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N.B.: When citing this work, cite the original article.

Original Publication:

A V Ponomareva, Yu Kh Vekilov and Igor Abrikosov, Effect of Re content on elastic properties of B2 NiAl from ab initio calculations, 2014, Journal of Alloys and Compounds, (586), S274-S278.

<http://dx.doi.org/10.1016/j.jallcom.2012.12.103>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-102967>

Effect of Re content on elastic properties of B2 NiAl from *ab initio* calculations

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The effect of substitutional alloying of Re on elastic properties of B2 NiAl has been studied using first-principles electronic-structure calculations by the exact muffin-tin orbitals method and the coherent potential approximation. Our calculations have shown that elastic constants C_{12} , C_{44} and bulk modulus B of $(Ni_{1-x}Re_x)Al$ alloys increase with Re composition almost linearly, but concentration dependence of elastic constants C_{11} , Young modulus E , shear modulus G , G/B ratio and the Cauchy pressure P_C is strongly nonmonotonously and has peculiarities near the concentration $x=30$ at. % Re. Analyzing the density of states and Fermi surface sections we establish a direct connection between the behavior of the elastic constants of $(Ni_{1-x}Re_x)Al$ alloys and changes in the interatomic bonding and Fermi surface topology.

I. INTRODUCTION

The intermetallic compound B2 NiAl has high melting temperature ($T=1911$ K) [1], low density, good oxidation resistance and therefore it widely used in aerospace applications. Low temperature brittleness inherent to B2 NiAl is the main limitation for the use of this intermetallic compounds as a high temperature structural material. Various techniques such as fiber reinforcement, precipitation strengthening, microalloying and macroalloying can improve room-temperature ductility by a formation of specific microstructure [2], [3], [4], [5]. In our previous paper [6] we analyzed substitutional alloying on brittle vs. ductile behavior of B2 NiAl-X ($X = \text{Sc, Ti, V, Cr, W, Re, Co}$) alloys examining at atomic level the role of interatomic bonding in the ductility enhancement. We studied the site preference of

impurities X, elastic constants C_{11} , C_{12} , C_{44} , bulk modulus B , the Young's modulus E , the shear modulus G , G/B ratio and the Cauchy's pressure ($P_C = C_{12} - C_{44}$) for NiAl-X alloys in the dilute limit, as well as for some nondilute systems to estimate the trend of changes in the elastic properties. Our results demonstrated that Re has a strong preference for the Ni sublattice in NiAl in good agreement with available experimental and theoretical data [7], [8].

We predicted that the addition of W, V, Ti, and Re atoms could yield improved ductility for B2 NiAl-X alloys without significant changes in the macroscopic elastic moduli. At the same time we found that concentration dependence of C_{11} , Young's modulus E , shear modulus G , G/B ratio and the Cauchy pressure P_C in $(Ni_{1-x}Re_x)Al$ alloys has strongly nonmonotonic character. For this reason we carried out a more detailed study of the effect of Re on elastic properties of B2 NiAl. Investigating the density of states and Fermi surface cross sections we demonstrate that the anomalies in the behavior of the elastic constants have an electronic origin associated with the disappearance of antibonding e_g states of nickel.

II. DETAILS OF CALCULATION

The calculations were performed using the exact muffin-tin orbital (EMTO) method including the full charge-density technique [9] within the coherent potential approximation (CPA) for modeling substitutionally disordered alloys [10]. The charge density was calculated within the local density approximation (LDA) and the total energy was obtained using the generalized gradient approximation (GGA) [11]. We used a basis set including valence *spdf*- orbitals and 29x29x29 grid of k-points. The energy integration was carried out in the complex plane using a semi-elliptic contour comprising 24 energy points. In our CPA calculation we included the screening contribution to the electrostatic potential and energy to take into account the effect of charge transfer between the alloy component using screening constants [12] obtained by the locally self-consistent Greens-function (LSGF) method [13]. The calculations of total and projected densities of states (DOS) for B2 $(Ni_{1-x}Re_x)Al$ were performed using the Korringa-Kohn-Rostocker (KKR) method within the atomic sphere approximation (ASA) [14], [15]. The Fermi surface cross sections for the alloys were obtained using the peak positions of the Bloch spectral density function (BSD) [16], which was calculated on the grid of k-points lying in Γ XM and XM Γ M planes of the Brillouin zone.

