Main research results of the 84078 OTKA project

1. Elastic properties of alloys, occasionally including those of the alloying elements
2. Various Steels, which are nowadays complicated alloys
3. Surface properties of composites, including surfaces and interfaces of bulk materials as well as nanocomposites of overlayer systems
4. Magnetic properties of bulk materials
5. Mechanical properties of alloys systems, including High Entropy Alloys (HEA)

Some publications were related to other theoretical and methodological advancemets wich were necessarily in the pathway of the research.

1. Elastic properties of alloys, occasionally including those of the alloying elements

The one of the most interesting result of this research topic is the interplay between magnetism and surface stress. Because of the increased electron density within the surface layer, metal surfaces are generally expected to have tensile surface stress. Using first-principles density functional calculations, we demonstrated that in magnetic 3d metals surface magnetism can alter this commonly accepted picture. We find that the thermodynamically stable surfaces of chromium and manganese possess compressive surface stress. The revealed negative surface stress is shown to be ascribed to the enhanced magnetic moments within the surface layer relative to the bulk values.

By using density-functional theory in combination with the coherent-potential approximation and the disordered local magnetic moment picture, we also demonstrated that the competing high-temperature cubic phases of paramagnetic Fe correspond to two distinct total energy minima in the tetragonal (Bain) configurational space. Both the face-centered-cubic (fcc) and the body-centered-cubic (bcc) lattices are dynamically stable, and at static conditions the fcc structure is found to be the thermodynamically stable phase. The theoretical bcc and fcc bulk parameters are in agreement with the experimental data. Due to the shallow energy minimum around the bcc structure, increasing temperature is predicted to stabilize the bcc phase against the fcc one, in line with the phase diagram of Fe.

We also studied the elastic properties of Fe-, Co-, and Cu-doped Ni2MnGa alloys, both the doping preferences, and their effect on the ellastic properties. We found that Fe atoms prefer to occupy the Mn and Ni sublattices even in Ga-deficient alloys; Co has strong tendency to occupy the Ni sublattice in all types of alloys; Cu atoms always occupy the sublattice of the host elements in deficiency. For most of the alloys with stable site occupations, both the electron density n and the shear modulus C′ can be considered as predictors of the composition dependence of the martensitic transition temperature of the alloys. The physics underlying the composition-dependent stress tensors are discussed based on the calculated density of states.

We also studied effect of Cr and Ti on the fundamental mechanical properties of V-Cr-Ti alloys h using the all-electron exact muffin-tin orbitals method in combination with the coherent-potential approximation. The static lattice constant and elastic parameters have been calculated for the body-centered-cubic V-Cr-Ti random solid solution as a function of composition. Our theoretical predictions are in good agreement with the available experimental data. Alloys along the equicompositional region are found to exhibit the largest shear and Young’s modulus as a result of the opposite alloying effects obtained for the two cubic shear elastic constants. The classical solid-solution hardening (SSH) model predicts larger strengthening effect in V-Ti than in V-Cr. By considering a phenomenological expression for the ductile-brittle transition temperature (DBTT) in terms of Peierls stress and SSH, we showed that the present theoretical results can account for the variations of DBTT with composition.

Improving the strength and ductility of materials is an eternal challenge in materials design. The strength of most structural materials is determined by the complex micro-structural properties associated with defects, such as vacancies, dislocation networks, and grain boundaries. A realistic description of strength involves accurate modeling of the dislocation activity for long periods of time, which is an enormous task for ab initio methods. However, the mechanical strength of solids is bounded from above and the limit is referred to as the ideal strength. The ideal tensile strength (ITS) is the stress at which a perfect crystal in tension becomes unstable with respect to an infinitesimal homogeneous strain. The ITS has been accepted as an essential intrinsic mechanical parameter of single crystal materials. The ideal strength connects aspects of chemical bonding and crystal symmetry with the mechanical properties of ideal lattices, such as the failure mode or common slip systems and is involved in fracture theory and the nucleation of defects. The ideal strength can be approached in systems with very low defect density like whiskers or thin films, and in graphene. Against this background, several fundamental issues call for in-depth investigation: Why is the ITS of Fe so much lower than those of Mo and W? Can the ideal strength of Fe be increased by alloying? Will the failure mode in Fe alloys be changed? What role does magnetism play in the attainable ITS of Fe and its alloys? we applied ab initio alloy theory to shed light onto the above questions. Studying pure Fe and six Fe-based binary alloys, we predict that the ITS of Fe can be significantly altered by alloying. We demonstrated that alloying Fe with frequently utilized solutes with concentrations up to 10% is an effective means to alter the intrinsic upper bound of the mechanical strength in tension along (001). Vanadium turns out to be one of the most efficient alloying agents producing an enhancement of the ideal tensile strength by 2.3% per atomic percent of V. All binary systems considered here fail by cleavage under (001) loading. The predicted ITSs form a consistent starting point for establishing useful limits on the attainable combination of strength and toughness of Fe-based alloys. We have shown that both the anomalously low ITS of pure Fe, in comparison with other bcc elements exhibiting the same failure mode, and the unexpected alloying effects are ascribed to the weak ferromagnetism of Fe. We have found that the present solutes alter the magnetic response of the Fe host during tension from the weak towards a stronger ferromagnetic behavior. The underlying driving force is shown to originate from the alloying-induced effects on the peculiar electronic structure of Fe. The fact that a small amount of Al or early 3d metal enhances the stability of ferromagnetism in Fe is in contrast to the commonly accepted scenario based on the phenomenological Slater-Pauling curve, and calls for revision of the existing picture of magnetism in dilute Fe alloys.

