Final Project Report

Ductility Enhancement of Molybdenum Phase by Nano-sized Oxide Dispersions

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Project Summary

The objective of this research is to understand and to remedy the impurity effects for room-temperature ductility enhancement of molybdenum (Mo) based alloys by the inclusion of nano-sized metal oxide dispersions. This research combines theoretical, computational, and experimental efforts. The results will help to formulate systematic strategies in searching for better composed Mo-based alloys with optimal mechanical properties.

For this project, majority of the research effort was directed to atomistic modeling to identify the mechanisms responsible for the oxygen embrittling and ductility enhancement based on fundamental electronic structure analysis. Through first principles molecular dynamics simulations, it was found that the embrittling impurity species were attracted to the metal oxide interface, consistent with previous experiments. Further investigation on the electronic structures reveals that the presence of embrittling species degrades the quality of the metallic chemical bonds in the hosting matrix in a number of ways, the latter providing the source of ductility. For example, the spatial flexibility of the bonds is reduced, and localization of the impurity states occurs to pin the dislocation flow. Rice's criterion has been invoked to explain the connections of electronic structure and mechanical properties. It was also found that when impurity species become attracted to the metal oxide interface, some of the detrimental effects are alleviated, thus explaining the observed ductility enhancement effects. These understandings help to develop predictive capabilities to facilitate the design and optimization of Mo and other high temperature alloys (e.g. ODS alloys) for fossil energy materials applications.

Based on the theoretical and computational studies, the experimental work includes the preparation of Mo powders mixed with candidate nano-sized metal oxides, which were then vacuum hot-pressed to make the Mo alloys. Several powder mixing methods were evaluated, however, the Mo alloys produced showed little improvement of room-temperature ductility. Finally, toward the end of the research project, a particle mixing process (Hosokawa mechano chemical bonding technology) was applied and the sample Mo alloys showed much improved room-temperature ductility. Follow-up mechanical properties evaluations on the as-processed Mo alloys were carried out using an in-house developed micro-indentation technique which is suitable for in-situ material mechanical properties measurement and ductility/brittle evaluation on small-size sample alloys. Relevant experimental results of the micro-indentation tests are presented.

PUBLICATIONS

Journal Papers

1. B. Kang, Z. Yao, and E.J. Barbero, "Post-Yielding Stress-Strain Determination Using Spherical Indentation," *Mechanical and Advanced Materials and structures*, vol.13, 129-138 (2006).
2. N. Ma, B.R. Cooper, and B.Kang, "Tight-binding Study of Thermal Expansions for Mo_3Si ," *Journal of Applied Physics*, 99, 053514, (2006).
3. C. Feng and B. Kang, "A transparent Indenter Measurement Method for Mechanical Property Evaluation," *Experimental Mechanics*, vol. 1, 1-14, (2006).
4. C. Feng, and B. S. -J. Kang, "Residual Surface Deformation Analyses Using Spherical Indentation", *Journal of Experimental Mechanics*, pp. 314-322, Vol.22, No.3-4, (Z1), (2007).
5. Ning Ma, Bernard Cooper , James Lewis , and Bruce Kang, "Criteria for Ductility in Cr Alloys based on Electronic Structures", accepted by *Appl. Phys. Letter*.

Conference Proceedings

1. Bruce S Kang, Chuanyu Feng, "Development of a Transparent Indenter Measurement System and indentation analysis for material mechanical property evaluation," 2005 ASME International Mechanical Engineering Congress and Exposition, Orlando, Florida, November 5-11, (2005).
2. Chuanyu Feng, Bruce S Kang, Ning Ma and Bernard R. Cooper, "Study of fracture behavior of molybdenum alloys using moiré interferometry," 2005 ASME International Mechanical Engineering Congress and Exposition, Orlando, Florida, November 5-11, (2005).
3. C. Feng, B. S. Kang, "A Transparent Indenter Measurement Method for Mechanical Property Evaluation, *Experimental Mechanics*," p91-103, Vol.46, No.1, Feb (2006).
5. Chuanyu Feng, Bruce S. Kang, "Young's Modulus Measurement Using a Transparent Indenter Measurement Method," *Proceedings of the 2006 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, St Louis, MO, June 4-7, (2006).
6. C. Feng, J. A. Noriega, and B. S.-J. Kang, "A Multi-Scale Transparent Indenter Measurement Technique for Surface Mechanical Property Evaluation", 2006 ASME International Mechanical Engineering Congress and Exposition, IMECE2006-15804, Chicago, Illinois, November 5-10, 2006.
7. N. Ma, B.R. Cooper , C.-Y. Feng, and B. S.-J. Kang, "Mechanisms of impurity effect and ductility enhancement of Mo and Cr alloys," *University Coal Research / Historically Black Colleges and Universities & Other Minority Institutions (UCR/HBCU) Conference*, Pittsburgh, PA, June 5-6, 2007.

8. N. Ma, B.R. Cooper , C.-Y. Feng, and B. S.-J. Kang “Mechanisms of Impurity Effect and Ductility Enhancement of Mo and Cr Alloys,” 21st Annual Conference on Fossil Energy Materials, Knoxville, TN , April 30-May 2, 2007.
9. B. S.-J. Kang, C.-Y. Feng, A. Manivannan, N. Ma, and B.R. Cooper , “In-Situ Mechanical Property Measurement and Influence of Impurity Elements on Grain Boundary Strength of Cr and Mo Alloys,” 22nd Annual conference on Fossil Energy Materials, Pittsburgh, PA, July 8-10, (2008).

*Invited Presentation

B. S.-J. Kang,” Development of A Multi-Scale Transparent Indenter Measurement Technique for Surface Mechanical Property Evaluation,” Invited Presentation, ASME McMAT 2007 Kobayashi Symposium, University of Texas in Austin, TX, June 7, 2007.

M.S Theses

AiLing Lin, Development of a Micro Depth Sensing Indentation Technique with Constant Load Control, West Virginia University, December 2008.

Ph.D Thesis

Julio A. Noriega, A Portable Transparent Indenter Instrumentation for Material Surface Characterization, West Virginia University, August 2006.

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Introduction

In developing ultra-high temperature structural materials for hot components in fossil energy conversion and combustion systems, there are two important factors to consider: oxidation resistance and mechanical properties. A number of molybdenum-silicide-based intermetallics have attracted considerable interest for many years due to their high melting point ($>2000\text{ }^{\circ}\text{C}$) and excellent high-temperature strength and oxidation resistance [1-5]. However, a major setback for these alloy systems' practical usage is their poor room-temperature ductility [4,5]. A large proportion of the current efforts in developing these high-temperature structural materials has been focused on the ductility enhancement of molybdenum phase.

