INTEGRATED DESIGN AND RAPID DEVELOPMENT OF REFRACTORY METAL BASED ALLOYS FOR FOSSIL ENERGY APPLICATIONS

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ABSTRACT

One common barrier in the development of new technologies for future energy generating systems is insufficiency of existing materials at high temperatures (>1150°C) and aggressive atmospheres (e.g., steam, oxygen, CO_2). To overcome this barrier, integrated design methodology will be applied to the development of refractory metal based alloys. The integrated design utilizes the multi-scale computational methods to design materials for requirements of processing and performance. This report summarizes the integrated design approach to the alloy development and project accomplishments in FY 2008.

INTRODUCTION

In order to improve efficiency and reduce environmental emissions in fossil power generation systems, new technologies are being developed such as oxy-fuel gas turbines, hydrogen turbines, and syngas turbines that will require new materials that can withstand high temperatures (Turbine blade substrate metal temperatures are predicted to be 1450°C for oxy-fuel turbines, and 1175°C for hydrogen turbines) and aggressive environments (e.g., steam, oxygen, CO, etc.). Even the state-of-the-art nickel based superalloys cannot meet these demands as they are unsuitable for use above 1150°C. Accordingly, alloys based on refractory metal elements such as Nb, Mo, Cr and W are being investigated as potential solutions.[1,2] This is partly because these elements have significantly higher melting temperatures than Ni, 2469°C, 2623°C, 1863°C and 3422°C respectively. Of those possibilities, we selected Cr to demonstrate that integrated design methodology works well in developing new high temperature materials based on refractory metals. Furthermore, Cr based alloys show considerable promise due to (i) the relatively low cost, (ii) the relatively low density and (iii) good high temperature strength. However, there are important challenges with use of Cr and other refractory metals: low ductility and fracture toughness at room temperature are the most significant issues that need to be dealt for important structural applications. In addition, alloying strategies should be applied so that the excellent oxidation resistance of Cr alloys[3] can be extended to higher temperatures and improved creep strength can be achieved. Therefore, if successful alloy systems are to be developed, improving these properties is an important area of research.

There are two main difficulties in developing refractory alloys: (i) lack of basic experimental data on thermodynamics, mechanical, and physical properties of most of these alloy systems, and (ii) difficulties associated with processing of these alloys. In order to avoid traditional trial-and-error experiments that are also time consuming and expensive, it has become essential to develop theoretical modeling to guide experimental alloy development. Such theoretical modeling can be multiscale in nature, which include first principles density functional theory (DFT) calculations, and atomistic, mesoscale and continuum simulations. Due to their interpretative and predictive capacities, first principles calculations are widely employed to study alloy lattice stability, interfacial energies,

defect structures, etc.[4-16] In this report, we present first principles calculations on a series of Cr-based binary alloys for initial screening alloying elements to improve the intrinsic ductility of Cr.

APPROACH

Materials development process encompasses three major sequential steps: Design, synthesis, and evaluation. Traditionally, this iterative process has been accomplished primarily using experimental methods. However, computational methods have been utilized increasingly throughout the process in recent years. Our approach of the rapid development of refractory metal based alloys begins with the concept of integrated design.[15] The integrated design utilizes the multi-scale computational methods to design materials for requirements of processing, microstructure, and performance. For example, a material can be designed for its improved ductility for processing, for a certain average grain size, and for creep strength utilizing computational techniques and experimental verification before the stage of synthesis. Therefore, the integrated design reduces significantly the number of iterations in the materials development process that one has to perform to reach to an optimized product. As a result of the integrated design, the rapid development of materials requires much less experimental work thus reducing the time and cost involved in alloy development.