We also studied the ideal strength of random alloys. The all-electron exact muffin-tin orbitals method in combination with the coherent-potential approximation was employed to investigate the ideal tensile strengths of elemental V and Mo solids, and V- and Mo-based random solid solutions. Under uniaxial [001] tensile loading, we found that the ideal tensile strength of V is 11.6 GPa and the lattice fails by shear. If assuming isotropic Poisson contraction, we obtained that the ideal tensile strengths are 26.7 and 37.6 GPa for V in the [111] and [110] directions, respectively. The ideal strength of Mo is 26.7 GPa in the [001] direction and decreases when a few percent of Tc is introduced in Mo. For the V-based alloys we found, that Cr increases and Ti decreases the ideal tensile strength in all principal directions. Adding the same concentration of Cr and Ti to V leads to ternary alloys with similar ideal strength values as that of pure V.

2. Various Steels, which are nowadays complicated alloys

The elastic properties of paramagnetic (PM) Fe-M (M = Al, Si, V, Cr, Mn, Co, Ni, and Rh) solid solutions in the body-centered-cubic (bcc) and face-centered-cubic (fcc) structures were investigated using the exact muffin-tin orbital density functional method in combination with the coherent-potential approximation and disordered local-magnetic-moment model. All impurities considered enlarge or leave nearly constant the equilibrium volume of PM Fe. At the same time, however, they produce both positive and negative changes in the elastic parameters. Some of the alloying elements induce opposite effects on cubic shear elastic parameters of PM bcc and fcc Fe. With a few exceptions, we find that the alloying effects on PM bcc Fe are smaller than on PM fcc Fe. Trends in the tetragonal elastic constant show a general correlation with the trends obtained for the bcc-fcc lattice energy difference.

Iron–chromium is the base material for most of the stainless steel grades. Recently, new insights into the origins of fundamental physical and chemical characteristics of Fe–Cr based alloys have been achieved. Some of the new results are quite unexpected and call for further investigations. The present study focuses on the magnetic contribution in the atomic driving forces related to the chemical composition in Fe–Cr when alloyed with Al, Ti, V, Mn, Co, Ni, and Mo. Using the *ab initio* exact muffin-tin orbitals method combined with an Ising-type spin model, we demonstrate that the magnetic moment of the solute atoms with the induced changes in the magnetic moments of the host atoms form the main factor in determining the mixing energy and chemical potentials of low-Cr Fe–Cr based alloys. The results obtained in the present work are related to the designing and tuning of the microstructure and corrosion protection of low-Cr steels.

