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First principles calculations of the effect of Pt on NiAl surface energy

and the site preference of Pt

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Abstract

Pt-modified NiAl is widely used as a coating material in industry.   In this study, the surface energies of NiAl with and without Pt are investigated using first-principles calculations.   The presence of Pt in NiAl takes the surface electronic states to higher energies, resulting in an increased surface energy, which explains some of the beneficial effects of Pt on the oxidation resistance of NiAl.   The electronic structure of NiAl-Pt alloys is also analyzed in terms of the site preference of Pt in NiAl.   Results show that Pt bonds strongly to Al, giving its site preference on the Ni site.

The B2-type intermetallic NiAl has good oxidation resistance, in that it forms a slow-growing Al_2O_3 film at elevated temperatures, which acts as a diffusion barrier to protect the alloy from continued oxidation. Addition of Pt has been known to significantly improve the Al_2O_3 film adhesion [1], such that even under thermal stresses of several GPa, the film reminds in contact with the alloy [2]. For this reason, Pt-modified NiAl is widely used as a coating material on Ni-based superalloys [3].

Recent studies have shown that the major effects of Pt on improving scale adhesion are to reduce the number of pores that form at the oxide/alloy interface [3], and to reduce bond-weakening sulfur impurity in the alloy or coating from segregating to that interface [4,5]. However, there has not been any indication as to why Pt should exert these effects. It is our goal that first principles calculations could provide some insights on the role of Pt in NiAl alloys. This paper reports results on the effect of Pt on NiAl surface energy. Before the surface energy calculations, we first determined the site preference of Pt in NiAl.

The site preference of Pt in NiAl has been studied recently [6]. From thermal conductivity measurements [6], Pt was found to occupy the Ni site, but atom probe results together with a statistical analysis [5] showed that Pt occupies Ni and Al sites, with a slight preference for the Al site. Jiang et al [7], using a statistical-mechanical model based on first-principles calculations, showed that Pt occupies the Ni site, in accordance with their X-ray results [7]. Here we analyze the electronic structure of NiAl-Pt alloys and show that the site preference of Pt can be attributed to a stronger bonding interaction between Pt and Al than that between Pt and Ni. With Pt on the Ni site, we found that it increases the surface energy of NiAl (110), where this would make the formation of NiAl surfaces energetically more expensive.

The full-potential linearized augmented plane waves (FLAPW) method [8] within density functional theory [9,10] was employed to calculate the site preference of Pt in NiAl. Augmented plane wave plus local orbitals (APW+lo) [11] were used for the valence states, and LAPW for other states. A fully relativistic calculation was performed for the core states, whereas the valence states were treated in a scalar relativistic scheme. The generalized gradient approximation (GGA) exchange correlation functional [12] were employed. Calculations were performed for pure NiAl and NiAl alloys containing 6.25, 12.5 and 18.75 at.% Pt. The Pt atoms are presumed to be located in ordered arrays, so that the investigated alloys corresponded to the following chemical formulae: Ni_7Al_8Pt, Ni_3Al_4Pt and $Ni_5Al_8Pt_3$ for the (Ni,Pt)Al alloys, and Ni_8Al_7Pt, Ni_4Al_3Pt and $Ni_8Al_5Pt_3$ for the Ni(Al,Pt) alloys. The three supercells for the (Ni,Pt)Al alloys are shown in Figs. 1a-c. Supercells for the Ni(Al,Pt) alloys are similar to these, but with the Ni and Al positions in Fig. 1 reversed. Any effect on the total energy from lattice relaxation was neglected, because it has been shown to be small (less than 1 mRy/atom) [13,14] in comparison to that from atom substitution.
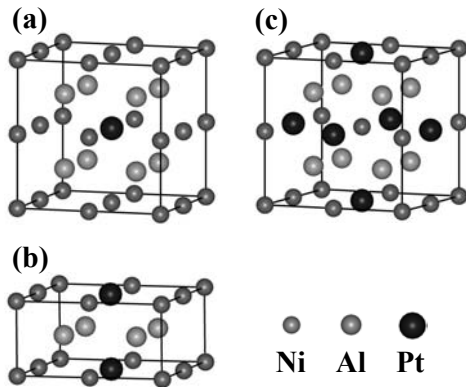

Fig. 1. Supercells for different amounts of Pt additions to NiAl. (a) Ni_7Al_8Pt (6.25 at.% Pt); (b) Ni_3Al_4Pt (12.5 at.% Pt); (c) $Ni_5Al_8Pt_3$ (18.75 at.% Pt).