Several schemes have been attempted to enhance the metal phase ductility, the most promising one being the incorporation of a small amount of oxide dispersions (such as MgO and/or MgAl_2O_4), which has recently been demonstrated to significantly improve the room temperature ductility of chromium[6,7]. It has been suggested that the presence of ceramic dispersion can cause detrimental impurities (such as N, O and S) to segregate or precipitate near the oxide-metal interface, which purifies the bulk and grain boundaries of metal, leading to detrimental impurity management (DIM) for ductility enhancement. However, the corresponding microscopic mechanism behind DIM is still not fully understood, and the ductility enhancement seems to sensitively depend on the nature and composition of the ceramic dispersions. For example, the incorporation of La_2O_3 , TiO_2 and Y_2O_3 in Cr, which displays similar DIM effects, does not yield enhanced ductility [7]. Even for the same dispersion material, the ductility enhancement critically depends on the particle size and processing time, etc. *Without a fundamental understanding of the mechanism, these problems can only be solved by trial-and-error based experimental efforts.*

The overall research objective of this three-year research project is to investigate the ductility enhancement of molybdenum by nano-sized oxide dispersions. The research work distinguishes from previous works in its emphasis on (1) *a deeper understanding of the mechanism at the microscopic level*, (2) *tailoring the dispersion material's properties by variations of composition and particle size*, and (3) *using nano-sized dispersions for optimal ductility enhancement*. In particular, nanotechnology and multi-scale modeling techniques are to be developed and employed in the simulating and manufacturing ceramic-metal alloys for improved performance. The research effort involves combined theoretical and experimental approach. On the theoretical side, we utilize our unique capabilities and past experience in the atomistic modeling of molybdenum silicide materials, and extend them to the study of ceramic-metal interfaces to determine the microscopic mechanism responsible for the desired ductility enhancement. Simulations at atomistic-scale were carried out to try to predict the optimal composition and particle size of the metal oxide dispersions for improved ductility enhancement. On the experimental side, based on the guidance from the atomistic modeling studies, we aim to develop a synthetic method to produce ductile molybdenum-based intermetallics with optimized nanosize MgO and MgAl_2O_4 dispersions. Toward this goal, a new powder mixing processing technique has been successfully applied to coat a thin layer of metal oxides on Mo particles and preliminary test results showed much improved

room-temperature ductility of the sample Mo alloy. The related mechanical properties were conducted to verify the enhanced ductility and structural properties of the Mo alloys with MgO or MgAl₂O₄ nano-oxide dispersions. To facilitate mechanical property evaluation on the as-processed small-size sample alloys, we have also developed a simple multiple partial unloading micro-indentation testing method for in-situ surface material Young's modulus measurement and ductile/brittle evaluation on small-size alloys. The research project contains three research tasks.

1. Task 1: First Principles Study of Ductility Enhancement Mechanisms in Cr and Mo Based Alloys with Metal-oxide Dispersions

Introduction

Due to their ultra-high working temperature (>1000°C) and excellent oxidation and corrosion resistance, a number of Cr and Mo based alloys are being developed as the next generation structural materials for fossil energy applications. However, a severe drawback with these materials is their limited room temperature ductility. It has been known that certain species of trace elements, including nitrogen (N) and oxygen (O), can cause embrittlement of Cr and Mo. For example, the ductile-to-brittle transition temperature (DBTT) of pure Cr (with less than 0.0001 atomic pct of N) is within the ambient temperature range, while that of unalloyed recrystallized Cr with commercial purity can rise to approximately 150°C [8].

There have been numerous studies concerning improving the ductility of Cr and Mo-based alloys at ambient temperature. In order to stabilize or remove the interstitial impurities, scavenging elements, such as tungsten, molybdenum, and rhenium were alloyed with Cr [9]. In 1965, Shruggs surprisingly found that the ductility of Cr and Mo can be increased by mixing with suitable amount of MgO dispersions. Although brittle by itself, MgO is thought to getter the nitrogen impurities out of the Cr and Mo phase, thus leaving the metal matrix clean and ductile. More recently, Brady *et.al.* [7] repeated the experiment and observed the room temperature tensile ductility to increase by 10-20%. Through microstructure analysis, they found that the oxide dispersions attracted the detrimental agents (notably N and S) to precipitate near the oxide-metal interface. Therefore, detrimental impurity management mechanism (i.e., by preventing the detrimental impurities from segregating to the Cr grain boundaries) has been invoked to explain the ductility enhancement. Interestingly, in their later experiments using La₂O₃, TiO₂, and Y₂O₃ as dispersions, similar microstructures were discovered, but none displayed any ductility improvement. This suggests that microstructure alone is not adequate to cause the ductilization; other factors must have contributed to the Cr's ductility enhancement. It is therefore crucial to understand these mechanisms before systematic strategies can be made to improve the material's mechanical properties in a controllable way.

On the theoretical side, the classic theory of Griffith [10] demonstrates that brittle fracture will occur when the hosting material can stably sustain an atomically sharp crack in the lattice without breakdown by dislocation generation. Therefore, the characteristic failure mode of a material depends on the relative easiness of creating new surfaces

compared with forming and emitting dislocations. Based on this theory, Rice [11] proposed a criterion to quantitatively measure the tendency of a material to be brittle or ductile in terms of the ratio of the energies for surface and dislocation formation. In practice, however, it is difficult to obtain the relevant energetics, due to the lack of *ab-initio* knowledge of the rich variety of interactions among the imperfections within the system, including impurities, dislocations, cracks, surfaces, and grain boundaries at quite different length scales. Therefore, Rice's criterion has limited applications. At the basic fundamental level, the mechanisms responsible for the impurity and additive effects are still largely unknown.

In this work, we attempt to extend the Rice's criterion and proposed several hypotheses that enable us to conveniently study the impurity effects on material's ductility properties. These new hypotheses are based on the properties of the valence electrons that participate in forming chemical bonds between atoms in solids. The knowledge of the valence electrons will then translate into that of the chemical bonds, and hence their ductility or brittleness mechanical properties through Rice's criterion. Comparing to the energetics approach, the one based on electronic structure analysis will provide a more comprehensive understanding of the mechanisms from a deeper level, yet it involves standard techniques that are readily available with many electronic structure software packages.