Heterophase interfaces between face-centered-cubic (fcc) and body-centered-cubic (bcc) phases exist in many important alloys, such as Fe-Cu, Fe-Ni, Fe-Ag, Ni-Cr, Cu-Cr, or duplex stainless steels. The interfacial properties are very important, for example, when studying the precipitate growth kinetics and interface strengthening or failure mechanisms. It has been shown that the interfacial energy is a key parameter determining the nucleation barrier and also the shapes of precipitates. However, the interfacial energy is often not experimentally accessible. Due to the lack of measured data, ab initio calculations have been extensively applied to determine the metal-ceramic interfacial energy. However, for the metallic fcc/bcc interface theoretical studies are very limited. Experimental observations have shown that the real semi- coherent fcc/bcc interface has various orientation relationships deviating from the Kurdyumov-Sachs (KS) or NW orientation relationships. The actual interface structure is highly dependent on the characteristics of the misfit dislocation arrays. Experimentally, it is very difficult to describe accurately the atomistic structure of the fcc/bcc interface even with today’s powerful high-resolution transmission electron microscopy. Without knowing the exact structure of the interface, to accurately determine the interfacial energy theoretically is almost impossible. Actually, the core structure of dislocation and its energy have been a mystery for many years. When misfit dislocations are close, their cores interfere with each other, and then the main contribution to interfacial energy would come from the dislocation core energies which cannot be determined by ab initio calculations at present. However, in the present work, we show that by performing ab initio calculations we can accurately determine the interfacial energy and work of separation of the coherent interface and estimate these energetic parameters for the commensurate incoherent interface. The interfacial energies (work of separation) of the coherent and the incoherent interfaces represent the lower and upper (upper and lower) bounds for the real semicoherent interfaces. By establishing these bounds, we can reasonably assess the contribution to the interfacial energy or work of separation from the misfit dislocations. Explicitly, we have calculated the work of separation(W) and interfacial energy(Y) of the coherent Fe/Ag interfaces. These parameters are very important especially when studying the Fe/Ag multilayer or the Fe/Ag core/shell nanoparticles. For the coherent Fe(001)/Ag(001) interface with taking Ag as the underlying lattice, W and γ are calculated to be 2.30 and 0.89 J/m2, respectively. For the coherent Fe(110)/Ag(111) interface, taking Ag or Fe as the underlying lattice, the largest W and smallest γ are calculated to be 2.21 and 0.36 J m2 2.24 and 0.79 J/m2, respectively. The significant difference in the interfacial energy when using different underlying lattices is due to the magnetism. We propose an averaging scheme to estimate the work of separation and interfacial energy for the semicoherent/commensurate incoherent interface. We justify the use of the averaging scheme by performing large supercell calculations for a semicoherent interface. We have shown that taking either Fe or Ag as the underlying lattice, the averaging scheme can yield a reasonable estimation of the work of separation of the semicoherent interface. However, when taking Ag as the underlying lattice the averaged interfacial energy of the semicoherent interface is significantly underestimated due to the magnetism. When taking Ag (Fe) as the underlying lattice, applying the averaging scheme we get 1.86 (1.96) J/m2 for the work of separation and 1.27 (0.99) Jm2 for the interfacial energy of the incoherent interface. We studed the crystal and magnetic structures at the coherent and semicoherent interfaces and show that at a real semicoherent interface the atomic plane is wavelike and there is spin wave coupled with the interface Fe layer

3. Surface properties of composites, including surfaces and interfaces of bulk materials as well as nanocomposites of overlayer systems

The L12-type IrMn3 is a triangular antiferromagnet (AFM) with a noncollinear spin ground state, called a T1 Neel state. It exhibits a large second-order magnetic anisotropy due to anisotropic exchange interactions. This high effective anisotropy entails an easy plane (111), to which the ground state is confined. When IrMn3 is capped by fcc Co (feroomagnet (FM)), the magnetic properties of both the AFM and FM are modified close to the interface. In particular, sizable Dzyaloshinskii-Moriya (DM) interactions arise between the Co and Mn atoms, owing to the breaking of inversion symmetry at the interface. The (111) interface is perfectly compensated, with an equal number of atoms belonging to the three magnetic sublattices of the AFM. We focused our efforts on addressing the origin of the Exchange-Bias (EB) in compensated IrMn3/Co111 bilayers by performing numerical calculations of the hysteresis loops and identifying the roles played by different types of exchange interactions between Mn and Co atoms. In particular we studied using multiscale modeling from *ab initio* to atomistic spin model calculations. We evaluated numerically the out-of-plane hysteresis loops of the bilayer for different thicknesses of the ferromagnetic layer. The results showed the existence of a perpendicular exchange bias and an enhancement of the coercivity of the system. To identify the origin of the exchange bias, we analyzed the hysteresis loops of a selected bilayer by tuning the different contributions to the exchange interaction across the interface. Our results indicate that the exchange bias is primarily induced by DM interactions, while the coercivity is increased mainly due to a spin-flop mechanism.