For cubic crystals there are three independent elastic constants C_{11} , C_{12} , C_{44} [17]. To determine the tetragonal ($C' = (C_{11} - C_{12})/2$) and the trigonal (C_{44}) elastic constants we calculate the internal energy response on a volume-conserving orthorhombic and monoclinic distortions [18] respectively. Then the two cubic elastic constants C_{11} and C_{12} are splitted from the relation between C' and bulk modulus $B = (C_{11} + 2C_{12})/3$. To estimate elastic moduli for polycrystalline materials, the Voigt-Reuss-Hill (VRH) approximation is used [17]. Brittle vs. ductile behavior of alloys is analyzed by using values of the Cauchy's pressure $P_C = (C_{12} - C_{44})$ [19] and the Pugh's relationship (G/B ratio) [20] phenomenologically linking the plastic properties of materials with their elastic moduli.

If in a material the Cauchy relation $C_{12} = C_{44}$ is fulfilled then the interatomic forces are central-symmetric and the total energy may be reasonably described by the pair potential approximation. But for metals and covalent solids the Cauchy relation is not satisfied experimentally. In these cases we must take into account the directionality of bonds via many-body potentials [21] and the angular character of atomic bonding relating to the brittle or ductile properties of materials could be described by the Cauchy pressure $P_C = (C_{12} - C_{44})$ [19]. Therefore for covalent materials where the material resistance to a shear (C_{44}) is much stronger than a volume change (C_{12}), Cauchy pressure $P_C = (C_{12} - C_{44})$ should be negative (vice versa for metallic materials). Another empirical representation which may be considered as a measure of the ductility is G/B ratio [20]. Bulk modulus B is associated with the resistance to bond-length change and shear modulus G corresponds to bond-angle change. Therefore, if $G/B < 0.5$ a material behaves in a ductile manner, while if $G/B > 0.5$ a material should be brittle and the higher the value of G/B , the more brittle the material should be. Thus, the use of these physical criteria allows to estimate brittle vs. ductile behavior in alloys and compounds [22], [23].

III. RESULTS AND DISCUSSION

Following recipe of Ref. [24] we have established that Re at low concentration should have a strong preference for Ni sublattice [6]. Our results are in good agreement with available experimental data. Indeed, using the atom probe field ion microscopy (APFIM) [7] it was found that Re had a strong preference for the Ni sublattice in NiAl. In principle, a reversal of the site preference could occur with increasing temperature and concentration [6] but as

demonstrated in Ref. [8] this was more common for additions which did not have any site preference and were randomly distributed between Al and Ni sites. So we consider Re only on Ni sublattice.

To analyze alloying effect of Re on the elastic properties of NiAl we calculate the elastic constants C_{11} , C_{12} , C_{44} , Young's modulus E and the shear modulus G of NiAl-Re alloys (Fig. 1). It is found that for $(Ni_{1-x}Re_x)Al$ alloys the well-known criteria for mechanically stable cubic crystals are satisfied, that is $(C_{11} - C_{12}) > 0$, $C_{44} > 0$. For NiAl the good correlation between our theoretical and experimental lattice parameter, bulk modulus, elastic constants C_{11} and C_{44} is found (Table I). C_{12} obtained in our calculation is slightly smaller than the experimental result so the Pugh ratio (G/B) is overestimated in comparison with the experimental data. On the contrary Cauchy pressure is underestimated. But though in our calculations NiAl turns out to be "more brittle" than it actually is, we can still analyze and qualitatively estimate the Re additions effect on the ductility of B2 NiAl. For more details see Ref. [6].

