Elastic Property Maps of Austenitic Stainless Steels

L. Vitos,[1] P. A. Korzhavyi,[1] and B. Johansson[1,2]

[1]*Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden*

[2]*Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden*

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The most recent advances in theory and methodology are directed towards obtaining a *quantitative* description of the electronic structure and physical properties of alloy steels. Specifically, we employ *ab initio* alloy theories to map the elastic properties of austenitic stainless steels as a function of chemical composition. The so generated data can be used in the search for new steel grades, and, as an example, we predict two basic compositions with outstanding properties among the austenitic stainless steels.

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The stainless steels are Fe based alloys containing a minimum of 12 atomic percentage of Cr and are the most important materials of our technological society. They supercede other materials in strength, stiffness, toughness, and corrosion resistance in relation to their prime cost. In particular, the austenitic stainless steels, which are widely used in both industrial and everyday applications, provide the best corrosion resistance of the stainless group having excellent mechanical properties. The austenitic stainless steels are low carbon contained, compositionally disordered, Fe, Cr, and Ni alloys (they often contain other alloying elements such as Mo, Si, Al, etc.) and have the face-centered cubic (fcc) crystallographic structure of the γ-Fe (the austenite).

Most of the stainless steel grades still in use today were developed at the beginning of the 20th century. The success of the first standard grades shifted attention towards finding cheap mass-production methods, which quashed the development of new categories of alloys. However, due to the rapidly increasing market and scope of steels, at the end of the last century the emphasis focused again on the invention of new specialized alloys. Previously new alloy steels were exclusively developed by empirical correlation of chemical composition, manufacturing processes, and technological properties. In the present work we adopt a completely different approach: we use alloy theory to describe austenitic stainless steels at a quantum mechanical level and to predict possible candidates for future materials.

The very limited use of quantum theory in industry and specifically in metallurgy was attributed to the crude approximations made in the solution of the fundamental equations of quantum mechanics [1]. The dramatic change perceived in the last decade [2,3] can be ascribed to the considerable developments based primarily on the density functional (DF) theory [4,5]. Several full potential (FP) methods have been designed to provide the exact DF description of solid materials, clusters, or molecules. However, these methods are restricted to ordered systems and, therefore, in order to simulate the compositional and/or magnetic disorder [6] present in many alloys, one has to carry out extremely time-consuming FP calculations for big and numerous model systems. Up to now the most powerful technique allowing one to treat systems with disorder is the coherent potential approximation (CPA) [7,8]. Until recently, the CPA was implemented in conjunction with less accurate computational methods, which, due to the employed approximations, limited its application to densely packed undistorted underlying crystal structures. During the last year, within the framework of the exact muffin tin orbitals (EMTO) theory [9,10], a basically new implementation of the CPA has been put forward [11]. This new method, which we refer to as the EMTO-CPA method, makes it possible to extend the accurate DF calculations from ordered structures to the case of concentrated random alloys.

Knowledge of the elastic properties of materials promotes understanding of the fundamental aspects of mechanical deformation and structural stability of crystals. At the macroscopic level empirical correlations exist between the engineering elastic moduli and technologically important properties such as strength, hardness, and wear. Particularly, the shear modulus (G) encompasses a large set of materials as a general indicator of mechanical hardness [12,13]. Recently, Clerc and Ledbetter [13] have shown that the hardness of annealed alloys, to a good approximation, is proportional with G. The bulk modulus (B) is a measure of the average bond strength and it shows strong correlation with the cohesive energy or the binding energy of the atoms in the crystal [14]. Assuming that the chemistry of the protective chromium-oxide surface film on the stainless steels is not altered upon changing the Cr and Ni contents, an increase in the cohesive energy, and thus in the bulk modulus, indicates improved resistance of steels to various forms of localized corrosion damage, and in particular to the stress-corrosion cracking [15].