Similar to the approach used on site preference, we estimated the surface energies of NiAl by total energy calculations, where we used the linear combination of atomic orbitals method (LCAO), as implemented in the SIESTA code [15,16], because this method is computationally more efficient in dealing with defects. The local density approximation (LDA) exchange correlation functional [17] was employed. The pseudopotentials were constructed considering relativity and core charge correction and were tested with bulk NiAl and Pt. The double-ζ plus polarization (DZP) basis functions were used in the calculations. In order to simulate a surface, we considered supercells consisting of periodically repeated crystal slabs (8 atomic layers and 32 atoms in total) separated by vacuum 10 Å wide. Two equivalent surfaces were thus created above and below each crystal slab. Surface energies were calculated by substracting the energies of supercells without vacuum from those with vacuum. In order to obtain more accurate energies, positions of all the atoms were allowed to relax untill the interatomic forces were less than 0.005 eV/Å^{-1}.

By fitting the Birch-Murnaghan equation of state [18] to the total energies as a function of unit cell volume, the equilibrium lattice constant and the bulk modulus of NiAl were found to be 0.2892 nm and 160 GPa, respectively, which are very close to their experimental values of 0.2887 nm and 166 GPa [19]. The slight overestimate of lattice constant and underestimate of bulk modulus are typical for GGA calculations [20]. The calculated lattice constant was used to construct the supercells of NiAl alloys.

The heats of formation of NiAl alloys are plotted as a function of Pt concentration, as shown in Fig. 2. For alloys with Pt occupying Ni sites, the heats of formation decrease with increasing Pt. On the other hand, the heats of formation of alloys with Pt occupying the Al sites increase with increasing Pt. The result clearly

shows that Pt has a preference to occupy the Ni positions, and this conclusion is consistence with the experimental and calculation results reported in refs. [6,7].
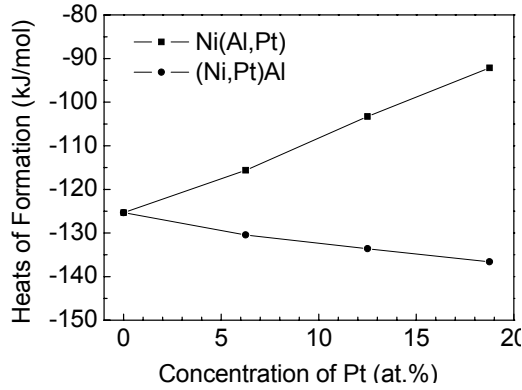

Fig. 2. Heats of formation for NiAl, Ni(Al,Pt) and (Ni,Pt)Al alloys. The heats of formation of (Ni,Pt)Al decrease with increasing Pt, indicating that Pt tends to occupy the Ni site.

In the following, we analyze the electronic structure of the (Ni,Pt)Al and Ni(Pt,Al) systems and show that the site preference of Pt in NiAl is due to a stronger bonding interaction between Pt and Al than that between Pt and Ni. We reveal the bonding interactions using partial (or site-projected) densities of states (DOS) and the difference charge densities, which describes the reordering of electrons upon the formation of chemical bonds between atoms. In general, a large overlap in DOS's of neighboring atoms indicates a strong hybridization between the orbitals of the atoms and thus a strong bonding interaction; likewise, high charge accumulation between neighboring atoms also indicates strong bonding. The partial DOS's and difference charge densities of NiAl are shown in Fig. 3. When Pt occupies the Ni sites, there is a significant overlap between the partial DOS's of Pt and Al, and the electrons accumulate to the interatomic areas, indicating a strong bonding interaction. In contrast, DOS overlapping between Pt and Ni and the charge accumulation between atoms are much less when Pt occupies the Al sites, suggesting a weaker bonding interaction, which

explains why Pt has a tendency to occupy the Ni sites.
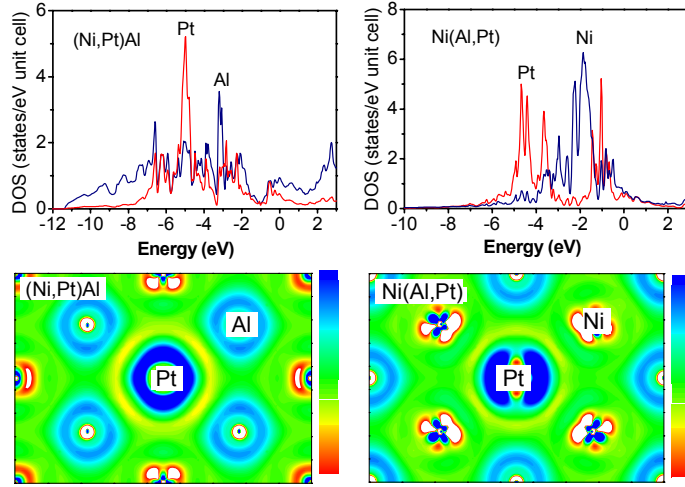

Fig. 3. Densities of states (DOS) and the difference charge densities of NiAl containing Pt. When occupying the Ni sites, Pt has a strong bonding interaction with the Al neighbors, as indicated by the large overlap between their partial DOS and the charge accumulation to the areas between Pt and Al. In contrast, the bonding interaction between Pt and Ni is much weaker when Pt occupies the Al sites. The Fermi level lies at 0.