In the following sections, we shall first present these hypotheses starting from the Rice's criterion, followed by our results of electronic structure analysis on Cr- and Mo- based alloy systems, where we will explain in detail about the impurity embrittlement and the observed ductility enhancement with the inclusion of MgO/spinel, as demonstrated in Brady's experiments. We conclude in the final section of Task 1 with some brief discussions.

The Extensions of Rice's Criterion

In transitional metals such as Cr and Mo, chemical bonds are formed by sharing valence electrons. According to Rice criterion, a ductile material will cost less energy to form a stacking fault than to break the bonds. The stacking fault configuration has layers of misaligned atoms, in which the chemical bonds need to be stretched and distorted. To make this configuration energetically more favorable than the cleavage, we anticipate that the electrons making up these bonds need to be delocalized and mobile so that they can easily follow the misaligned ions and refill the voids whenever necessary to preserve the bonds. To characterize the relevant properties of valence electrons, we analyzed the following electronic properties:

(a) *Electronic charge distribution (real space distribution)*

A more globally shared (delocalized) electron state is easier to reshape to adapt to the ionic displacement (like the stacking faults) than a localized state. In a FP-LMTO calculation, the electronic charge is partitioned into muffin-tin (MT) spheres and interstitial areas. Charge in interstitial area is considered as being shared by ions, which contributes to ductile chemical bonds. Charge in the MT spheres may still be considered delocalized and beneficial to ductility if it is uniformly shared by many different MT spheres. To distinguish between

localized and delocalized charge in the latter case, we calculate the variance of its population distribution among all MT spheres, and the smaller variance indicate better sharing. The extent of delocalization for a given electronic state may also be measured by the entropy, defined as $S = - \sum n_i \log n_i$, where n_i is the partition of the charge on the i th ionic site. States with larger entropy are more scattered in space, and therefore more delocalized. This method is used in our larger scale molecular dynamic simulations.

(b) *Electronic density of states (energy space distribution)*

The electronic density of state (DOS) provides another measure of mobility across the Fermi level. Due to Pauli's exclusive principle, most of electrons are frozen in the low lying energy levels, while a small population of electrons immediately below the Fermi level may be excited into the empty orbitals (conduction bands) above the Fermi level. Electronic states in conduction bands are generally more delocalized and mobile. Therefore, the shape of DOS near the Fermi level can provide useful information for the characterization of chemical bonds and their mechanical properties.

(c) *Angular momentum projected population (angular momentum space distribution)*

Chemical bonds formed by s electrons tend to be more flexible than those formed by d electrons. This is because the spacial distribution of s electron is more isotropic, which facilitate the formation of unstable stacking fault configuration. In contrast, chemical bonds formed by d electrons are strongly angular dependent, and cost more energy to bend. This is why most sp-bonded metals are soft and ductile while transition metals are hard and brittle. By analyzing the population of occupied angular channels, we may predict the ductile/brittle properties of the materials.

Methodology and Results

In analyzing the electronic structures, we employed the following two first principle techniques: the all-electron full potential linear muffin-tin orbital (FP-LMTO) method [12], and an *ab-initio* tight-binding method called FIREBALL. Both methods are based on the density functional theory (DFT) implemented in the local density approximation (LDA). The FP-LMTO method uses a set of muffin-tin orbitals to expand the wavefunctions, and is particularly convenient to describe the d states in transition metals. Due to its extensive computing resource consumption, this method is currently suitable for small systems with less than 100 atoms. The FIREBALL method, on the other hand, employs the pseudopotential scheme and a set of localized pseudoatomic basis. In addition, the Hamiltonian matrix elements are expanded into one-, two-, and three-center integrals that are pre-computed into database for run-time interpolation. The manybody exchange-correlation potential and energy are treated similarly using a combined multi-center expansion (Horsefield) and linearization approximation (HXS) approach. All these schemes make FIREBALL particularly efficient and capable of simulating larger scale systems such as nanostructures and DNAs. In the results presented in this paper, the FP-LMTO methods are used on small-scale systems mainly to test the

extensions of Rice's criterion, while the FIREBALL method is used in molecular dynamics simulations of a much larger scale systems.

To study the mechanisms of the impurity and additives effects using FP-LMTO techniques, we considered the following model systems (see Figure 1):

- (a) A 1x1x3 Cr/Mo supercell containing one nitrogen/oxygen impurity at the center (Fig. 1a)
- (b) A 1x1x3 Cr/Mo supercell interfaced with 6 stacks of MgO layers, with nitrogen/oxygen impurities near the interface (Fig. 1b)

Between the two models, system (a) represents the impurity embrittled metal, while system (b) represents the ductility enhancement due to the inclusion of MgO. A three-kappa linked base is used to expand the muffin-tin tail functions. The energies for these bases are set to be -0.9, 0.3, and 1.2, respectively. Iterations are repeated until a convergence of 10^{-5} rydberg is achieved, after which properties of the electrons and chemical bonds are analyzed.

Figure 1: The schemes of the simulated systems: (a) a 1x1x3 Cr or Mo supercell (red spheres) containing a nitrogen or oxygen impurity (yellow sphere) at the center; (b) a 1x1x3 Cr or Mo supercell (top and bottom parts) interfaced with 6 stacks (figure only show 3 for simplicity) of MgO layers (center part, Mg and O atoms are represented by blue and green spheres, respectively), with two nitrogen or oxygen impurities (yellow spheres) near the interface.

First we calculated and compared the spacial distribution of electronic charge. In the FP-LMTO calculations, the charge distribution of any electronic eigenstate is conveniently partitioned into the interstitial region and the muffin-tin spheres. The interstitial charge is the delocalized part of the electronic state and contributes the most to the ductile bonds. The average proportion of the interstitial charge for electronic states within 0.1Ryd. across the Fermi level is tabulated in Table I (for Cr alloys) and Table II (for Mo alloys). Comparing system (a) and (b), we found that the ductility enhanced systems generally have higher proportion of charge in the interstitial region than the impurity embrittled systems. This is because the interstitial charge can easily adapt to the ionic motion in response to external stress, so that the stacking fault configuration may be stabilized by preserving the chemical bonds.

Table I. The overall proportion of interstitial charge in Cr alloys.

	System (a)	System (b)
Proportion of interstitial charge	14%	16%

Table II. The overall proportion of interstitial charge in Mo alloys.

