Quarterly Management Report

WBS Element	Project Title	Contract Number	Contract Start	Contract End
	In-Situ Mechanical Property Measurement and Influence of Carbon and Oxygen on Grain Boundary Strength of Molybdenum Alloys	4000042127	06/23/05	06/30/08

Performer Name and Address	Principal Investigator(s)
Bruce S. Kang Mechanical and Aerospace Engr. Dept. West Virginia University Morgantown, WV 26506	Bruce S. Kang

BUDGET AND COST REPORT

Prior Year Funds [$K]	100
Total Current Year Commitment $K]	100
Projected Current Year Costs [$K]	100

	O	N	D	J	F	M	A	M	J	J	A	S
Planned Costs	0	0	0	0	0	0	0	0	0	0	0	0
Actual Costs	0	0	0	0	0	0	0	0	0	0	0	0
Variance	0	0	0	0	0	0	0	0	0	0	0	0

MILESTONE REPORT

Milestone Designation	Milestone Description	Due Date	Revised Due Date	Completion Date
	Quarterly Progress Report for the first quarter of 2007			05/06/07

TECHNICAL HIGHLIGHTS

Quarterly technical report is in pages 3 to 14 of this report.

ISSUES

None

Report Prepared By	Date
Bruce S. Kang	05/06/07

Summary of project status

The objective of this three-year research project is to understand and minimize the impurity effect for room-temperature ductility improvement of Mo- and Cr-based alloys by the inclusion of suitable metal oxide dispersions. The project includes two tasks: (i) to conduct atomistic modeling on the impurity embrittlement and mechanism of room-temperature ductility enhancement with metal oxide dispersions of Mo and Cr alloys, and (ii) to conduct in-situ mechanical property measurement of the developed Mo and Cr alloys with suitable nano-size metal oxides as well as other alloys relevant to the Fossil Energy Materials Program.

Mo- and Cr-based alloys are brittle at room temperature due to oxygen and nitrogen embrittlement, respectively. Past research showed that suitable amount of MgO or $MgAl_2O_4$ dispersion can improve the room temperature tensile ductility of Cr or Mo alloys. However, the experimental results were not consistent. MgO dispersions are also potentially useful for ductility enhancement of Mo since the electronic structures and physical properties of the two elements are very similar. The purpose of this research is to identify the mechanisms responsible for the impurity embrittling and to tailor ductility enhancement based on fundamental electronic structure analysis, which will guide the selection of suitable nano-sized metal oxides to be incorporated in the Mo or Cr alloys to achieve the desirable room-temperature ductility. The results will help to formulate systematic strategies in searching for better composed Mo and Cr alloys with optimal mechanical properties.

On the atomistic modeling analyses, using *ab-initio* FP-LMTO techniques, we investigated the electronic structures of Mo and Cr, with possible embrittling impurities and/or MgO layers. We found that the electronic structures and chemical bonds near the surface boundaries in the ductile alloys and brittle alloys are quite different. Specifically, in the ductile alloys the metal/MgO surface is dominated by chemical bonds formed by d electrons with $3z^2$-r^2 geometry, which are not found in brittle systems. We speculate that these $3z^2$-r^2 d bonds are responsible for the ductility enhancement. Further investigations on chemical and mechanical properties associated with these bonds are conducted. In addition, we developed *ab-initio* database for more efficient tight-binding schemes. Such schemes are suitable to study some of the dynamic effects, such as impurity gettering and defects transport, that are pertinent to the ductility enhancement mechanism. For year-three research, we will conduct large scale simulations (10^4-10^5 atoms) to understand the qualitative effects of varying the dispersion particle sizes.

On the experimental task, we have developed a micro-indentation technique suitable for in-situ material mechanical properties and ductility/brittleness evaluation of sample alloys. For year-three research, we plan to develop a high-temperature micro-indentation test apparatus to further investigate mechanical properties of Mo and Cr alloys and other alloys relevant to the Fossil Energy Materials Program.