From Fig. 1 we see that C_{12} , C_{44} and bulk modulus B are increasing functions at all concentrations although C_{12} and B have a slightly lower rate of increase at low Re concentrations. On the other hand, C_{11} decreases up to a concentration about 30 % of Re and then substantially increases. The shear modulus G and Young's modulus E almost do not change their values at low Re concentration, and then decrease sharply near 30 at.% Re and finally increase monotonously up to their original values. The G/B ratio slightly increases and then decreases with increasing rhenium content. The Cauchy pressure P_c becomes less positive at low Re concentration and then increases. Thus, using the Pugh criterion and the values of the Cauchy pressure one could expect an increase in ductility of the alloy for Re fraction above 30 at.%. (or the Re content 15 at.%.)

In order to understand the reason for the non-monotonous change of elastic properties of NiAl-Re alloys we analyze the electronic density of states (DOS) and Fermi Surface (SF) cross-sections near the singularity. Figs. 2 and 3 show the calculated total and projected DOS for B2 NiAl and NiAl-Re alloys, respectively. From Fig. 2 we can see that the major contribution to DOS in NiAl around E_f comes from narrow d-band of Ni, which consists of the so-called nonbonding [25] ($t_{2g} + e_g$ located from -0.25 to -0.1 Ry) and antibonding (e_g close to E_F) states, separated by a pseudogap. Note, that the t_{2g} (d_{xy}, d_{yz}, d_{zx}) electrons are directed toward the eight nearest neighbors in the bcc lattice, e.g. in NiAl toward Al and Ni

located on different sublattice of B2 structure. The e_g ($d_{x^2-y^2}$ and d_{z^2}) electrons are directed toward the next-nearest neighbors atoms located on the same sublattice (Ni-Ni and Al-Al). The addition of Re leads to the smearing of total DOS due to the increase of disorder on Ni sublattice (Figure 3, upper panels). The main effect observed at low Re concentration is that the peak corresponding to Ni e_g states begins to decrease (Fig. 3, $(Re_{10}Ni_{90})Al$ and $(Re_{20}Ni_{80})Al$) and at about 30 at.% Re it disappears (Fig. 3, $(Re_{30}Ni_{70})Al$). Simultaneously, C_{11} decreases and reaching its minimum causes a drop in G and E moduli. In the same concentration interval the Pugh criterion and the values of the Cauchy pressure indicate a possibility for a slight decrease in ductility. Also, this indicates that the reduction of the Ni concentration increases a partial covalent component in the bonding, although the metallic type of bond still dominates ($C_{12} > C_{44}$, Fig. 1). A small dip in P_c curve is also related to the decrease of occupation of Ni e_g states. Indeed in B2 NiAl t_{2g} and e_g states are almost fully occupied (Fig. 2), and therefore there is no specific directionality in the distribution of electron density. In $(Re_xNi_{1-x})Al$ at low x e_g states of Ni start to disappear. Thus electron density distribution becomes more directional. With further increase of Re concentration, d-electrons of Re, which occupy a wide band and have large spatial extension begin to provide an increase of the bond strength. So C_{11} , the shear modulus G and Young's modulus E start to increase. We can see that with increasing Re concentration central peak is smeared out, broadens and shifts to the right as compared to the NiAl case. Such delocalization of electrons increases metallic component of bonding at $x > 30$ at.% Re. At the same time, a type of interactions remains mixed: the increasing value of C_{44} indicates the presence of covalent component of bonding. We can see strong hybridization between t_{2g} states of Re and p-electrons of Al which is much stronger than in the case of d-electrons of nickel. This strengthens covalent component of bonding and enhances the shear resistance.