Low ductility and fracture toughness at room temperature is one of the most important issues needed to be dealt in the design stage of the Cr alloys. Improving these properties is both process and performance requirement. Therefore, we began in FY 2008 with searching for alloying elements that have ductilizing effect on chromium[16] utilizing first principles quantum mechanical calculations. This work is described in detail in the next section. After identifying ductilizing elements in several binary, ternary, and quaternary systems, a multi-component alloy system will be selected. While most of the binary equilibrium phase diagrams are available within the refractory metal systems, a few binaries and most of the ternaries have not been established. In order to study stability of phases as a function of composition and temperature, the phase diagrams of the relevant systems have to be investigated. While this can be a daunting task if done purely experimentally, it can be achieved efficiently and reliably utilizing CALPHAD (acronym of Calculation of Phase Diagrams) methodology coupled with first principles quantum mechanical calculations and critical experiments. At the same time, kinetic parameters such as diffusivities in these alloy systems will be compiled where available, calculated when possible, or measured experimentally. These kinetic parameters will be used in predicting phenomena such as coarsening rates of second phase particles and growth of oxide scales. Once we establish the thermodynamic and kinetic databases, designing new alloy compositions within this multi-component system for sufficient creep resistance and high temperature oxidation resistance becomes feasible. For creep resistance, an ideal alloy composition can be designed such that second phase particles are stable at high temperatures, coherent with matrix, and slow to coarsen, and form at sufficiently high volume fractions. For oxidation resistance, the alloy composition can be adjusted to cause it to form protective oxide scale on the surface of the alloy when exposed to high temperatures and oxidizing environments. The following sections describe the computational work performed in two of the main tasks in FY 2008: ductility and fracture toughness and thermodynamics.

DUCTILITY AND FRACTURE TOUGHNESS

It is well known that the Poisson's ratio is well correlated with ductility of crystalline alloys[17,18] (see Fig. 1) and amorphous metals.[19,20] The higher the Poisson's ratio is, the better ductility the crystalline or amorphous metal has at low temperatures. For example, gold has a Poisson's ratio of 0.42 and it has an elongation of 50%; niobium has a Poisson's ratio of 0.40 and it has an elongation of 44% at room temperature. Other ductile metals (e.g. silver, palladium, copper) also have high values of Poisson's ratio. In contrast, commonly known brittle metals have low values of Poisson's ratio. For example, beryllium has a Poisson's ratio of 0.08 and its tensile elongation is only 1%; Cr has a Poisson's ratio of 0.21 and it is very brittle below its DBTT which is about 150^{o}C. Similar trends are also observed in wholly or partially amorphous metallic alloys.[19,20] Therefore, Poisson's ratio is chosen as the first screening tool to gauge ductility in this project. Moreover, it can be evaluated completely from first principles calculations with virtually no empirical information.

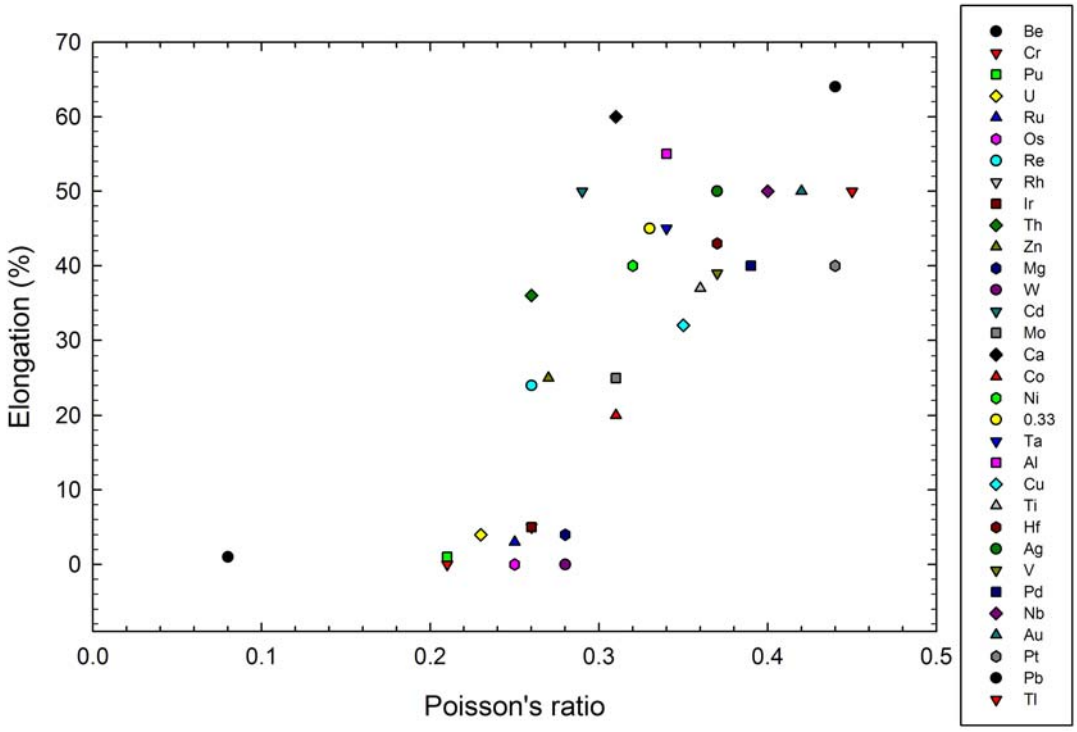

Fig. 1: Elongation vs. Poisson's ratio for selected pure elements (purity>99.95%) at annealed state. The data are taken from Refs. 17 and 21.