1. Introduction

The computational simulation part of this research is focused on the understanding of the microscopic mechanisms behind the impurity embrittling and ductility improvement effects on Cr- and Mo- based alloys which are used for ultra-high temperature (>1000°C) applications beyond those presently attainable with nickel-based superalloys. Based on these understandings, systematic strategy to enhance the ductility improvement may be formulated, for example, by either varying the dispersion composition, or by changing the dispersion sizes.

The source of brittleness or ductility properties inherent from a material can be traced back to the characteristics of the chemical bonds at the microscopic level. One may use the Rice criterion, by comparing the surface formation energy and the stacking faults energy, to predict ductile or brittle behaviors for a specific material system. In practice, however, this criterion has limited applications because a system's total energies can be affected by many other non-relevant factors, which makes it difficult to obtain the relevant energetics for the ideal cleavage and stacking fault configurations, especially when impurity effects are also involved.

In view of these difficulties, we extended the Rice's criterion and proposed several hypotheses that enable us to 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. These hypotheses not only help us to understand the material's mechanic properties from a deeper and more fundamental level, but also serve as a basis to form the strategy for a systematic approach to enhance the material's properties for better performance.

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 or ductility improvement effects. We conclude with discussions and a brief future work plan.

2. Overview of the atomistic modeling analysis

In transitional metal such as Cr and Mo, atoms are bonded by sharing their valence electrons. The Rice criterion tells that if it costs less energy to assume a stacking fault configuration than to break the bonds, the material would be ductile. The stacking fault state creates layers of misaligned atoms, in which the chemical bonds between layers need to be stretched and distorted. To make this configuration energetically more

favorable than the cleavage (bonds broken state), 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 to preserve the bonds. To assess the mobility of the valence electrons near the Fermi level, 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 results of this analysis are provided in Section 3.1.

(b) *Density of states (energy space distribution)*
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. The results of this analysis are provided in Section 3.2.

To study the mechanisms of the impurity and addictives effects, we considered the following model systems (see Figure 1):

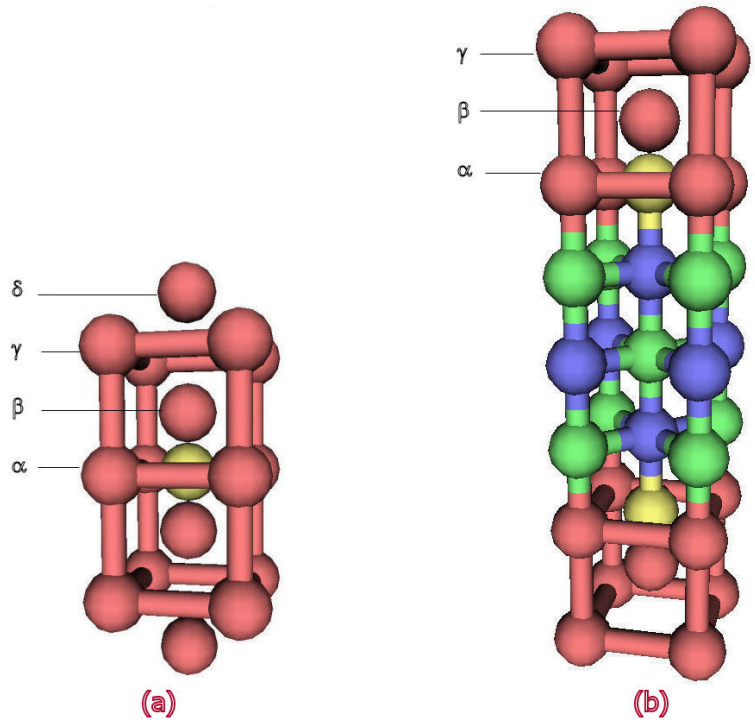


Figure 1: The schemes of the simulated systems: (a) a 1x1x3 Cr or Mo supercell (red spheres) containing a nitrogen or oxygen impurity (yellow sphere) at the center; (c) a 1x1x3 Cr or Mo supercell (top and bottom parts) interfaced with 6 stacks (figure only show 3 for simplicity) of MgO layers (center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

(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 these models, system (a) represents the impurity embrittled metal, while system (b) represents the ductility enhancement due to the inclusion of MgO.

