloys, the composition changes become dominant in the lattice misfit for temperatures above $0.6T_{\mathrm{melt}}$; in this case, $\delta(T)$ is mostly determined by the shape of the γ–γ' gap in the phase diagram.

The lattice misfit is defined as:

$$\delta = \frac{a_{\gamma'} - a_\gamma}{\frac{1}{2}(a_{\gamma'} + a_\gamma)}, \tag{1}$$

where a_γ and $a_{\gamma'}$ are the lattice parameters for the γ and γ' phases, respectively. In general, the temperature dependence $\delta(T)$ is determined by (i) the difference in coefficients of thermal expansions (CTE), $\alpha(T)$ of the corresponding phases, and (ii) lattice dilatations due to composition changes and vacancy formation, $\varepsilon^C(T)$ and $\varepsilon^V(T)$:

$$\delta(T) = \delta^{(0)} + \frac{1}{3}\int_0^T (\alpha_{\gamma'}(T') - \alpha_\gamma(T'))\mathrm{d}T' + (\varepsilon^C_{\gamma'} - \varepsilon^C_\gamma) + (\varepsilon^V_{\gamma'} - \varepsilon^V_\gamma), \tag{2}$$

where $\delta^{(0)}$ is the lattice misfit at $T = 0$ K for the reference composition A/A_3B.

Modern computational methods allow one to calculate thermal expansion from first-principles, based on ab initio considerations of the electronic structure and crystal lattice dynamics (for a review, see Ref. [11]). The CTE is determined by the phonon and electronic contributions

$$\alpha = \alpha^{(ph)} + \alpha^{(e)} \tag{3}$$

$$\alpha^{(ph)} = \frac{1}{VB_{\mathrm{T}}}\sum_v \gamma_v \left(\frac{\hbar\omega_v}{T}\right)^2 n_v(1+n_v),$$

$$\alpha^{(e)} = \frac{1}{TB_{\mathrm{T}}}\frac{\partial}{\partial V}\int \mathrm{d}\varepsilon N(\varepsilon)[(\varepsilon-\mu)f_\varepsilon - T\ln f_\varepsilon]$$

where V is the volume, B_{T} the isothermal bulk modulus, $n_v = (\exp(\hbar\omega_v/T) - 1)^{-1}$ and $f_\varepsilon = (1 + \exp(-(\mu-\varepsilon)/T))^{-1}$ are the Planck and Fermi functions, respectively, $\gamma_v = -\partial\ln\omega_v/\partial\ln V$ is the microscopic Grüneisen parameter, and $N(\varepsilon)$ is the electronic density of states (see Ref. [12] for details of the computational procedure).

Usually, the electronic contribution, $\alpha^{(e)}$, to the thermal expansion is small in comparison with the phonon one and is neglected. However, it may become significant in alloys with large $N(\varepsilon)$ at or near the Fermi level, such as in Ni and Ni-based alloys [13]. Here, we take into account the $\alpha^{(e)}$ for all metals and alloys under consideration.

Since $L1_2$ intermetallics are antisite disordered alloys [14], a contribution to the lattice dilatation in Eq. (2) from the vacancy formation, $\varepsilon^V(T)$, can be neglected. Indeed, the concentration of the equilibrium vacancies does not exceed 10^{-4} at the melting temperature and their contribution cannot be larger than 0.001%, which is significantly smaller than the observed $\delta(T)$ variation. A contribution from composition changes, in the form of the concentration dependence of the lattice parameters, can be presented as follows:

$$\varepsilon^C_\gamma = C^B_\gamma\beta_\gamma, \quad \varepsilon^C_{\gamma'} = (C^B_{\gamma'} - 0.25)\beta_{\gamma'}. \tag{4}$$

Here, $\beta = (1/a)\delta a/\delta C^B$ is the coefficient of the lattice expansion due to changes in the concentration C^B_γ, $C^B_{\gamma'}$ of the minor alloy component B in the corresponding phase (in our case, $B = \mathrm{Al}$ or Nb). The temperature dependence of ε^C is determined by the variation with temperature of the alloy component $C^B(T)$ in the γ and γ' phases.

We employ the all-electron full-potential linearized augmented plane wave (FLAPW) method [15] for high-precision calculations of the equilibrium lattice parameters and bulk moduli of the γ and γ' phases at 0 K with the GGA-corrected exchange-correlation functional [16]. The concentration expansion coefficients β were calculated from the equilibrium volume changes of the 32-atom supercells due to Al (Nb) substitutions in the Ni (Ir) matrix (β_γ) and antisite atoms in the γ' phase ($\beta_{\gamma'}$). The first-principles implementation [11] of linear response theory with ultra-soft pseudopotentials [17] was used for the phonon spectra calculations [18] in Ni, Ir, Ni_3Al and Ir_3Nb (see Ref. [12] for details of the computational procedure).

The calculated temperature dependence of the CTE for Ni, Ni_3Al, Ir and Ir_3Nb is presented in Figure 1 (the linear CTE, $\alpha_l = \alpha/3$, is plotted to allow for direct comparison with experiment). The results of the calculations are in good overall agreement with available experimental data for Ni, Ni_3Al and Ir [19–21], namely within 5% at low temperatures and within 10% (for Ir) or 15% (for Ni and Ni_3Al) at higher temperatures. For Ir_3Nb, the experimental data indicate that the CTEs are close to $8 \times 10^{-6}\ \mathrm{K}^{-1}$ within a broad temperature range [22] – which also agrees well with the results of our calculations. The largest disagreement between the calculated CTEs and the experimental data is for Ni and Ni_3Al at high-temperatures; this is connected with the decreased accuracy of the quasiharmonic approximation, and with the contributions of magnetic degrees of freedom, i.e. spin fluctuations [23], which are beyond the scope of this work. Note that for Ni, the calculations were done both for the spin-polarized and non-spin-polarized cases, where the latter models the state of

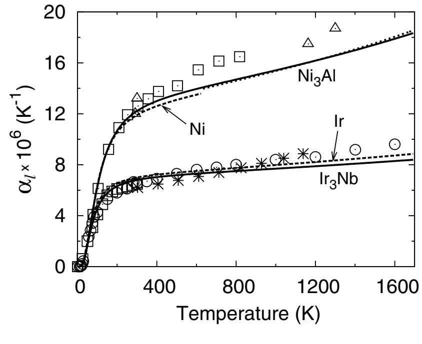

Figure 1. Calculated linear coefficients of thermal expansion for Ni and Ir (dashed lines), and for Ni_3Al and Ir_3Nb (solid lines). Symbols denote the experimental data for Ni [19] (squares), Ni_3Al [20] (triangles), and several sets of data for Ir [21]. For Ni, the results of both spin-polarized (for $T < T_C$) and non-spin-polarized calculations (for $T > T_C$, $T_C = 630$ K) are shown.