	System (a)	System (b)
Proportion of interstitial charge	27%	35%

The muffin-tin (MT) charge belongs to different MT spheres. In the following, we calculated the average variance of the MT charge distribution for electronic states within 0.1Ryd. across the Fermi level, and tabulated the results in Table III (for Cr alloys) and Table IV (for Mo alloys). Compared to the impurity embrittled system, the MgO dispersed system has lower average variance, indicating the electronic state is more evenly scattered among the muffin-tins. The higher proportion of interstitial charge and more uniformly distributed MT charge together contribute to stabilize the stacking fault configuration. Therefore, we conclude that delocalized and uniformly distributed electronic states tend to form ductile bonds that resist to cleavage and improve ductility.

Table III. The average variance of MT charge distribution in Cr alloys.

	System (a)	System (b)
average σ^2	0.0139	0.0124

Table IV. The average variance of MT charge distribution in Mo alloys.

	System (a)	System (b)
average σ^2	0.0120	0.0039

Next, we turn to look at the charge distribution in the angular momentum space. In this analysis, the total charge (including the interstitial and muffin-tin charge) is decomposed into s, p, and d channels. We pay special attention to Cr's 4s and 3d channels, and the results are tabulated in Table V. Comparing the brittle and ductile systems, we find that both channels have increased charge population as a result of the inclusion of MgO. Evidentially, the bond strength is enhanced. In addition, the increase of population in s channel is more prominent, and the s to d population ratio is increased from 5.8% to 6.7%. States with s angular momentum are isotropic in space. Correspondingly, bonds formed

by sharing electrons in the s channel behave more like metallic bonds, i.e., they do not depend on the angular direction and are more flexible. On the other hand, bonds formed by sharing electrons in the d channel have strong directional preferences, which behave more like covalent bonds. The fact that metallic bonds render ductility and covalent bonds cause brittleness can be understood through Rice's criterion. In systems where metallic bonds dominant, the uniformly shared electrons are more tolerant with stacking faults; whereas in covalent materials, dislocation flow usually means breaking and reconnecting bonds with significant higher energy barrier. Assuming an equal energy cost to create new surfaces by cleavage, the Rice ratio γ_{us}/γ_0 will be higher in metallic systems than in covalent systems. Therefore, the ratio of s and d channel population is an indicative of material's mechanical properties. By changing the balance of s and d channel charge population, MgO helps to improve Cr's mechanic properties.

Table V: Calculated charge population in s and d channels (Cr alloy).

	System (a)	System (b)
s-channel	1.306	1.596
d-channel	22.503	23.738
Ratio s/d (%)	5.8%	6.7%

We also calculated and compared the DOS near the Fermi levels. In Figure 2 and Figure 3 we present the results of DOS calculations for the Cr and Mo alloys systems, respectively. In the impurity embrittled systems, DOS curves cross the Fermi line near the local minima, while in the MgO dispersed systems, DOS cross at local maxima. Due to Pauli's exclusion principle, states below the Fermi level are mostly occupied, and the states above the Fermi level are less occupied and hence more mobile. The mobile states are easily adapted to the ionic displacements, and hence are beneficial to ductility. Therefore, in the MgO dispersed systems, where DOS crosses Fermi level at maximum, it is easier to promoted electrons across the Fermi line to assume a mobile state, and consequently the systems are more ductile, and vice versa. This further explains the impurity imbrittlement and ductility enhancement effects.

Figure 2: The DOS for Cr alloys.

Figure 3: The DOS for Mo alloys.

Finally, using the FIREBALL package, we were able to extend the simulated system to a much larger scale. Molecular dynamics simulations are carried out for Cr and Mo systems with the inclusion of MgO or spinel phase. An impurity (N for Cr and O for Mo) is initially placed within the metal matrix. We then let the system freely evolve at constant temperature (set as 600°K), and watch the dynamics of the impurity atom. Figure 4 shows the initial and final configurations of Cr/MgO system after 1000 simulation steps (~1ps). The nitrogen impurity (marked as the orange sphere) was seen to gradually diffuse to the Cr/MgO interfacial boundaries. This result is consistent with Brady's experiments, where they found the MgO tends to cause precipitations of N near the interface rather than actual getter of N as proposed by Schruggs. Similar results have been found in the Cr/spinel system. In contrast, the Mo/MgO and Mo/spinel systems do not exhibit any oxygen diffusion. Therefore, alternative explanations of the observed ductility enhancement may be needed. Schneibel has argued that grain size control among other issues is more important in affecting the mechanical properties for Mo-based systems. The inclusion of some other metal oxides has been tried in Cr-based alloys, and similar impurity precipitation effects have been found, however, resulting in none ductility improvement. This suggests the complexity of the problem, and necessary further investigations.

Figure 4: The diffusion of N in Cr/MgO system (109 atoms). Blue, green, red, and orange spheres represent, respectively, the Cr, Mg, O, and N species. The temperature is 600°K. Shown on the left is the initial system configuration, where the nitrogen impurity is placed inside the Cr matrix. The final system configuration after 1000 simulation steps (1ps) is shown on the right. The diffusion length is about 0.2 nm.

To understand how the position of the detrimental impurity affects the system's mechanic properties, we carried out the electronic structure analysis and compared the initial and final configurations, which represent the non-gettered (initial) and gettered (final) systems, respectively. We focus on the properties of the electron orbitals due to the embrittling impurity and study their effects on the hosting materials, in the non-gettered and gettered environments.

The initial, non-gettered system was shown in Figure 5, where a nitrogen atom was placed in the chromium matrix as an interstitial impurity. The electronic wave functions within a cube centered at the nitrogen impurity were analyzed, and those correspond to the nitrogen's 2s and 2p orbitals were selected and plotted in Figure 6. The 2s orbital, which is almost spherical, lies deep (-17.5eV) under the Fermi surface, and is slightly bonded with N's six nearest Cr neighbors. The bonds are strongly polarized, though, since majority of the electron charge is centered at nitrogen atom. The nitrogen's 2p states lie immediately below the chromium's 3d bands, having energy ranging from -7.4eV to -6.9eV below Fermi surface. Two of the three 2p orbitals are aligned within the diagonal directions of the xy plane, where they bond with six nearby Cr atoms, two of which are σ bonds formed with Cr's 4s orbitals, and the rest four are π bonds formed with Cr's 3d orbitals. The third 2p orbital is aligned parallel to the z axis and are

similarly connected to the six neighboring Cr atoms through two σ and four π bonds. All of these bonds are very much localized in space, their average entropy being 21.7 (higher entropy means more delocalized). As comparison, the occupied Cr electronic states were mostly 3d orbitals with an average energy of -3.4eV below the Fermi surface and an average entropy of 56.5.