We made a detailed study of the magnetic properties also of a monoatomic layer of Mn on W(110). By comparing multiscale numerical calculations with measurements we evaluate the magnetic ground state of the system and its temperature-dependent evolution. We find that the ground state consists of a cycloidal spin spiral (CSS) that persists up to the Néel temperature with a temperature-independent wavelength. However, by continuously increasing the temperature, that CSS becomes thermally depinned. This results in a time-averaged absence of magnetic order, a process that can be viewed as the antiferromagnetic analog of superparamagnetism. Our results for the ground-state magnetic configuration of Mn/W(110) agreed remarkably well with measurements, especially the wavelength of the cycloidal spin spiral. Experimental observations (performed in collaboration) as well as numerical results show that up to the Neel temperature no magnetic transition from CSS to an antiferromagnetic state exists and the wavelength of the CSS remains practically constant.

4. Magnetic properties of bulk and overlayer systems

Fe in the form of thin film may have entirely different magnetic ground state than bulk, mostly because the host material. We studied the dependence of the magnetic ground state of Fe thin films on Ir(100) surface. First we performed relativistic self-consistent calculations on Fe(n)/Ir(100) films, then by using the so called spin-cluster expansion, we obtained tensorial exchange parameters of a Heisenberg Hamiltonian. These in turn were used to performed a detailed study of the ground-state magnetic structure of ultrathin Fe films on the surface of fcc Ir(001). We determined the favored magnetic structure of the system by means of a mean-field approach as well as by atomistic spin dynamics simulations. For the case of a single monolayer of Fe, we find that layer relaxations very strongly influence the ground-state spin configurations, whereas Dzyaloshinskii-Moriya (DM) interactions and biquadratic couplings also have remarkable effects. To characterize the latter effect, we introduced and analysed the spin collinearity maps of the system. While for two monolayers of Fe we obtained a single-q spin spiral as ground state due to DM interactions, for the case of four monolayers, the system shows a noncollinear spin structure with nonzero net magnetization. These findings are consistent with experimental measurements indicating ferromagnetic order in films of four monolayers and thicker.

The magnetic ordering and its effect on the physical stability of X2Mn1+xSn1−x ($0 \le x \le 0.5$, and X=Ru, Os, Co, Rh, Ni, Pd, Cu, and Ag) Heusler alloys were also investigated quite systematically by the use of our first-principles method. We found that the ferromagnetic (FM) coupling between Mn on Mn sublattice (Mn1) and Mn on Sn sublattice (Mn2) is favorable over the antiferromagnetic (AFM) coupling for X with the number of valence electrons [Nv(X)] of 8 and 9, and vice versa for X with Nv(X)=10 and 11, originated from the competition of the exchange interactions between X-Mn2 and Mn1-Mn2. In comparison with the FM Mn1-Mn2 coupling, the AFM coupling decreases significantly the shear elastic constant C′ but increases slightly C44, which results in increasing elastic anisotropy (A=C44/C′) and consequently may facilitate the tetragonal shear lattice deformation.

4. Alloy theory

Landau phenomenological theory in combination with first-principles calculations was used to reveal the origin of the meta-magnetic nature and the unusually strong dependence of the ordering temperature with doping of the Fe2P compound. We show that the magnetism of the two sublattices occupied by Fe atoms has an entwined codependency, which is strongly influenced by alloying.

Similar ab-initio calculations were applied to determine the lower and upper bounds of the interfacial energy and work of separation of a fcc-Ag/bcc-Fe interface. The strain-free interfacial energy of the coherent interface was taken to be the lower bound and the interfacial energy of the commensurate incoherent interface the upper bound of the interfacial energy of a realistic semicoherent interface. The latter was estimated by applying an averaging scheme based on the interfacial energies obtained for the coherent interfaces. Similar calculations were performed for determining the bounds of the work of separation. We justified the use of this averaging scheme by carrying out large supercell calculations for a semicoherent interface. For a Fe(110)/Ag(111) semicoherent interface, we showed that taking either Fe or Ag as the underlying lattice, our averaging scheme can yield a reasonable estimation of the work of separation of the semicoherent interface. However, when taking Ag as the underlying lattice, the averaged interfacial energy of the semicoherent interface is significantly underestimated due to the magnetism. The structure and magnetism at the coherent and semicoherent interfaces are discussed.

Based yet again on our first-principles alloy theory, we predicted that at room temperature the paramagnetic NiCoFeCrAlx high entropy alloys adopt the face centered cubic (fcc) structure for $x \lesssim 0.60$ and the body centered cubic (bcc) structure for $x \gtrsim 1.23$, with an fcc-bcc duplex region in between the two pure phases. The calculated single- and polycrystalline elastic parameters exhibit strong composition and crystal structure dependence. We concluded that alloys around the equimolar NiCoFeCrAl composition have superior mechanical performance as compared to the single-phase regions.