Full potential linear muffin-tin orbital (FP-LMTO) techniques[1], which accurately treat the muffin-tin's interstitial region, have been used to calculate the electronic structures for the above systems. 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 the electronic charge density and DOS are obtained and analyzed.

3. Results and discussion of the atomistic modeling analysis

3.1 Electronic charge distribution

The charge distribution of a given electronic state gives one some idea about how localized or delocalized an electron is. As illustrated in Section 2.1, the distribution of a delocalized electron is easy to deform so as to preserve the chemical bonds should ions be misaligned. Therefore delocalized electrons contribute to the system's ductility. In FP-LMTO calculations, the charge distribution is conveniently partitioned into interstitial regions and muffin-tin spheres.

The Interstitial charge is shared by ions in system. Thus, they contribute the most to the ductile bonds. Tables 1 and 2 give the overall proportion of interstitial charge for electronic states within 0.1Ryd. across the Fermi level. In both tables, the impurity embrittled system has lower proportion of charge in the interstitial than the ductility enhanced system.

Table 1. The overall proportion of interstitial charge in Cr alloys.

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

Table 2. The overall proportion of interstitial charge in Mo alloys.

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

The muffin-tin (MT) charge is distributed among the different MT spheres. Compared to the interstitial charge, it is more localized to ions. However, if a given electronic state has a uniform distribution among the MTs, it is still considered as being shared, and helps to "glue" the system together. Tables 3 and 4 show the average variance of MT charge distribution for electronic states within 0.1Ryd. across the Fermi level. In both tables, the system (b), with MgO layers, has lower variance, indicating the charge is shared more uniformly among the muffin-tins. This is in consistent with the system's ductile behavior. Therefore, we conclude that the delocalized and uniformly distributed electrons tend to form ductile bonds that resist to cleavage.

Table 3. The average variance of MT charge distribution in Cr alloys.

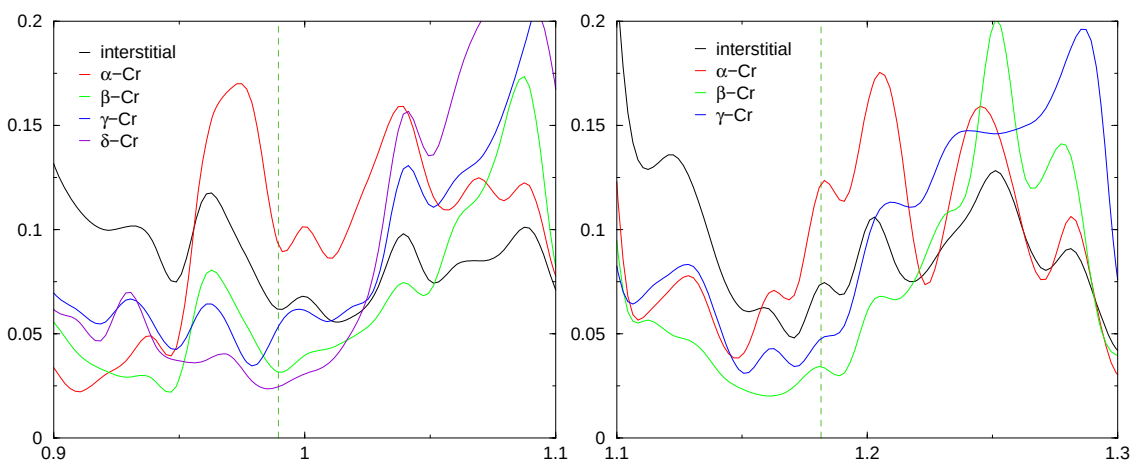
	System (a)	System (b)
average σ^2	0.0139	0.0124

Table 4. The average variance of MT charge distribution in Mo alloys.