As comparison, the final configuration of the system is shown in Figure 7. The nitrogen impurity was attracted to the MgO and diffused to the Cr/MgO interfacial boundary. The electronic states of Ni's 2s and 2p levels are plotted in Figure 8. The deep 2s orbital does not change very much, whereas the 2p orbitals undergo substantial changes due to the new chemical environments. The two orbitals on the xy plane rotate about 45 degrees so that they are now aligned parallel with the x and y axes. This rotation apparently is due to the presence of the four nearby oxygen atoms sitting below the nitrogen. The electronic wave function can be seen to change phase along the nitrogen-oxygen line, and the resulting anti-bonding configuration suggests the oxygen refuse to form chemical bonds with the nitrogen. The N-O anti-bonding configuration would have been impossible without the rotation. The rotation, however, also prevents the nitrogen atom from forming π bonds with any of the four chromium neighbors in the xy plane. As a result, four of the N-Cr bonds are σ type. Similar N-O anti-bonding configuration is found in nitrogen's p_z orbital, which requires no rotation due to the azimuthal symmetry. However, the lower branch of the orbital is tilted by the unevenness of the interfacial plane, and only two of the π bonds in the xy plane remain; the rest two are converted to σ bonds with the upper branch. In terms of energy, these states are -6.5eV to -6.2eV below the Fermi surface. The average entropy is 17.8, compared to the average entropy for Cr: 62.0.

Figure 5: The non-gettered system. The light blue, dark blue, red, and green spheres represent chromium, nitrogen, oxygen, and magnesium atoms, respectively. The right panel is the enlarged cubic volume centered at the nitrogen impurity, which was initially placed in the Cr matrix.

Figure 6: The spatial distribution and bonding of nitrogen's 2s and 2p states. The yellow and purple volumes represent the opposite phases within the electronic wave function.

Figure 7: The gettered system. The light blue, dark blue, red, and green spheres represent chromium, nitrogen, oxygen, and magnesium atoms, respectively. The right panel is the enlarged cubic volume centered at the nitrogen impurity, which has diffused to the Cr/MgO interfacial boundary

Figure 8: The spatial distribution and bonding of nitrogen's 2s and 2p states. The yellow and purple volumes represent the opposite phases within the electronic wave function.

Lastly, we compare the distribution of the electronic states in the energy space, i.e., the density of states. The results are presented in Figure 9. As explained earlier, DOS measures the mobility of the electrons while entropy depicts the overall spreading of charge in space. The total number of states within $\pm 1\text{eV}$ of the Fermi level is found to increase from 73 to 76 as the impurity diffused from metal matrix to the Cr/MgO boundary. The average entropy for these states has also increased from 81.4 to 83.9. Evidentially, the diffusion of nitrogen atom indeed promotes both the mobility and uniform space distribution of the charge within the system. According to our hypothesis, the ductility is predicted to increase in the final state. This explains the ductility enhancement effects observed in Brady's experiments.

Figure 9: The density of states (solid black) and entropy (red pluses) plots. Upper panel: the initial (non-gettered) system; lower panel: the final (gettered) system. Energies are measured from the Fermi level.

Conclusions – Task 1

Through atomistic modeling using FP-LMTO techniques, we obtained and compared the electronic structures of selected Cr/Mo systems containing N/O impurities and/or MgO layers. Several microscopic criteria have been identified to connect with material's ductile/brittle property. These include the extent of delocalization of the electronic state, the shape of the DOS curves near the Fermi level, and the angular momentum projected population. These criteria are shown to be in consistency with the Rice's criterion based on energetic arguments. Based on these criteria, we explained the impurity embrittlement and ductility enhancement effects due to N/O and MgO. These criteria are then used in larger scale (nano-scale) simulations to study the dynamic effects of impurity diffusion and related mechanic property change. As an application, we compared the two systems in which the nitrogen impurity is either placed in the bulk of Cr matrix (the non-gettered case) or diffused to the Cr/MgO interfacial boundary (the gettered case). In the former case, the nitrogen's three 2p orbitals were found to form 18 chemical bonds with its six nearby Cr neighbors; of which 1/3 are σ bonds and 2/3 are π bonds. In the latter case, however, the nitrogen's 2p orbitals are forced to rotate around the z axis by the nearby oxygen neighbors. After the rotation, the nitrogen were

found to form 15 chemical bonds with its five nearby Cr neighbors; of which 2/3 are σ bonds and 1/3 are π bonds. Because σ bonds are symmetric with rotations around the bond line, they are more flexible and tolerant with lattice distortions induced by, for example, dislocation flows than π bonds. Therefore, having more σ bonds is certainly beneficial to the system's ductility property.

After understanding the microscopic mechanisms for ductility enhancement, future research will be focused on studying the size effects of the nano-particles on ductility improvement. Techniques to prepare uniform nano-particle coating samples have been developed and are discussed in the following sections of the report. How the size of the nano-particles will affect the electronic structural properties, and eventually the efficiency of the oxides to getter impurities, remains unclear, and will be subjected to our further investigations. In addition, we will compare different metal oxides on their abilities to alter the hosting material's mechanical properties.

2. Task 2: Mo-based Alloys Development

In year-three research, based on the numerical modeling studies (as a guideline), we have also attempted to produce Mo-based alloys with improved room-temperature ductility performance. We have prepared some Mo powders mixed with various nano-sized oxides using conventional ball-milling process or high power ultrasonic mixing procedure, which are discussed in Task 3 section. The processed powder mixes were then vacuum hot-pressed to make the Mo alloys. We then conducted mechanical properties evaluations using an in-house developed micro-indentation technique. However, these as-processed Mo alloys showed little improvement of room-temperature ductility. From SEM microstructural analyses of these Mo alloys, we conclude that the main reason for the unsatisfactory results is that the nano-sized oxides were not uniformly dispersed to the Mo matrix.

Toward the end of this research project, we had an opportunity to try out a new particle mixing process developed by Hosokawa. The Hosokawa mechano chemical bonding (MCB) technology belongs to a type of mechanochemistry process (MCP) which has a long history of development and the materials produced using this procedure have found a number of technological applications, such as hydrogen storage materials, heaters, gas absorbers, fertilizers, catalysts, cosmetics, pharmaceutical drug powders, etc. The Hosokawa mechano chemical bonding technology is a unique powder processing technique that can bond particles together using only mechanical energy established under solid state conditions. The basic operating principle of the mechano chemical bonding technology is illustrated in Figure 10. In this concept, the powder mixture introduced into the internal cavity of the equipment is subjected to a centrifugal force which transports them to the inner wall of the rotating chamber. The powder mixture is then subjected to additional compression and shear mechanical forces as they rotate and pass through a gap between the chamber wall and what is referred to as a press head. This results in the smaller particles being dispersed and bonded onto the surfaces of larger base particles without using any binders. The MCB technique does not use ball media

and is much easier and cheaper to scale up than ball mills. This technique can also be applied to improve particle sphericity and for precision mixing of nano and submicron powders.

