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Alloying effect on the ideal tensile strength of ferromagnetic and paramagnetic bcc iron

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ABSTRACT

Using *ab initio* alloy theory formulated within the exact muffin-tin orbitals theory in combination with the coherent potential approximation, we investigate the ideal tensile strength (ITS) in the [001] direction of bcc ferro-/ferrimagnetic (FFM) and paramagnetic (PM) $Fe_{1-x}M_x$ (M = Al, V, Cr, Mn, Co, or Ni) random alloys. The ITS of ferromagnetic (FM) Fe is calculated to be 12.6 GPa, in agreement with available data, while the PM phase turns out to posses a significantly lower value of 0.7 GPa. Alloyed to the FM matrix, we predict that V, Cr, and Co increase the ITS of Fe, while Al and Ni decrease it. Manganese yields a weak non-monotonic alloying behavior. In comparison to FM Fe, the alloying effect of Al and Co to PM Fe is reversed and the relative magnitude of the ITS can be altered more strongly for any of the solutes. All considered binaries are intrinsically brittle and fail by cleavage of the (001) planes under uniaxial tensile loading in both magnetic phases. We show that the previously established ITS model based on structural energy differences proves successful in the PM Fe-alloys but is of limited use in the case of the FFM Fe-based alloys. The different performance is attributed to the specific interplay between magnetism and volume change in response to uniaxial tension. We establish a strong correlation between the compositional effect on the ITS and the one on the shear elastic constant C' for the PM Fe-alloys and briefly discuss the relation between hardenability and the ITS.

1. Introduction

The mechanical properties of engineering materials are of primary interest because they determine the ability to withstand loads without failure. High strength and good ductility are characteristic of metallic materials. Both properties are controlled by the occurrence or propagation of dislocations, cracks, grain boundaries, and other microstructural defects. In the absence of defects, the ideal strength of a material is the strength at which a perfect crystal itself becomes unstable with respect to a homogeneous strain. This strength defines the intrinsic upper bound strength and has been accepted as an essential mechanical parameter of single crystal materials [1–3].

The ideal strength is involved in the theory of fracture and the nucleation of defects [3–6]. The local inhomogeneous stress distribution close to the tip of a crack, and thus the transgranular cleavage behavior of materials, is related to the ideal tensile strength (ITS) [3,4]. The stress necessary for the nucleation of a dislocation loop can be identified with the ideal shear strength [4,7]. The ideal strength determines whether a material is intrinsically brittle or ductile [7,8]. In the former case, the tensioned lattice fails by cleavage of interatomic planes in the direction perpendicular to the applied load. Even under strict uniaxial tensile loading, an immaculate crystal may, however, not cleave but rather yield under the circumstance that a shear instability along another direction occurs first. This scenario defines intrinsically ductile

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materials and occurs, for example, for the bcc metals V and Nb loaded along the [001] direction, where a shear instability is activated in the {112}⟨111⟩ slip system before the cleavage strength of the (001) planes is reached [2,9].

Further, the ideal strength is relevant in situations where dislocation activity is suppressed or for systems with very low defect density. The plastic deformation behavior of a multicomponent solid solution based on the Ti–Nb binary ("gum metals") is believed to be governed by the ideal strength rather than conventional dislocation mobility [10]. The second mentioned situation is frequently met in the deformation behaviors of filamentary crystals or graphene sheets, the mechanical properties of nanowires and nanopillars, and in nanoindentation experiments on thin films and nanostructures [3,11–14]. In some cases the measured maximum strength approximates the theoretically predicted ideal strength. For example, the maximum shear strength of Mo has been measured by nanoindentation on single-crystalline nanopillars [12]. The experimental value is 15.8 – 16.7 GPa, which is close to the theoretical prediction 17.6 – 18.8 GPa [15].

In recent years, considerable attention has been paid to the theoretical determination of the large-strain response and the ITS of elemental solids and intermetallic compounds by *ab initio* methods [2,16–20].

Among the bcc metals, elemental Fe as the basic ingredient in steel received great scientific interest [1,9,21–26]. The picture that has evolved for FM ordered Fe is that the [001] direction is the weakest one in response to uniaxial stress. The deformation is governed by a primary tetragonal deformation path, but a bifurcation to a secondary orthorhombic deformation path, triggered by a shear instability, occurs after the ITS on the primary path is reached. Accordingly, bcc Fe strained along the [001] direction fails by cleavage as opposed to V and Nb [2,9]. If the failure mode in tension were restricted to cleavage of the (001) plane, the ITS of Fe turned out to be the lowest among all bcc transition metals [1,2,21,27].

Alloying plays an essential role in material and steel design as the alloy properties are usually superior to those of the pure constituents. As regards the ideal strength, tuning its magnitude and the ductile versus brittle failure mode are of obvious interest. The *ab initio* description of the ITS in substitutional alloys is, however, rather limited. One early attempt [10] employed the virtual-crystal approximation (VCA) to study the ITS of the Ti–V binary.