Finally in Figure 4 we present fragments of Fermi surface cross sections by ΓXMX and $XMRM$ planes in $(Re_xNi_{1-x})Al$ alloys with $x=0, 10, 20, 30, 50$ at.% Re. The figures allow us to see the evolution of the Fermi surface (FS) topology with increasing Re concentration. The ΓXMX and $XMRM$ sections of the Fermi surface show a hole pocket at the center of the zone and electron sheets around the perimeter (Fig.4, ΓXMX plane, upper panel), as well as small fairly spherical hole pockets around R points of the Brillouin zone (BZ) (Fig.4, $XMRM$ plane, lower panel). At small Re concentration peaks of Bloch spectral function (BSF) are smeared out and the electronic parts of the Fermi surface sheets become smaller

(Fig.4, $(Re_{10}Ni_{90})Al$). At $x=20$ at. % Re the sheet touches the BZ boundary near the X point forming a neck (Fig.4, $(Re_{20}Ni_{80})Al$). Also in the FS of $(Re_{20}Ni_{80})Al$ a formation of a new electron sheet around the Γ point begins. At $x=30$ at.% Re, when e_g peak of the DOS vanishes, a part of the original electronic sheet near XM line disappears in Γ XM plane, and only the electronic pockets around the M point remain. At the same time a new cavity near the Γ point with arms along Γ X direction grows. So changes in the topology of Fermi surface take place also near 30 at. % of Re.

IV. CONCLUSION

We have investigated effect of rhenium content on the elastic properties and on ductility enhancement of $(Ni_{1-x}Re_x)Al$ alloys. We have shown that singularities of DOS and BSF peaks are observed at the same concentrations as the peculiarities in the behavior of the elastic properties of NiAl-Re alloys. We have linked this correlation with the disappearance of antibonding e_g states of nickel at low Re concentration. Metallic-covalent (mixed) bonding in the alloys together with a growing metallic component with increasing Re concentration leads to the fact that all three elastic constants C_{11} , C_{12} , C_{44} increase at $x > 30$. Compared with elastic constants of B2 NiAl C_{11} , C_{12} , C_{44} increase by about 15%, 25% and 50%, respectively. Analyzing the calculated values of the Cauchy pressure and the Pugh criterion one can expect an increase in the ductility of the alloy for Re fraction beyond 30 at. %.

V. ACKNOWLEDGEMENTS

Financial support from RFBR (Grant # 10-02-00-194a), from the Ministry of Education and Science of the Russian Federation within the framework of Program "Research and Pedagogical Personnel for Innovative Russia (2009-2013)" (project no. 14.37.21.0890 of 10.09.2012), as well as from the Swedish Foundation for Strategic Research (SSF) program SRL10-0026 is acknowledged. Calculations are performed on the Joint Supercomputer Center of RAS (Moscow, Russia) and National Supercomputer Centre (NSC) in Linköping,

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FIG. 1: (Color online) Calculated elastic constants C_{11} , C_{12} , C_{44} , Pugh G/B ratio, Cauchy pressure $P_C = (C_{12} - C_{44})$, shear moduli G , bulk moduli B , and Young's moduli E of NiAl-Re alloys.

FIG. 2: (Color online) Calculated total and projected densities of states for B2 NiAl. The Fermi level is set to zero.

TABLE I: Young's modulus (E), shear modulus (G) of B2 NiAl. The experimental values for NiAl [26] are given in parentheses.

a, Å	C_{11} , GPa	C_{12} ,GPa	C_{44} , GPa	B,GPa	E, GPa	G, GPa
2.89	233	121	114	159	218	86
(2.89)	(212)	(143)	(112)	(166)	(184)	(70)

FIG. 3: (Color online) Calculated total and projected densities of states for B2 $(Re_xNi_{1-x})Al$ alloys. Shadowed area correspond to DOS of B2 NiAl.

FIG. 4: (Color online) Γ XM and XM Γ sections of Fermi surface in $(Re_xNi_{1-x})Al$ alloys with $x=0, 10, 20, 30, 50$ at.% Re.

NiAl

 $(\text{Re}_{10}\text{Ni}_{90})\text{Al}$ $(\text{Re}_{20}\text{Ni}_{80})\text{Al}$ $(\text{Re}_{30}\text{Ni}_{70})\text{Al}$ $(\text{Re}_{50}\text{Ni}_{50})\text{Al}$