A batch trial was carried out at Hosokawa USA Nanoparticle Technology and Micro Products R&D Center (Summit, NJ), where 450 gram of Mo-MgAl₂O₄ powder mixes (Mo-97.25wt%, MgAl₂O₄ – 2.75wt%) were processed by Hosokawa's MCB processing equipment.

Figure 10: Hosokawa Mechano Chemical Bonding Technology

SEM, FIB and EDS experiments were carried out on the Hosokawa MCB-processed Mo-MgAl₂O₄ powder mix. As shown in the following figures, Mo particles were coated with a layer of MgAl₂O₄ consisting of fine particles (-100nm). The thickness of the MgAl₂O₄ layer varies from place to place. The thinnest areas are close to the junctions between Mo grains.

Figure 11: Figure Energy-Selected Back SEM (inlens) image Scattering SEM image
Brighter areas have thinner AlMgO

Figure 12: MgAl₂O₄ coverage

Figure 13: MgAl_2O_4 coverage (Energy-selected backscattering detector)

Figure 14: More SEM image: MgAl_2O_4 coverage (SE detector)

Figure 15: SEM image (Inlens detector) Mo particle is cut by FIB

The Hosogawa MCB-processed Mo powder mix was then vacuum hot pressed (1800 °C, one hour, 15 ksi) to produce a sample alloy. As shown in Figures 16 and 17, the Mo alloy sample was examined using Vickers indentation under 1kg of dead weight and 15 seconds of dwelling time. An average of HV230 is obtained consistently over 8 tests. The indentations were carefully inspected after the tests. It was observed that all the indentations showed significantly pileup around the indentation sites, which apparently shows certain degree of ductility of the alloy.

Frame size (a) 321 x 240 micrometer

(b) 129 x 96 micrometer.

Figure 16: Indentation No.1 with 20x and 50 x magnification.

Frame size (a) 321 x 240 micrometer (b) 129 x 96 micrometer.

Figure 17: Indentation No. 5 with 20x and 50x magnification

The alloy was also examined using scanning electron microscope (SEM) for the particle distribution and detailed surface morphology examination, as shown in Figures 18 to 20.

Figure 18: SEM observation of distribution of the $MgAl_2O_4$ particles.

Figure 19: Indentation No. 1, SEM observation

Figure 20: Indentation No. 5, SEM observation

Finally, we also carried out a simple three-point-bend test of the sample Mo alloy. As shown in Figure 21, improved room-temperature ductility is demonstrated.

Figure 21: Simple bend test

3. Task 3: In-Situ Material Mechanical Property Measurement and Ductile/Brittle Characterization

In new alloys development using vacuum hot-pressed process such as the Mo and Cr alloys, many sample alloys are developed and needed to be tested for mechanical property evaluation. Current practice requires to prepare test specimen (with sufficient specimen size) in order to conduct tensile test to obtain the material Young's modulus and stress/strain curve. It would be advantageous to develop a suitable material testing technique that is capable of obtaining mechanical properties and ductile/brittle evaluation on small-size (i.e. mm-size, such as 6 mm diameter and 6 mm long) sample alloys, this

will greatly facilitate new alloys development. In this research task, a simple micro-indentation technique is developed to meet this goal.

Background

In material nano- and micro-indentation research, among all the indentation parameters, load-depth relation and unloading characteristics have been studied extensively either experimentally or numerically to elucidate the relevant mechanical behavior or properties. For example, it is well accepted to use the initial unloading stiffness of the load-depth curve to determine the material's Young's modulus [13-17]. This approach can be traced back to Sneddon's [13] classical elastic indentation solutions which describe the general relationship among the load, displacement and contact area for any punch that can be treated as a solid of revolution of a smooth function. In the 1970s, Bulychev and co-workers [14] defined the initial unloading slope and reduced modulus, thus providing a theoretically sound methodology for determining the Young's modulus. This method is applicable to both spherical and pyramidal indenters. Using instrumented indentations, Doerner and Nix [15] further investigated the unloading characteristics. In 1992, Oliver and Pharr [16] showed that Bulychev's technique can be applied to any indenter that can be described as a body of revolution of a smooth function.

In the indentation research for Young's modulus measurement, the contact area and initial unloading stiffness are the key parameters to be determined. However, in most cases, direct measurement of the contact area is not applicable or not possible. Typically, the unloading stiffness is used to estimate the contact area through some iterative algorithm [17-19]. Furthermore, high-precision displacement sensors are needed in order to accurately obtain load-depth curve and the unloading stiffness data [14-16]. As for the direct measurement of contact area, Kleesattel [20] designed a special apparatus for direct measurement of the contact region through a spherical sapphire indenter while conducting indentation tests, but the scanning method yields only one line of the contact region, and real-time access of the indented surface is not possible. By applying a special lighting technique, Frank [21] developed a transpyramidal indentation viewing system. It was also implemented by Sakaia et al [22] using a similar technique. Recently, with the support from the DOE/NETL Advanced Research Materials (ARM) Program, we have developed a Transparent Indenter Measurement (TIM) technique [23-26]. By integrating a Twyman-Green type interferometer into the spherical transparent indenter head, the TIM system can directly measure the indentation-induced out-of-plane deformation as well as the indented surface. It was found that by using the difference of out-of-plane deformation, Young's modulus can be evaluated without unloading stiffness measurement. Recently, a similar TIM approach was also done by Miyajima and Sakia [27] using sapphire spherical indenters on Aluminum and Zirconium oxide materials.

In this research, based on the experience learned from the research and development of the

TIM technique, we have further developed a simple multiple partial unloading micro-indentation method for material's Young's modulus measurement. Experimental validation tests of several metallic alloys and related theoretical discussions are presented.

Multiple Partial Unloading Micro-Indentation Experimental Setup

Figure 22 shows the schematic of a simple indentation system. As shown, a spherical indenter assembly is attached to one end of the load cell, which is then attached to a PZT actuator. The PZT actuator serves as both loading apparatus and displacement sensing device. For the research work done in this paper, 1.5 mm diameter spherical indenters made of tungsten were used.