Using the EMTO-CPA *ab initio* electronic structure calculation method [10,11] we have determined the shear and bulk moduli [16] of the $Fe_{100-(c+n)}Cr_cNi_n$ alloys as a function of the chemical composition for the interval $13.5 \leq c \leq 25.5$ and $8 \leq n \leq 24$ (here and throughout the paper the concentrations are expressed in atomic

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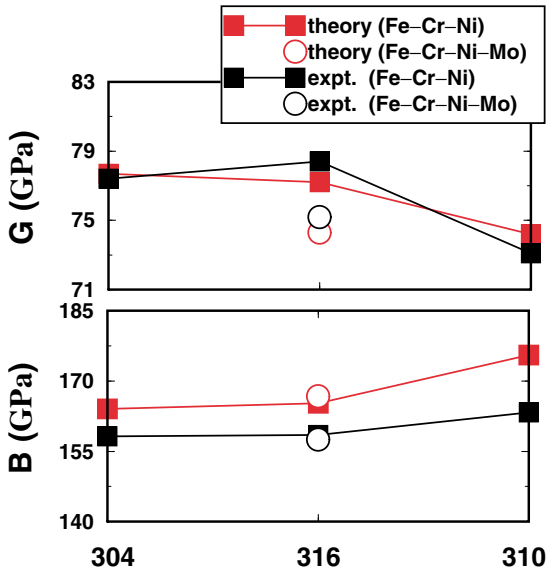

FIG. 1 (color). Comparison between the theoretical [16] (present results) and experimental [19,20] shear and bulk moduli of the alloy steels 304: Fe9.7Cr8.9Ni, 316: Fe18.6Cr12.2Ni, and 310: Fe26.2Cr19.4Ni. The experimental values correspond to commercial stainless steels without molybdenum (black squares connected by black line) and with 1.2% of molybdenum (black open circles). The theoretical calculations were performed for the Fe-Cr-Ni alloys (red squares connected by red line), and for an alloy with composition corresponding to austenitic steel 316, where 1.2% Fe was substituted by Mo (red open circles).

percentage, at. %). This interval includes the basic compositions of the well-known commercial grades from the AISI (American Iron and Steel Institute) 300 austenitic stainless steel series. At room temperature the above Fe-Cr-Ni alloys are paramagnetic metals [17]. Here we describe the paramagnetic state by the so called disordered local moment model [18], i.e., we treat the Fe-Cr-Ni system as a quaternary $Fe^{\uparrow}_{50-(c+n)/2}Fe^{\downarrow}_{50-(c+n)/2}Cr_cNi_n$ alloy with a random mixture of two magnetic states of Fe.

In order to demonstrate the accuracy and reliability of our calculations, in Fig. 1 we compare the present theoretical elastic moduli with available experimental data [19,20]. The average deviation between the theoretical and experimental shear and bulk moduli are 1.0% and 5.1%, respectively. Such small errors are typical for what has been obtained for the elemental $3d$ transition metals [21–23] in conjunction with the widely used generalized gradient approximation for the exchange-correlation energy functional [5] also employed in the present calculation. It is most significant how well the experimentally observed trends, including the effect of additional Mo, are reproduced by the theory. Thus, from Fig. 1 we conclude that the present theoretical results can be used for prediction of new data. In the following we discuss the calculated composition-elastic moduli maps presented in Figs. 2–4.

In terms of the shear modulus, shown in Fig. 2, one can clearly distinguish three families of alloys. Compounds

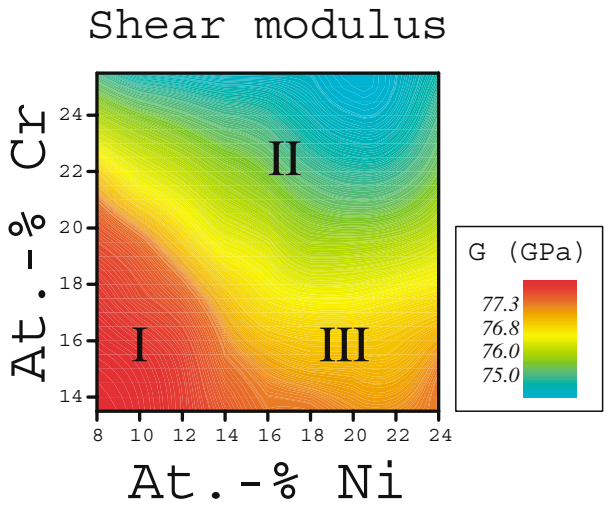

FIG. 2 (color). The calculated [16] shear modulus of austenitic stainless steels as a function of the chromium and nickel contents (balance iron).