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

3.2 Density of states (DOS)

In Figures 2 and 3 we present the results of DOS calculations for the Cr and Mo alloys systems, respectively. Both figures show enhanced DOS for Cr/Mo atoms near the impurity. A very distinctive feature is that the majority of DOS curves cross the Fermi line at their minima in system (a) while those crosses at maxima in system (b). Due to Pauli's exclusion principle, the electrons will first occupy the levels below the Fermi line and leave those above Fermi line mostly unoccupied. The states corresponding to the unoccupied levels are less crowded and usually more mobile. As illustrated in Section 2.1, the mobile electrons are easy to deform and are beneficial to the ductility property. Thus, for systems with larger DOS at Fermi level (whose DOS crosses Fermi line at maxima), electrons will be easier to cross the Fermi line and assume such a mobile state, and consequently the system is ductile, and vice versa. This further explains the impurity imbrittlement and ductility enhancement effects.



(a) (b)

Figure 2: The DOS for Cr alloys.

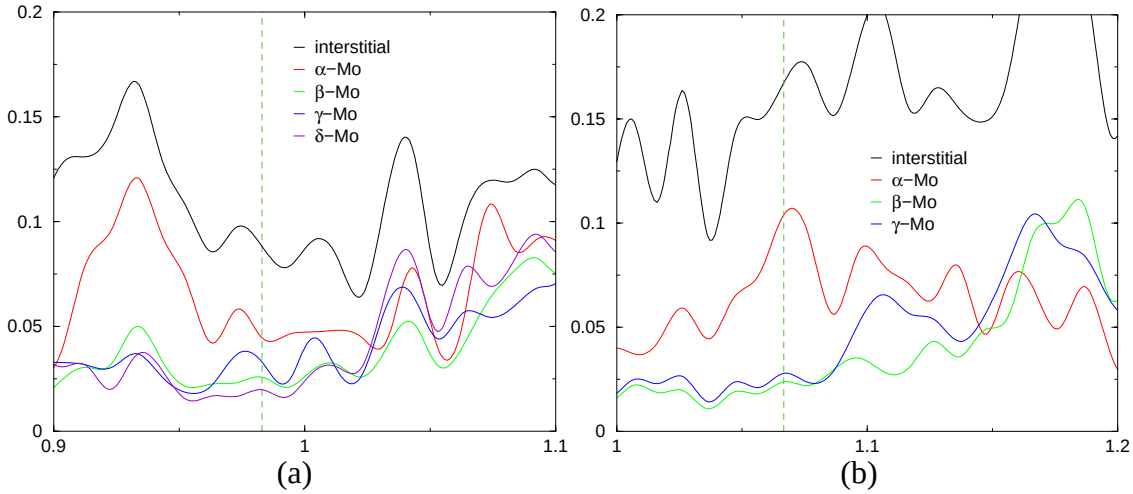


Figure 3: The DOS for Mo alloys.

4. Development of a micro-indentation technique for in-situ mechanical property measurement

Relevant to this project, we have developed a micro-indentation technique for in-situ mechanical property measurement.

4.1 Technical background

Figure 4 shows schematics of the micro-indentation system and a prototype micro-indentation test apparatus. As shown, a spherical indenter (diameter 1.5 mm) assembly is attached to a load cell, which is then attached to a PZT actuator. Using a multi-partial-unloading technique recently developed at WVU, a LabVIEW™ program is developed to conduct the indentation tests. The program will first detect the contact position between the indenter and the sample with a given load threshold, 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 compliance. After the completion of the indentation test, the program will process the data to determine the surface stiffness response of the bond coat/substrate.