Survey of established Cr-based binary phase diagrams[22] indicates that feasible alloying elements are Ti, V, Fe, Co, Ni, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir, Pt, Al, Si, Ga, Ge. These elements are soluble to varying extents in bcc Cr up to very high temperatures whereas all other elements in the periodic table exhibit essentially negligible solubility. Therefore, all 22 elements were evaluated as potential substitutional alloying elements in this study. For comparison purpose, the elasticity of pure Cr with 6.25at% vacancies was also calculated. The first principles calculations use the plane-wave code VASP[24,25] which solves for the electronic band structure using electronic density functional theory. Projector augmented-wave[26] pseudopotentials are used as supplied with VASP. We use the Perdew-Burke-Ernzerhof[27] gradient approximation to the exchange-correlation functional.

Reciprocal space (k-point) meshes are increased to achieve convergence to a precision of better than 1 meV/at. All structures are fully relaxed (both lattice parameters and atomic coordinates) until energies converge to a precision of 0.25 meV/at. A "high precision" setting is used since the derivative of total energy is required for calculation of elastic properties. The plane-wave energy cutoff is held constant across each binary system at 500 eV. The semi-core 3p, 4p and 5p electrons of selected transition metals are explicitly treated as valence electrons. Spin polarization with collinear magnetization or anti-ferromagnetism is considered in all calculations since Cr is known to be as anti-ferromagnetic at its ground state.

To obtain enthalpy of formation values ΔH_f, a composition-weighted average of the pure elemental cohesive energies is subtracted from the cohesive energy of a given compound. The resulting energy is an "enthalpy" because its volume is relaxed at zero pressure. The phase stability at 0 K is evaluated by a convex hull plot (see Figs. 4-5 for example). Vertices of the convex hull of a scatter plot of ΔH_f versus composition identify stable structures. Points above the convex hull represent thermodynamically unstable structures at T=0 K, though they may become metastable, or stable at higher temperatures in some cases.

To examine the substitutional effect on the elasticity of Cr, a 2x2x2 bcc supercell is built and then one Cr atom is replaced with one alloying element. Thus we fix the alloy composition at $Cr_{15}X_1$ (X=6.25 atomic %) in the present study. The computational details on the bulk modulus, elastic constants and Poisson ratio are presented in Ref. [16].

Fig. 2 shows that calculated bulk modulus and Poisson's ratio for selected pure elements agree with experimental ones.

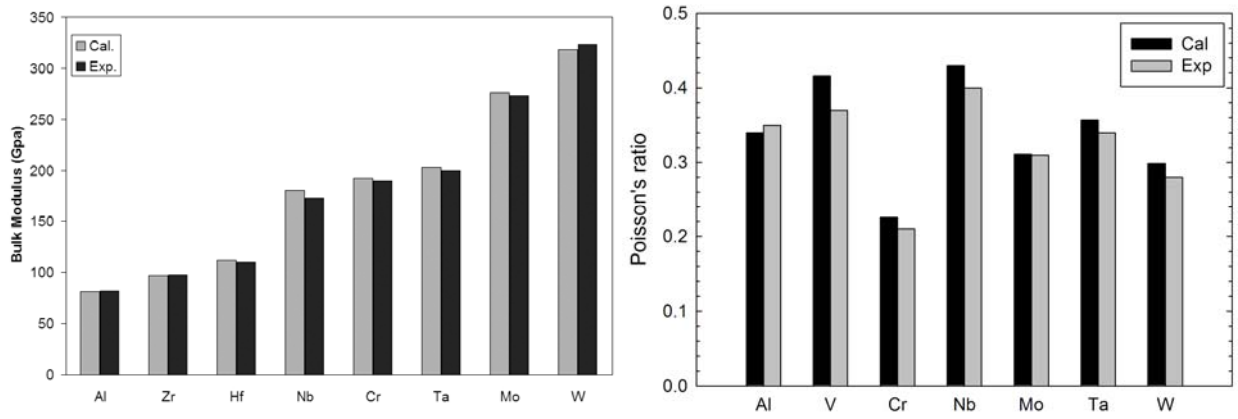

Fig. 2: Calculated bulk modulus (left) and Poisson's ratio (right) of selected pure elements in comparison with experimental data.