We also performed fully relativistic first-principles calculations of the exchange interactions and the magnetocrystalline anisotropy energy (MAE) in an Fe/FePt/Fe sandwich system in order to elucidate how the presence of Fe/FePt (soft/hard magnetic) interfaces impacts on the magnetic properties of Fe/FePt/Fe multilayers. We compared thoroughly the geometrically fully relaxed system to the geometrically unrelaxed one. We found that the Fe layer at the Fe/FePt interface plays a crucial role inasmuch as its (isotropic) exchange coupling to the soft (Fe) phase of the system is substantially reduced. Moreover, this interfacial Fe layer has a substantial impact on the MAE of the system. We showed that the MAE of the FePt slab, including the contribution from the Fe/FePt interface, is dominated by anisotropic intersite exchange interactions. Our calculations indicate that the change in the MAE of the FePt slab with respect to the corresponding bulk value is negative, i.e., the presence of Fe/FePt interfaces appears to reduce the perpendicular MAE of the Fe/FePt/Fe system. However, we also found that for the relaxed system, this reduction is marginal. We calculated that the relaxed system exhibits a reduced interfacial exchange. Using a simple linear chain model, we demonstrated that the reduced exchange leads to a discontinuity in the magnetization structure at the interface.

Alloys traditionally have been based on a solvent element to which various solute atoms are added for improving specific properties. Thus, alloys are usually named after the major element in the alloy (e.g., Fe-,Al-, Cu-, Mg-, and Ni-base alloys). In recent times, Cantor and Yeh came up with equiatomic and nonequiatomic multicomponent alloys. They were christened as “high-entropy alloys (HEAs),” rightly so, as the configurational entropy of these alloys is expected to be very high at their random solution states. Such a high entropy is expected to drive the tendency to form simple solid solutions (crystalline or amorphous) rather than complex microstructures with many compounds. Besides the scientific curiosity, researchers also feel that HEAs can substitute conventional materials in advanced applications so that the limitations of the latter in service life and operational conditions could be overcome by providing superior performance of the former. A number of processing routes, including conventional melting and casting, mechanical alloying, various coating techniques, and even combinatorial materials science approaches are being used to synthesize and process this new class of alloys. There have been a lot of studies on understanding both the structural and functional properties of these alloys. The results of HEAs and HEA-related materials reported so far by various research groups are very encouraging for their applications in a wide range of fields such as materials for engine, nuclear plant, chemical plant, marine structure, tool, mold, hard facing, and functional coatings. In the view of these, we concentrated on the one of the important mechanical property thses alloys might have: hardness. We collected the available basic properties of nearly 100 high-entropy alloys (HEAs) with a single face centered cubic (fcc) or body centered cubic (bcc) phase. HEAs crystallizing in the fcc structure are mainly composed of the late 3*d* elements (LTM-HEAs), whereas HEAs consisting of the early (refractory) transition elements and the LTM-HEAs containing an increased level of bcc stabilizer form the bcc structure. Guided by the solid solution theory, we investigate the structure and hardness of HEAs as a function of the valence electron concentration (VEC) and the atomic size difference (δ). The fcc structure is found for VEC between 7.80 and 9.50, whereas the structure is bcc for VEC between 4.33 and 7.55. High strength is obtained for an average valence electron number VEC $\sim$ 6.80 and for an average atomic size difference $\delta \approx 6\%$. Based on these empirical correlations, one can design the high-entropy alloys with desired hardness.

The Al_xMoNbTiV ($x = 0$–1.5) high-entropy alloys adopt a single solid-solution phase, having the body centered cubic (bcc) crystal structure. Here we employ the ab initio exact muffin-tin orbitals method in combination with the coherent potential approximation to investigate the equilibrium volume, elastic constants, and polycrystalline elastic moduli of Al_xMoNbTiV HEAs. A comparison between the ab initio and experimental equilibrium volumes demonstrates the validity and accuracy of the present approach. Our results indicate that Al addition decreases the thermodynamic stability of the bcc structure with respect to face-centered cubic and hexagonal close packed lattices. For the elastically isotropic $Al_{0.4}$MoNbTiV HEAs, the valence electron concentration (VEC) is about 4.82, which is slightly different from VEC ~ 4.72 obtained for the isotropic Gum metals and refractory—HEAs.