We calculated energies of the (110) surface of NiAl with and without Pt. Two types of surface models were considered for NiAl containing Pt. In Model I, Pt atoms stay inside the crystal; in Model II, Pt atoms occupy surface sites. In light of the site preference results described above, we only considered models with Pt occupying the Ni sites. There are two Pt atoms in each model; with 32 atoms in total, this gives a composition of $Ni_{0.44}Al_{0.5}Pt_{0.06}$ in atomic percent.

The calculated energy of the (110) surface of pure NiAl is 1.80 J/m^2. This value is close to those obtained previously, at 1.79 J/m^2 [21] and 1.87 J/m^2 [22]. When Pt is added and stays inside the bulk (Model (Ni,Pt)Al-I), the surface energy increases to 2.44 J/m^2. In Model (Ni,Pt)Al-II, where all the Pt stays on the surface, the energy increase is

mitigated and the surface energy is reduced to 1.85 J/m^2. This lowered energy suggests a tendency for Pt to segregate to the NiAl surface, which was observed experimentally [4], where upon heating, Pt in Ni-37Al-5Pt and Ni-50Al-10Pt (all at%) segregated to the alloy surfaces up to about half a monolayer.

Figure 4 shows, for NiAl and Pt-doped NiAl, surface-projected densities of states, which are DOS's summed over atoms at the surfaces and hence reveal features of the surface states. As can be seen, the energies of the local electronic states at the surface shift toward higher energy upon Pt doping, which is another verification that Pt addition increases NiAl surface energy.
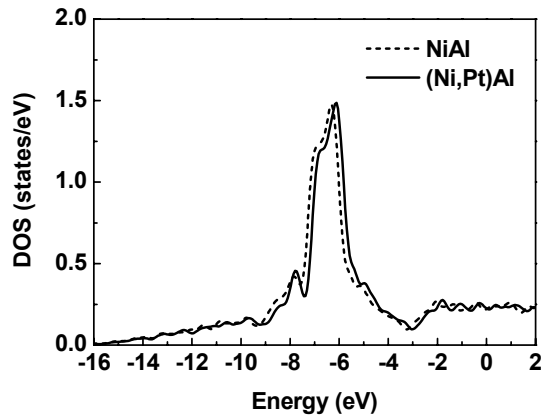

Fig. 4. The surface-projected densities of states of NiAl and (Ni,Pt)Al. The Pt atoms reside inside the bulk. The Fermi level lies at 0.

The increased surface energy of (Ni,Pt)Al, especially when Pt is present in the alloy, as in our model I, explains why Pt is found to segregate to NiAl surfaces when NiAl is heated in vacuum [4,23]. More importantly, in terms of oxidation and the adherence of oxide films that form above NiAl and NiPtAl alloys, this result can explain why the presence of Pt in NiAl prevents, or greatly reduces, the number of voids at the Al$_2$O$_3$/alloy interface [3,23]. It has been demonstrated repeatedly (see for example Ref. 3)

that the major effect of Pt in coatings is to reduce the number of voids that form at the oxide/alloy interface. Our own work [24] performed on Ni-50Al and Ni-50Al-3Pt alloys have also shown that after oxidation at 1000°C for 26 hrs, the void density at the Al_2O_3/alloy interface of the former was $(2.2\pm1.2)\text{x}10^{-5}/\mu\text{m}^2$, while that of the latter was an order of magnitude lower, $(2.9\pm2.6)\text{x}10^{-6}/\mu\text{m}^2$. The energy barrier to nucleate a void, according to the classical theory of hetero-nucleation [25], scales with $(\gamma_m)^3$, where γ_m is the alloy surface energy. Therefore, if adding Pt increases the alloy surface energy, it will certainly increase the void nucleation energy, hence making void formation more difficult.

In summary, we have investigated the electronic structure of NiAl containing Pt, and the effect of Pt on the surface energy of NiAl (110). It was found that the electronic states of Pt hybrid with those of Al more than those of Ni, giving the site preference of Pt on the Ni site. The surface energies of NiAl (with and without Pt alloying) have also been calculated. It was found that the alloying of Pt in NiAl pushes the local electronic states of the surface to higher energies, giving rise to an increased surface energy.

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