The applicability of the VCA is by construction restricted to binary solid-solutions composed of neighboring elements in the periodic table, which covers a tiny fraction of the physically interesting cases. A more general approach to multi-component random solid solutions is given by the coherent-potential approximation (CPA) [28]. Recently, Li et al. [29] investigated the composition-dependent ITS of bcc V–Cr–Ti solid solutions demonstrating the applicability of the CPA for this type of calculations. The V–Cr–Ti ternary is presently considered as one of the primary structural materials for the first wall and blanket structure of future fusion reactor [30,31].

In a recent study [25], we focused on the anomalously low ITS of Fe compared to other bcc transition metals, which can partially be ascribed to its weak FM behavior. By means of analyzing electronic structure and magnetism, we found that a small amount of alloying addition can turn the weak FM behavior in the Fe host more stable against structural deformations, resulting in anomalous alloying trends. The purpose of this paper is to give an in-depth investigation of the ITS of bcc Fe-based alloys in magnetically ordered [ferro-/ferrimagnetic (FFM)] and disordered [paramagnetic (PM)] phases and to establish a relation to other mechanical properties. Our results give useful limits on the attainable combination of strength and toughness of Fe-based alloys and provide a consistent theoretical guide to further optimization of the composition of Fe-based alloys in multiscale-materials design [6,32].

2. Computational method

2.1. Total energy calculations

The *ab initio* approach used in this work is based on density-functional theory (DFT) [33]. We adopted the generalized-gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) [34] functional to describe exchange and correlation, which is well known to give the correct FM bcc ground state for Fe. For the main part of the work, the Kohn-Sham equations were solved using the exact muffin-tin orbitals (EMTO) method [35,36]. The problem of chemical disorder was treated within the CPA and the total energy was computed via the full charge-density technique [28,37,38]. We point out that, due to its single-site nature, the CPA describes a homogeneous random solid solution and omits the inter-dependence between magnetic state and local environment. The magnetic state of the presently considered solute atoms in the FM Fe host is determined by the coherent Green function rather than by actual neighboring atoms.

The EMTO method is an improved screened Korringa-Kohn-Rostoker method [35], where the full potential is represented by overlapping muffin-tin potential spheres. The potential is spherically symmetric inside these spheres and constant in between. By using overlapping spheres, one describes more accurately the exact crystal potential compared to conventional muffin-tin methods. The accuracy of the EMTO method for the equation of state and elastic properties of metals and alloys was demonstrated in a number of previous works [29,39,40] and is assessed for the ITS of Fe in Sec. 3.1.

The PM state well above the magnetic transition temperature (where the magnetic short range order effects are negligible) was described by the disordered-local moment (DLM) model [41] in the CPA framework. Within the DLM picture, PM Fe and $Fe_{1-x}M_x$ binary alloys were simulated as a binary alloy Fe↑ Fe↓ and a quaternary $(Fe\uparrow\ Fe\downarrow)_{1-x}(M\uparrow\ M\downarrow)_x$ alloy, with an equal amount of spin-up (↑) and spin-down (↓) alloy components, respectively.

Additional test calculations for FM Fe were performed with the full-potential local orbital scheme FPLO-9 [42], the projector-augmented wave (PAW) method as implemented in VASP release 5.3.3 [43], and the full-potential linearized augmented-plane wave (FP-LAPW) code ELK version 2.2.9 [44] using PBE. The FPLO calculations were performed in the scalar-relativistic approximation. Convergence of numerical parameters, in particular integration meshes and the basis, was carefully checked. Linear-tetrahedron integrations with Blöchl corrections were done on a $24 \times 24 \times 24$ mesh in the full Brillouin zone and the valence basis comprised 3*d*, 4*spd*, and 5*s* states augmented by Refs. 5*pd* and 6*s* polarization states. The ELK scalar-relativistic calculations employed the default valence basis set. The muffin-tin radius was fixed to 2.100 Bohr for all calculations ensuring that there is no overlap between neighboring spheres. Brillouin zone integrations were done on a $18 \times 18 \times 18$ *k*-point mesh smeared by a Fermi-Dirac function and a small smearing parameter 5×10^{-4} Ha. The augmented plane-wave cutoff was set to 9.2 Ha, the angular momentum cut-off for the APW functions was set to 10, and the angular momentum cut-off the outer-most loop in the Hamiltonian and overlap matrix setup were set to 8 to ensure converged results. All VASP calculations were done with the default *spd*-valence state PAW potential and the global 'Accurate' precision switch. Total energies and the computed stress tensor were found converged for a plane-wave cutoff $\geq$500 eV. The unit cell was relaxed until residual stresses perpendicular to the applied force were smaller than 1×10^{-3} eV/Å.