Figure 22: Load-displacement sensing indentation system.

A schematic load-displacement curve from the aforementioned experimental setup is shown in Figure 23. The PZT actuator provides the overall indentation depth (h) measurement, which includes both the indentation penetration depth and system deformation, i.e.,

$$h = h_i + h_s \quad (1)$$

where h_i is the indentation penetration depth and h_s is the loading system deformation.

Figure 23: One indentation test with multiple partial unloadings.

At every unloading step (Figure 23), the unloading compliance is,

$$\frac{dh}{dp} = \frac{dh_i}{dp} + \frac{dh_s}{dp} = \frac{dh_i}{dp} + C_s \quad (2)$$

where C_s is the system compliance, which can be assumed to be a constant for a given system and within a given loading range.

Following the theoretical analysis of indentation [13,14, 17], the unloading compliance of a spherical indentation test can be expressed in terms of the indentation load, i.e.,

$$\frac{dh_i}{dp} = C \times \frac{1}{p^{1/3}} \quad (3)$$

where $C = (6RE_r^2)^{-1/3}$, R is the radius of the indenter, and E_r is the reduced modulus, defined by $\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_o^2}{E_o}$. E_i is the Young's modulus and ν_i is the Poisson's ratio of the test specimen, and subscript 0 denotes the indenter's mechanical properties. Substitute Equation (3) into Equation (2),

$$\frac{dh}{dp} = C \times \frac{1}{p^{1/3}} + C_s \quad (4)$$

Equation (4) shows that $\frac{dh}{dp}$ and $\frac{1}{p^{1/3}}$ has a linear relationship if C_s remains constant within a given loading range, and thus measurement of slope C provides an alternative method for material Young's modulus measurement. It should be noted that, after obtaining the Young's modulus, other mechanical properties, such as hardness, stress-strain curve can also be determined [18].

For mechanical property measurement using instrumented nano/micro indentation technique, the effect of the system compliance is always a concern and this is why in-situ high precision and sometimes sophisticated displacement sensor is often used to remedy this problem. In this research, a rather simple approach is proposed to try to alleviate this problem by making the assumption that within a selected loading range (of an indentation test where data are collected for mechanical property evaluation) the system compliance is constant (i.e. load versus load-line system displacement is linear within the loading range). It should be noted that, experimentally, it is difficult to conduct direct measurement of the system compliance and thus prove the validity of this assumption. However, we noticed the investigation work of Oliver and Pharr [16] on system compliance measurement. Their approach is similar to what described in this paper, the

difference is that instead of calculating the Young's modulus as proposed in this paper, it was used for system compliance determination.

In practice, Equation (4) also provides a convenient guideline to justify the validity of the proposed methodology, i.e., if the system compliance changes during the indentation loads, the linear relationship as depicted in Equation (4) can not be maintained.

Test Procedure

Based on the aforementioned multiple partial unloading technique, a LabVIEW™ software tool is developed to conduct the indentation tests. The program will first detect the contact position between the indenter and the sample within a given load threshold ($\sim 0.1\text{N}$), then it will conduct the multiple partial unloading indentation test using pre-defined parameters, such as the velocity of the indenter, the penetration depth and the unloading magnitude. After the completion of the indentation test, the program will process the data to determine the material Young's modulus from the slope measurement. For the results shown in this paper, all tests were conducted with six or ten loading/partial unloading steps, and each partial unloading displacement was either $0.5\mu\text{m}$ or $1\mu\text{m}$, nominally.

Materials

To verify the feasibility of this technique, indentation tests were carried out on Al 7075-T6 and Inconel 783. The published Young's modulus values for Al 7075-T6 and Inconel 783 are 71.7GPa and 177.3 GPa, respectively [28, 29]. The Inconel 783 alloy had standard heat treatment ($1120^\circ\text{C}/1\text{hr}/\text{AC} + 845^\circ\text{C}/8\text{hrs}/\text{AC} + 720^\circ\text{C}/8\text{hrs} + 50^\circ\text{C}/\text{hr} + 620^\circ\text{C}/8\text{hrs}/\text{AC}$). The Young's modulus of the sapphire indenter is 340GPa with Poisson's ratio equal to 0.29. Tests were then carried out on several research alloys, as listed in Table VI. As shown in Table VI, in addition to the ORNL alloys, three batches of Mo alloys were prepared at WVU using a sonication process. TiO_2 ($\sim 5\text{ nm}$) and Mo ($\sim 65\text{ nm}$) were taken as 5g and 95g respectively according to their weight percent ratio. Similarly 5g of MgO ($\sim 50\text{ nm}$ size) and 95g of Mo ($\sim 65\text{ nm}$) were taken for the other composite. Then we followed the following procedure for assuring uniform mixing of the components. Mo was dissolved in ethyl alcohol and sonicated for 10 minutes in presence of Ar. Then TiO_2 was mixed slowly to the Mo solution with continuous sonication. The total mixture was sonicated for 1 hour in Ar atmosphere. The mixture was kept at room temperature for 1 day to remove ethanol. Finally it was dried in vacuum. In the same way we prepared the $(\text{MgAl}_2\text{O}_4)_{0.05}(\text{Mo})_{0.95}$ composite ($\sim 35\text{ nm}$ particle size of MgAl_2O_4). The dried powder samples were kept in Ar-filled glove box and packed in presence of Ar. These are the as-prepared sample powders which were sent to Dr. J.H. Schneibel at ORNL for vacuum hot-pressed casting.

Table VI. Materials matrix

(Alloys received from M.P. Brady and J. H. Schneibel, ORNL)

#678, Mo-3.4wt%MgAl₂O₄ : 1800°C/4hr/3ksi/Vacuum, Mo powder 2-8µm, MgAl₂O₄, 1-5µm

#696, Mo-3.0wt%MgAl₂O₄ : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8µm, MgAl₂O₄, 1-5µm

#695, Mo only : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8µm

#697, Mo-6.0wt%MgAl₂O₄ : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8µm, MgAl₂O₄, 1-5µm

#698, Mo-3wt%MgO : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8µm, MgO, 1-5µm

Cast Re-(26-30) Cr wt% nominal: 1800°C/1hr/3ksi/Vacuum

(Powder mix prepared at WVU and sent to J.H. Schneibel for vacuum hot-pressed)

WVU-1, Mo-5.0wt%MgAl₂O₄ : 1800°C/0.5hr/3ksi/Vacuum

WVU-2, Mo-5wt%MgO : 1800°C/1.0hr/3ksi/Vacuum

WVU-3, Mo-5.0wt%TiO₂ : 1700°C/0.5hr/3ksi/Vacuum

Al 7075-T6

Several indentation tests were carried out on the Al 7075-T6 alloy. Figure 24(a) shows the typical indentation load and displacement data, in which ten partial unloading/reloading were introduced. Based on the unloading line data, compliances at each unloading step were calculated. They were then further processed according to the algorithm discussed in the multiple partial unloading procedure. Figure 24(b) shows data analysis results based on Equation (4). The processed data show the existence of a linear relationship within most of the applied indentation loading range. Using the linear unloading line, Young's modulus was calculated by applying Equation (4) and assuming a Poisson ratio of 0.3. An average value of 67.2 GPa was obtained. The experimental data obtained are in good agreement with the book value of 71.7 GPa.