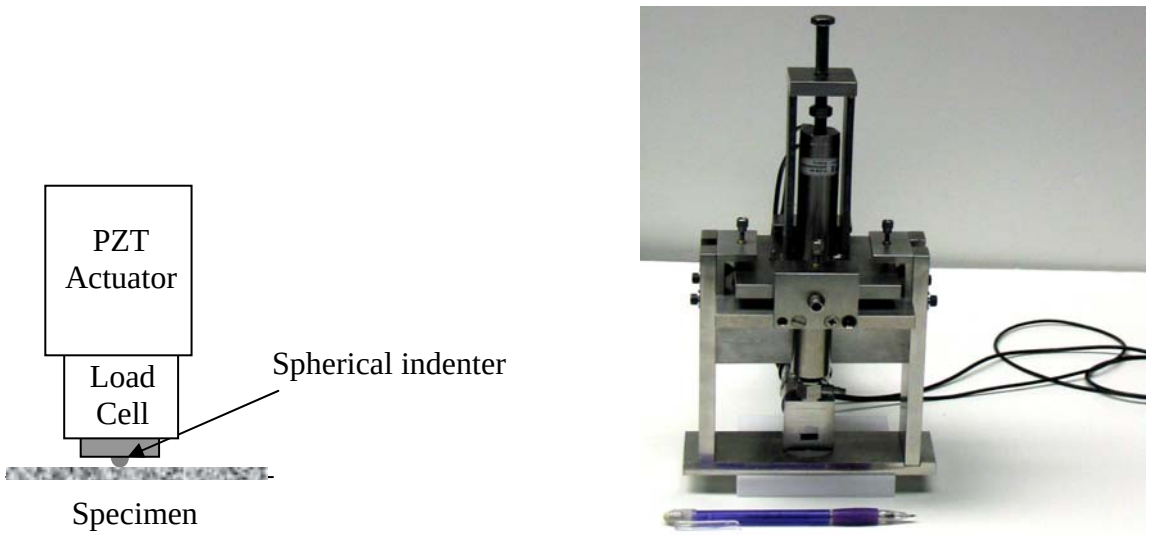


Figure 4: Micro-indentation system.

A schematic load-indentation depth curve is shown in Figure 5. The PZT actuator provides the overall indentation depth (h) measurement, which includes both the indentation penetration depth and system rigid-body displacement, i.e.,

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

where h_i is the indentation depth and h_s is the system displacement.

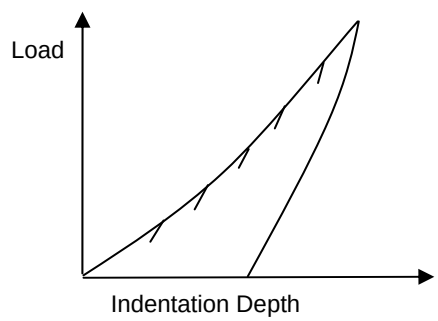


Figure 5: Indentation test with multiple partial unloadings.

At every unloading step (Figure 4), the unloading compliance is

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

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.

From theoretical indentation analysis [5], the unloading compliance of an spherical indentation can be expressed in terms of the indentation load, i.e.,

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

where $C = \left(6RE_r^2\right)^{-1/3}$, R is the radius of the indenter, and E_r is the reduced modulus, defined by $\frac{1}{E_r} = \frac{1-v_i^2}{E_i} + \frac{1-v_0^2}{E_0}$. E_i is the Young's modulus and v_i is the Poisson's ration of the specimen, and subscript 0 denotes the indenter's mechanical properties.

Substitute Equation (3) into Equation (2),

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

Equation (4) shows that $\frac{dh}{dp}$ and $\frac{1}{p^{1/3}}$ has a linear relationship if C_s remains constant within a indentation loading range, and thus material Young's modulus can be determined from the measured slope *C*. It should be noted that, after obtaining the Young's modulus, material hardness value and stress-strain curve can also be determined [5].

4.2 Validation test

Using the above-mentioned procedure, indentation tests were conduct on a Inconel 783 alloy sample. Figure 6 shows a typical load-indentation depth curve with multiple partial unloadings. The Young's modulus determined based on Equation (4) is 170.2GPa, which is in excellent agreement with the book value of 170 GPa.