The effect of alloying elements on Poisson's ratio of bcc $Cr_{15}X_1$ is shown in Fig. 3. All elements increase the Poisson's ratio of Cr except three elements (Al, Ge and Ga). Ti increases it by 21%, followed by V, Ta, Zr, Hf and Nb. It is worth noting that vacancy substitution increases the Poisson's ratio by 25% because vacancy substitution lowers the shear modulus by 36 GPa.[16]

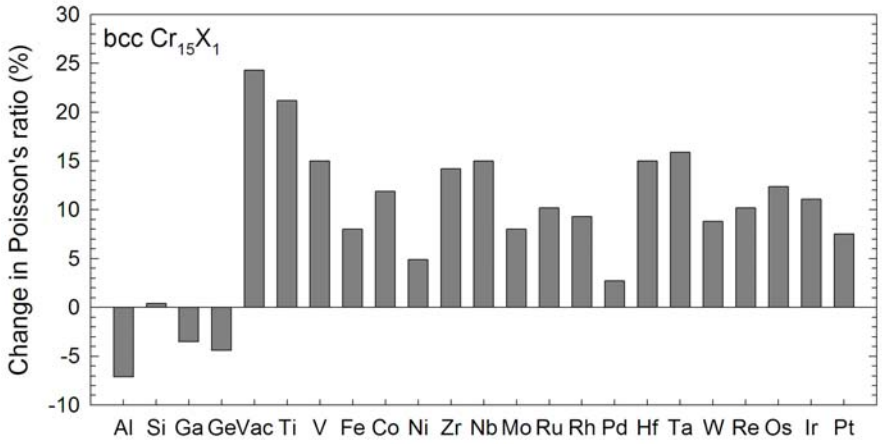

Fig. 3: the effect of alloying elements on the Poisson ratio of bcc $Cr_{15}X_1$.

Present theoretical calculations predict that all the transition metals selected tend to increase the Poisson's ratio moderately for the 6.25at% composition, thus improve the ductility of Cr. The results are supported by several experimental findings.[29-31,3] For example, our calculations predict that Cr-6.25at%V alloy enhance the Poisson's ratio of Cr by 15%, and Kurishita et al[29] found that properly processed V–52Cr–1.8Y (wt%) alloy achieved a yield strength of 610–740MPa and a total elongation of 10–19% at room temperature. Our study predicts that a Cr-6.25at%Re alloy can increase the Poisson's ratio of pure Cr by 10%, and it was reported that alloying of Re (≥ 20 at.%) to Cr can significantly improve the low-temperature ductility and fabricability of Cr.[30] Recently, Brady et al.[31] found that a eutectic microstructure that consists of an Fe-rich bcc matrix and brittle strengthening Cr_2Ta intermetallics at a relatively large volume fraction (Cr–30Fe–6.3Ta–4Mo-0.5Ti–0.3Si–0.1La) exhibited a toughness of 20 MPa√m at room temperature and a yield strength of 350 MPa at 1000°C. The present study predicts that Fe is a moderate ductilizer because $Cr_{15}Fe_1$ alloy increases the Poisson's ratio by 7%. The other advantages of choosing Fe are that Fe is very inexpensive, and that Fe and Cr forms an extensive solid solution over a wide range of temperature and composition. In order to enhance the oxidation resistance by forming Al_2O_3 surface scale, alloying Cr with Al was practiced by several research groups,[3,32,33] but it was found that addition of 5at% Al[32] or 10at%Al[3,33]

deteriorates ductility significantly. This is in excellent agreement with the present prediction that shows the bcc $Cr_{15}Al_1$ alloy has a 7% lower Poisson's ratio than pure Cr.

The present study also predicts that hexagonal-close-packing (hcp) metals (Ti, Zr, Hf) have potent ductilizing effect. This agrees with another theoretical study[10] that used the Rice-Thompson parameter[34] as the ductility prediction parameter for Mo alloys. However, these hcp metals have low solubility in Cr, so alloying strategies to enhance their solubility in ternary and higher-order systems will be needed. Again, there is little information on phase diagrams for these systems, which motivates further theoretical calculations.