with large shear modulus correspond to low and intermediate Cr ($< 20\%$) and low Ni ($< 15\%$) concentrations (indicated by I). Within this group of alloys G decreases monotonically with both Cr and Ni from a pronounced maximum of 81 GPa (near Fe14Cr8Ni, i.e., $c = 14$ and $n = 8$) to approximately 77 GPa. The high Cr content alloys define the second family of austenites (indicated by II) possessing the lowest shear moduli ($\lesssim 75$ GPa) with a minimum around the composition Fe25Cr20Ni. The third family of austenites, with intermediate G values, is located at moderate Cr ($< 20\%$) and high Ni ($> 15\%$) concentrations (indicated by III), where G shows no significant chemical composition dependence.

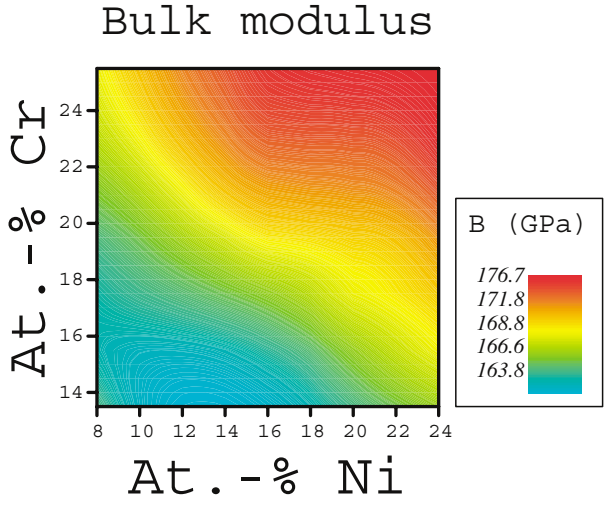

FIG. 3 (color). The calculated [16] bulk modulus of austenitic stainless steels as a function of the chromium and nickel contents (balance iron).

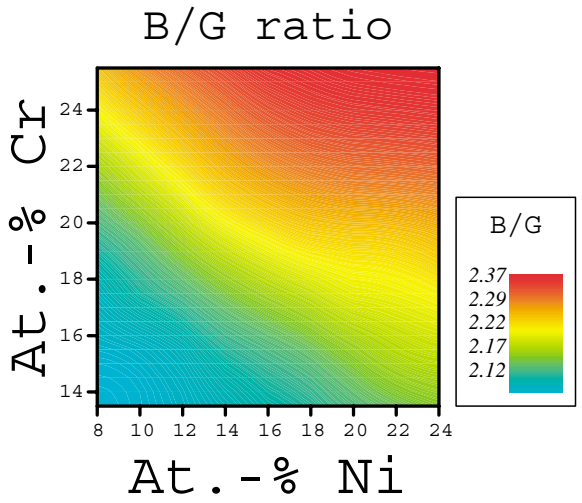

FIG. 4 (color). The calculated [16] B/G ratio for austenitic stainless steel as a function of the chromium and nickel contents (balance iron).

It is interesting to compare the effect of alloying elements on G with the composition dependence of the stability of the austenite (fcc) phase relative to the ferrite phase, which has a body centered cubic (bcc) crystallographic structure. We mention that in the case of transition metals the cubic elastic constant associated with the tetragonal distortion of the lattice, shows a proportionality to the energy difference between the bcc and fcc structures [23]. In the case of *austenitic stainless steels* we have found that Ni always stabilizes the austenitic phase (with $\sim$0.9 meV per at. %). However, even so, except for large concentrations, it decreases the cubic and, thus, the polycrystalline elastic moduli. On the other hand, Cr is a strong ferrite stabilizer ($\sim$1.3 meV per at. %), which correlates reasonably well with the trend of the shear modulus.