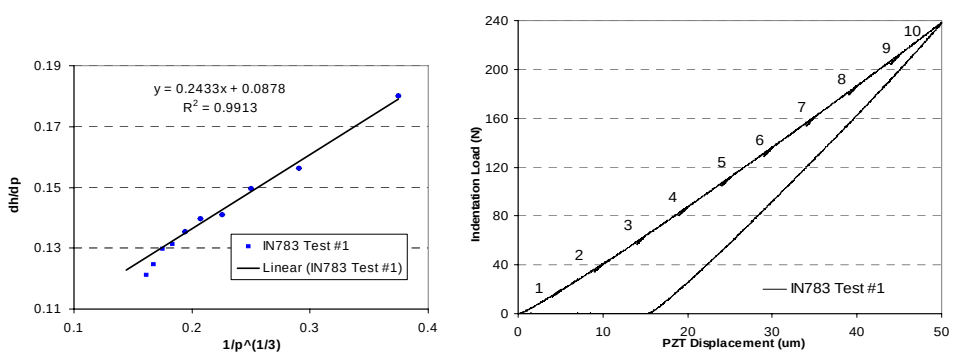


Figure 6: Load-indentation depth curve with partial unloadings, Inconel 783.

4.3 Results

Table 5 shows the measured Young's modulus of selected Mo alloys using the newly developed micro-indentation method. Alloys #678, #696, #697, and #698 were developed by Dr. J. Schneibel at ORNL with either $MgAl_2O_4$ or MgO micro-size oxide dispersions.

The results of #697 show favorable comparison to the tensile test result. The follow-up microstructural studies will be presented in the next quarterly report.

Table 5 Young's modulus using multi-partial unloading indentation technique

Material	Young's modulus (GPa)
#678, Mo-3.4wt%MgAl2O4	229
#696, Mo-3.0wt%MgAl2O4	200
#697, Mo-6.0wt%MgAl2O4	192 (Tensile test : 189)
#698, Mo-3wt%MgO	211
Mo-MgO (WVU)	254
Mo-MgAl2O4 (WVU)	202
Mo-TiO2 (WVU)	226

5. Conclusion and future work plan

Atomistic modeling

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, etc. 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 will be used in larger scale (nano-scale) simulations to study other metal oxide dispersions as well as their size effects.

Our future work include performing electronic structure analysis for a much larger, more realistic systems, possibly at the nano-scale, as well as other metal oxide ductilized Mo- and Cr-based alloys systems. The larger systems will be simulated using tight-binding (TB) method. We have developed a unique scheme to extend the capabilities of our existing FP-LMTO package, to extract the TB parameters directly from *ab-initio* calculations[2]. We also have access to the FIREBALL package[3], an ab-initio tight-binding molecular dynamic package that is suitable for studying both the static electronic structure properties and the dynamic effects of impurity diffusions and processing conditions, etc. Through these simulations, we will understand how various controlling factors, such as dispersion material's composition, size and morphology, can interplay and affect the ductility enhancement mechanism. While the optimal parameters may not be exactly predicted, the results of the numerical simulations can at least shed light on the tendency of varying sizes, and provide clues for experimentalists in searching for optimal size to improve the mechanical properties.

In-situ mechanical property measurement

A new micro-indentation technique has been developed for in-situ mechanical property measurement. Using an automated multiple-loading/unloading indentation testing sequence, the micro-indentation technique is capable of in-situ material mechanical property measurement and quick assessment of ductility/brittleness of the sample alloys under development. This technology has the potential to develop a hand-held portable device for on-site, in-situ mechanical properties evaluation of structural metallic components used in power system.

For Year-three research, we will continue the in-situ mechanical property evaluation of the Mo and Cr alloys developed with suitable metal oxides. We also plan to seek research collaboration with ORNL research scientist, Dr. M. Brady, on the new high strength steel alloys recently developed by him. Application of the newly developed micro-indentation method on the new high strength steel alloys can provide quick assessment of the alloy's mechanical properties using only tiny pieces of alloy samples. We plan to develop a high-temperature micro-indentation test apparatus for mechanical and creep property measurement (of the alloys under development) at elevated temperatures (up to 1200 ^{0}C).