THERMODYNAMICS

Phase diagrams and their inherent thermodynamic properties are the keys to alloy design and process. To achieve the desired function during processing, one requires the best possible knowledge of the relevant phase field and thermodynamic descriptions of all phases. For this purpose, CALPHAD method has been developed substantially in the past several decades, and CALPHAD techniques based on critically evaluated data are widely used as a basic tool in the development and optimization of materials and processes of many different types. Considerable time and cost can be saved in the experimental development work if the calculations involved can be made sufficiently reliable.

A successful modeling of thermodynamics requires an extensive body of reliable phase equilibria and thermochemistry data. Our approach will integrate first principles density functional theory (DFT) calculations, critical experiments and CALPHAD modeling in order to develop a physically meaningful thermodynamic database with high efficiency.[14] Although DFT calculations will provide enthalpy and entropy data for a wide range of compounds and solid solutions, key experiments are still needed to validate DFT predictions.

Since phase equilibria and thermochemistry data are scarce for ternary and higher-order systems based on Cr, a significant amount of work on critical experiments and CALPHAD modeling will need to be done in addition to DFT calculations. Typical experiments involve phase identification using SEM, XRD and TEM, and phase boundary measurement using thermal analysis. For unknown compound phases, structure refinement and simulations up to atomic positions in the unit cell may be required. A self-consistent thermodynamic database will be developed for the mutilcomponent system that is being studied will be carried out using the PARROT module of Thermo-Calc package.

During thermodynamic database development, it usually requires the energy data for hypothetical structures of various compositions for database compatibility purpose.[9,11-14] For example, there is no Laves compound formation in Cr-W binary, but W may partition into the Ta site of Cr_2Ta Laves phase in Cr-Ta-W ternary system. In this case the energies of Cr_2W Laves phases are needed but they cannot be obtained by experiments since they are not stable. Therefore, we calculate and then compare the total energy for common "likely" crystal structures for each compound Cr_xTM_y (TM=transition metals) in the complete Cr-TM binary series. For instance, we examined 3 structures for the Cr_2TM compound, including Cu_2Mg.cF24, $MgNi_2$.hP24, and $MgZn_2$.hP12 for all Cr-TM binary systems. The structure information is primarily taken from Refs.[22,23]

In this report, we only present DFT calculations on two binary phase diagrams (Cr-Zr and Cr-W) in comparison with experimental ones. Our calculation on the Cr-Zr system (Fig. 4) shows an excellent agreement with experiments.[21,22] Hcp Zr is predicted to be more stable over bcc Zr by 80 meV/at at 0K. Cubic α-Cr_2Zr.cF24 (prototype Cu_2Mg) lies exactly on the convex hull, and it is stable at $T \leq 1592^oC$.[21] Hexagonal β-Cr_2Zr.hP24 (prototype $MgNi_2$) and γ-Cr_2Zr.hP12 (prototype $MgZn_2$) lies slightly above the convex by 8.3 and 18.6 meV, respectively, and they become stable at $1592^oC \leq T \leq 1622^oC$ and $1622^oC \leq T \leq 1673^oC$, respectively. All other compounds examined (i.e. Cr_3Pt.P8, Cr_2Rh_3.hP2, $CrPt_3$.cP4) are predicted to be very unstable since their formation energies show a large positive value.

The convex hull plot of Cr-W binary is shown in Fig. 5. All the compounds examined show a large positive value of formation energies, suggesting that none of them is stable. In fact, the experiment[21] shows no compounds except a wide miscibility gap. Heat of mixing in bcc for a composition of $Cr_{15}W_1$ is +26.5meV/at, suggesting a positive regular solution constant and therefore a miscibility gap formation as the temperature goes up.