(a) Load-displacement curve with multiple-partial unloadings

Figure 24: Experimental results for Al 7075-T6 alloy.

Inconel 783

Figure 25 shows the typical indentation test results for Inconel 783. In Figure 25(a), there were ten partial unloading displacements of 0.5 μm each. Based on the linear unloading line data, compliances at each unloading step were calculated and then further processed according to the multiple partial unloading technique. Similar to the Al 7075-T6 test, a linear relationship is observed within most of indentation loads, as shown in Figure 25(b). However, the data starts to deviate from the linear relationship at higher indentation loads, indicating the breakdown of the constant system compliance assumption, as discussed earlier. Again, using only the linear part in Figure 25(b), and based on Equation (4), Young's modulus values were calculated. An average value of 168.4 GPa is obtained and agreed well with the book value of 177.3 GPa.

(a) Load-displacement curve with multiple-partial unloadings

(b) Linear relationship
Figure 25: Experimental results for Inconel 783 alloy.

Mo and Cr Alloys

Micro-indentation tests were carried out on several research alloys as listed in Table VI. The results were presented in Figure 26, Figure 27, and Table VII. As for ductile/brittle evaluation of these alloys, relatively larger indentation loads (400 N to 2000 N) were applied to the samples. The higher indentation load is to have a sufficient elastic rebounding (after indentation unloading) that may cause cracking at the region just outside the perimeter line of the indentation contact zone, if the material is brittle. Preliminary results show that for the ORNL alloys, alloy #678 is the only alloy with sufficient room-temperature ductility while other alloys are brittle as evidenced with indentation-induced cracking, as shown in Figure 28. The results are in consistent with the research work of ref. 3. As for the WVU alloys, preliminary results show that only WVU-3 has some degree of room-temperature ductility and the metal oxide dispersion is not uniform especially for WVU-1 and WVU-2, as shown in Figures 29 to 31. The non-uniform oxide dispersion may be due to the fact that the prepared powder mix was exposed in air for about 60 to 80 seconds when pouring the powder mix to the crucible for vacuum hot-pressed casting.

Figure 26. Typical load-displacement curve, ORNL Mo alloys, #678, #696, #697, #698.

Figure 27: Typical load-displacement curve, WVU Mo-MgO, Mo-MgAl₂O₄, Mo-TiO₂ alloys.

Table VII. Summary - Young's Modulus Measurement

Material	Young's modulus (GPa)
Cast Re-(26-30) Cr wt%	234
#678, Mo-3.4wt%MgAl ₂ O ₄	229
#696, Mo-3.0wt%MgAl ₂ O ₄	200
#697, Mo-6.0wt%MgAl ₂ O ₄	192 (from tensile test : 189)
#698, Mo-3wt%MgO	211
WVU-1, Mo-MgO	254
WVU-2, Mo-TiO ₂	226
WVU-3, Mo-MgAl ₂ O ₄	202

(Averaged value from five indentation tests, typical)

#695, brittle, indentation load 1500N, cracks are observed

#697, brittle, indentation load 1000N, cracks are observed

#678, Ductile, indentation 2000N, no cracks were observed

Figure 28: Material surface condition evaluation, ORNL Mo alloys.

Figure 29: Ductile/brittle characterization using spherical micro-indentation Mo-MgO (WVU-1), 400N indentation, cracking.

Figure 30: Ductile/brittle characterization using spherical micro-indentation Mo-TiO₂ (WVU-2), 400N indentation, cracking.

Figure 31: Ductile/brittle characterization using spherical micro-indentation Mo- MgAl₂O₄ (WVU-3), 400N indentation, no cracking.
Vickers hardness tests show plastic flow at the matrix region.

Conclusion – Task 3

We have developed a simple multiple partial unloading micro-indentation testing method for in-situ surface material Young's modulus measurement and ductile/brittle evaluation on small-size alloys. Test results of two metallic alloys, (Al 7075-T6, and Inconel 783) show the validity of this technique. The proposed micro-indentation method does not require the use of sophisticated displacement sensor for indentation depth measurement and has the potential for the development of a portable micro-indentation instrument for on-site, in-situ component inspection and surface mechanical property evaluation. Micro-indentation tests were carried out on several research alloys. The results show that for the ORNL alloys, alloy #678 is the only alloy with sufficient room-temperature ductility while other alloys are brittle as evidenced with indentation-induced cracking. The sample Mo alloy produced based on the Hosogawa MCB method (as discussed in Task 2 section) has similar room-temperature ductility characteristic as that of alloy #678.

Overall Research Summary

We have investigated the electronic structures of selected material systems, and based on Rice's criterion, proposed microscopic mechanisms to understand the experiment observed impurity embrittlement and ductility enhancement. The proposed mechanisms and criteria are being tested and verified, and can be applied for large-scale simulations for understanding and optimization the effect of nano-size oxides (i.e. MgO and MgAl₂O₄) to ductile/brittle characterization of Mo and Cr alloys.

A new powder mixing processing technique has been successfully applied to coat a thin layer of metal oxides on Mo particles. The Hosogawa MCB process can disperse submicron and nano-size particles and bonds them onto the surfaces of larger host particles, which has the desirable uniform dispersing of the nano-size oxides in the alloy matrix. Preliminary results show evidences of using the Hosokawa's MCB processing technique to produce cost-effective Mo alloys with improved room-temperature ductility.

To facilitate mechanical property evaluation on the as-processed small-size sample alloys, a load-based micro-indentation testing method couple with a multiple loading/partial unloading procedure has been developed for in-situ surface material Young's modulus measurement and ductile/brittle evaluation on small-size alloys.

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