The bulk modulus, presented in Fig. 3, varies between a minimum value of 161 GPa, corresponding to Fe13Cr12Ni, and a maximum value of 178 GPa, belonging to Fe25Cr24Ni. Both Cr and Ni enhance the bulk modulus, conferring the excellent corrosion resistance particular to austenites. Further enhancement of the resistance to various forms of corrosion of the austenitic stainless steels, relative to the straight compositions, is achieved by alloying them with, e.g., Mo or Si. According to the present calculations, a small amount of substitutional Mo and Si increase the bulk modulus of Fe17.5Cr12Ni by approximately 1.25 and 1.40 GPa per at. %, respectively, in good agreement with the experimental observation [19]. At the same time, we find that Mo, being a strong ferrite stabilizer, decreases the shear modulus of austenite by 2.40 GPa per at. % compared to 0.60 GPa per at. % found in the case of Si.

The polycrystalline shear modulus is associated with the resistance to plastic deformation while the bulk modulus represents the opposition to bond rupture. Hence, the ratio B/G may be considered as a measure of the ductility/brittleness performance of solids. Ductility (ability to change shape without fracture) is characterized by high B/G ratio ($\gtrsim$1.75) , while low B/G is representative of brittleness (fracture without appreciable plastic deformation) [24]. In Fig. 4 we have plotted the B/G ratio for the austenitic stainless steels. According to this figure additional Cr and Ni, relative to the commercial grades of 8%–13% Ni and 17%–19% Cr, provide high degrees of ductility. As an example, the basic composition of alloy 310 has about 10% larger B/G ratio compared to type 316 (for approximate compositions see the caption of Fig. 1).

Using the maps from Figs. 2–4 one can predict new alloy compositions, which have improved and controllable properties relative to the common commercial grades. Here we consider the following two prospects: (a) low Cr- and Ni-laden austenite with an approximate composition of Fe13Cr8Ni, and (b) high Ni content austenite with a composition around Fe18Cr24Ni. Stainless steels with high shear modulus (and hardness) can be obtained from low Cr and Ni alloys belonging to the first family of alloys (I) from Fig. 2. These alloys, however, have a low bulk modulus ($\sim$163 GPa) and a relatively low B/G ratio ($\sim$2.0), which reflects a reduced corrosion resistance and increased brittleness relative to the commercial grades 304 and 316. Both of these shortcomings can be eliminated or retrenched by alloying the basic composition with a small amount of Mo, for example. In particular, we have found that a 4% increase of the bulk modulus of Fe13.5Cr8Ni can already be achieved by substituting 2% Fe by Mo. A similar steel composition (Fe13Cr8Ni2Mo1Al) with high strength and toughness, has recently been developed by Allvac (British company for development of stainless steel grades).

Austenitic stainless steels from the third family of alloys (III) from Fig. 2 possess an intermediate shear modulus ($\sim$77 GPa) and, presumably, intermediate hardness. Their bulk moduli and B/G ratios increase gradually from 162 GPa and 2.1 to 171 GPa and 2.2, respectively, when proceeding from the composition Fe14Cr15Ni to Fe20Cr24Ni. In particular, alloys with compositions near 18% Cr and 24% Ni are more ductile compared to the ordinary low Ni austenites (e.g., 304 and 316) and, due to the relatively large bulk modulus ($\sim$170 GPa), they should exhibit excellent resistance to stress-corrosion cracking. Moreover, the relatively high Ni content, that renders the Fe-Cr alloys austenitic, allows for a reduction of the carbon content, thereby lowering the susceptibility of these steels to intergranular corrosion [15].

In summary, using the EMTO-CPA computational tool based on *ab initio* alloy theory, we have calculated the elastic moduli of a series of Fe-Cr-Ni alloys of great industrial relevance. From the chemical composition-elastic moduli maps we predict two new basic compositions for the austenitic stainless steels: one with excellent hardness and the other with remarkable resistance to various forms of localized corrosion and intermediate hardness. The present achievements open up new perspectives concerning

theoretical modeling of materials with direct implications for practical use.

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