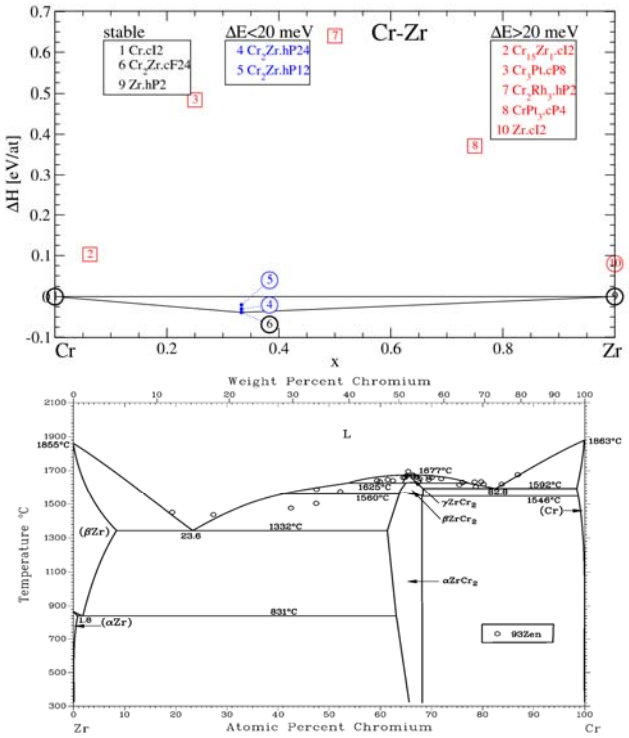

Fig. 4: (left) the convex hull plot of the enthalpies of formation of Cr-Zr binary system calculated at 0 K. The plotting symbol notation is: heavy circles for known stable phases; light circles for known high temperature phases; squares for imperfectly known, unknown or hypothetical structures. Tie-lines run along convex hull edges, joining low enthalpy structures at the vertices of the convex hull. (Right) experimental Cr-Zr binary phase diagram.[21]

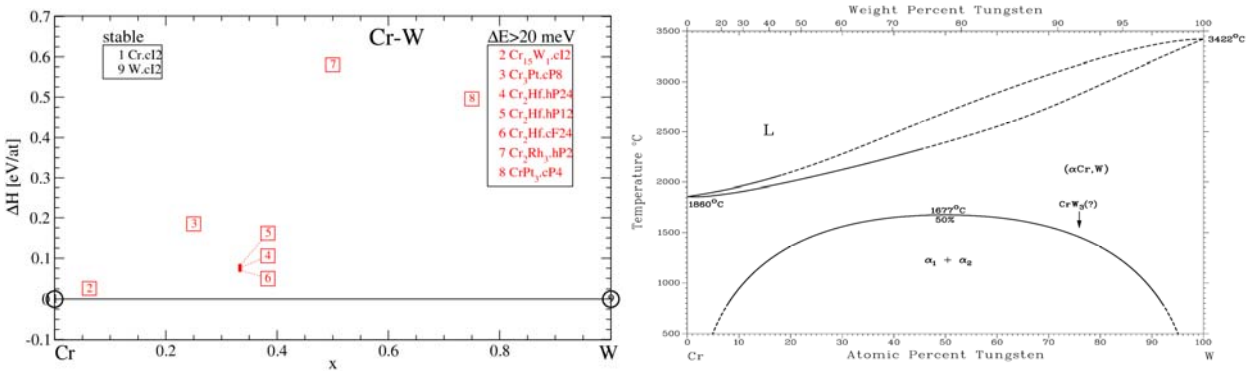

Fig. 5: (left) the convex hull plot of the enthalpies of formation of Cr-W binary systems calculated at 0 K; (right) experimental Cr-W binary phase diagram[21]. Plotting symbols as in Fig. 2

CONCLUSIONS

Based on the first principles DFT calculations on Cr-based binary phase diagrams and the Poisson's ratio of 22 bcc $Cr_{15}X_1$ alloys, the following conclusions are drawn:

1. The predicted phase stability of Cr-Zr and Cr-W at 0 K agree well with experimental phase diagrams.
2. On an atom-for-atom basis, Ti, V, Zr, Nb, Hf and Ta are predicted to be potent ductilizers in Cr. Recent experiments by Kurishita et al[29] demonstrated that alloying V to Cr with proper processing improved the room temperature ductility of Cr significantly.

3. Re and Fe are predicted to be moderate ductilizers in Cr. There is experimental evidence for ductilization of Cr by Re and Fe.[30, 31]
4. Al, Ge and Ga are predicted to embrittle Cr. Again, there is experimental evidence that Al degrades the ductility of Cr.[3,32,33]
5. The calculated elastic properties are found in good agreement with reported experiments, indicating that Poisson ratio can be used a screening parameter for alloy development.

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