As shown schematically in Figure 7, a high temperature module can be constructed to be integrated to a portable indentation system (with a supporting ceramic rod attached to the load cell for thermal insulation) for high temperature indentation test of the alloy samples. The commercially available high intensity focusing quartz lamp system has the capability for rapid isothermal heating (up to 1200°C) as well as cyclic heating of the test specimen.

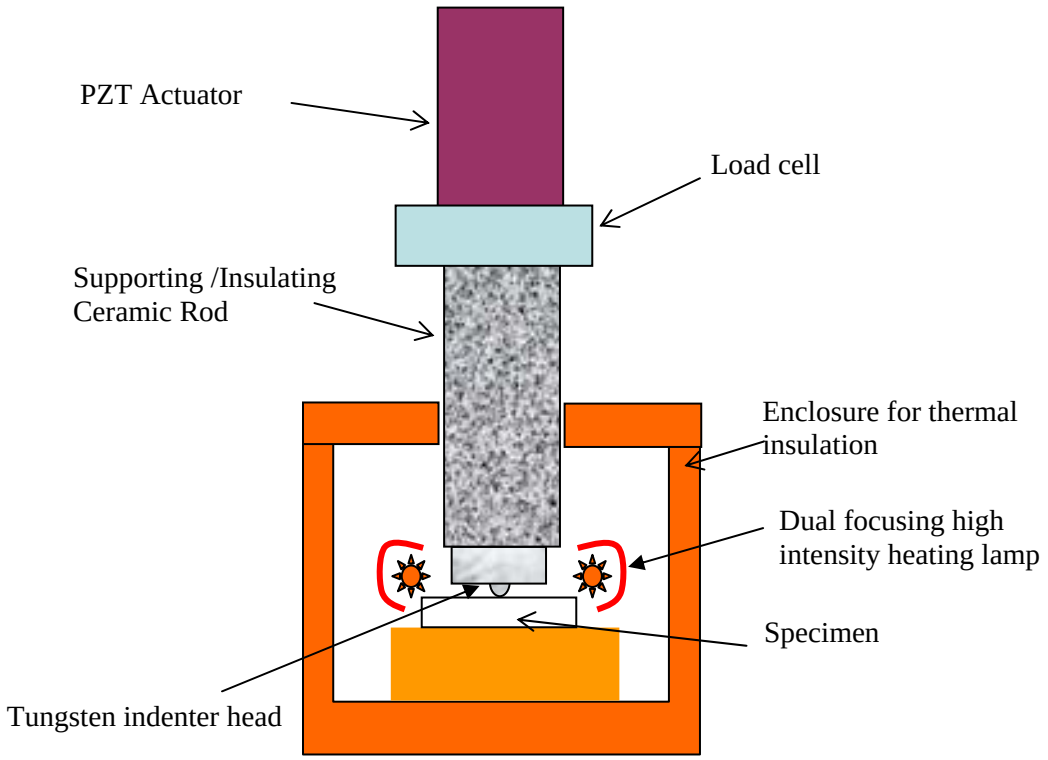


Figure 7: High temperature micro-indentation system.

Reference:

[1]M.P. Brady, I.M. Anderson, M.L. Weaver, H.M. Meyer, L.R. Walker, M.K. Miller, D.J. Larson, I.G. Wright, V.K. Sikka, A. Rar, G.M. Pharr, J.R. Keiser, C.A. Walls, Mater. Sci. & Eng. A358, 243-254 (2003)

[2] D.L. Price and B.R. Cooper, Phys. Rev. B 39, 4945-4957 (1989); D.L. Price, J.M. Wills and B.R. Cooper, ibid. 46, 11368-11375 (1992).

[3] N. Ma, B.R. Cooper, and B.S. Kang, J. App. Phys. 99, 053514 (2006)

[4] O.F. Sankey and D.J. Nikleswki, Phys. Rev. B. 40, 3979 (1989)

[5]C. Feng, B. 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.