



---

## Faculty Scholarship

---

2008

# Criteria for ductility in Cr alloys based on electronic structures

Ning Ma

Bernard R. Cooper

James P. Lewis

Bruce S. Kang

Follow this and additional works at: [https://researchrepository.wvu.edu/faculty\\_publications](https://researchrepository.wvu.edu/faculty_publications)

---

### Digital Commons Citation

Ma, Ning; Cooper, Bernard R.; Lewis, James P.; and Kang, Bruce S., "Criteria for ductility in Cr alloys based on electronic structures" (2008). *Faculty Scholarship*. 108.

[https://researchrepository.wvu.edu/faculty\\_publications/108](https://researchrepository.wvu.edu/faculty_publications/108)

This Article is brought to you for free and open access by The Research Repository @ WVU. It has been accepted for inclusion in Faculty Scholarship by an authorized administrator of The Research Repository @ WVU. For more information, please contact [ian.harmon@mail.wvu.edu](mailto:ian.harmon@mail.wvu.edu).

## Criteria for ductility in Cr alloys based on electronic structures

Ning Ma,<sup>1,a)</sup> Bernard R. Cooper,<sup>1</sup> James P. Lewis,<sup>1</sup> and Bruce S. Kang<sup>2</sup>

<sup>1</sup>Department of Physics, West Virginia University, Morgantown, West Virginia 26506, USA

<sup>2</sup>Mechanics and Aerospace Engineering Department, West Virginia University, Morgantown, West Virginia 26506, USA

(Received 28 June 2008; accepted 20 August 2008; published online 16 December 2008)

We proposed several hypotheses based on Rice's [Mech. & Phys. of Sol. **40**, 239 (1992)] brittle-ductile criterion to explain materials' mechanical properties from their electronic structures. These criteria were used in the study of mechanisms behind the ductility enhancement in Cr alloys by MgO dispersions through first principles methods and molecular dynamics simulations. The understanding of the mechanisms may help provide systematic strategy to further improve this and other related material's mechanical properties. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2981575](https://doi.org/10.1063/1.2981575)]

Due to their ultrahigh working temperature range ( $>1000$  °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.<sup>1–11</sup> However, a severe drawback with these materials is their limited room temperature ductility. A recent discovery found that the inclusion of MgO dispersions can improve the ductility of Cr alloys by 10%–20%.<sup>12</sup> The microstructure analysis reveals that the embrittling impurity species (notably N and S) in the Cr matrix are attracted by the MgO dispersions to segregate or precipitate near the Cr–MgO interfacial boundaries.<sup>12</sup> Therefore, the mechanism was speculated to be the cleaning up of the detrimental elements in the bulk of the metal matrix. Interestingly, no ductility improvement was found in Cr with other types of oxide dispersions (such as La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>) with similar microstructures. This fact suggests that some unknown factors must have contributed to the ductility enhancement effects. In this letter, we attempt to address these factors from a microscopic point of view based on electronic structure analysis.

Theories based on energetic arguments have been developed to relate the atomic crystal structures to mechanical properties. For example, the classic theory of Griffith<sup>13</sup> 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<sup>14</sup> 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 usually difficult to accurately determine 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 applica-

tions. At the basic fundamental level, the mechanisms responsible for the impurity and additive effects are still largely unknown.

To overcome the above difficulties, we extend the Rice's criterion and propose several hypotheses that enable us to conveniently study the impurity effects on material's ductility properties. The hypotheses are based on the properties of the valence electrons that participate in forming chemical bonds between atoms in solids. The knowledge on the valence electrons will then translate into that of the chemical bonds, and hence to their ductility or brittleness mechanical properties. Compared with the classical energetics approach, the electronic structure analysis provides more comprehensive information, yet it only involves standard techniques that are readily available with many electronic structure software packages. In this letter, the electronic structure analyses are carried out using the all-electron full potential linear muffin-tin orbital (FP-LMTO) method,<sup>15</sup> as well as an *ab initio* tight-binding method called FIREBALL.<sup>16</sup>

According to Rice's criterion, it costs less energy for a ductile material 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 the electrons making up these bonds to be delocalized and mobile so that they easily adapt to the motions of the ions and refill the voids whenever necessary to preserve the metallic bonds. To characterize the relevant properties of valence electrons, we use FP-LMTO method to analyze and compare a number of electronic structure features for two model systems (see Fig. 1): (a) a  $1 \times 1 \times 3$  Cr supercell containing an interstitial nitrogen at the center representing an impurity embrittled metal and (b) a  $1 \times 1 \times 3$  Cr supercell interfaced with six stacks of MgO layers with interstitial nitrogen impurities near the Cr–MgO interface, representing the ductility enhanced system due to the inclusion of MgO.

We first consider the spatial distribution of the electronic charge. Delocalized electrons are shared by many atoms; therefore, they contribute most to the metallic bonds and ductile properties. In an FP-LMTO calculation, the charge distribution of a given electronic state is conveniently partitioned into the interstitial region and the muffin-tin (MT) spheres. In the following analyses, we consider electronic

<sup>a)</sup> Author to whom correspondence should be addressed. Tel.: +1-304-293-3422ext1448. FAX: +1-304-293-5732. Electronic mail: ning.ma@mail.wvu.edu.

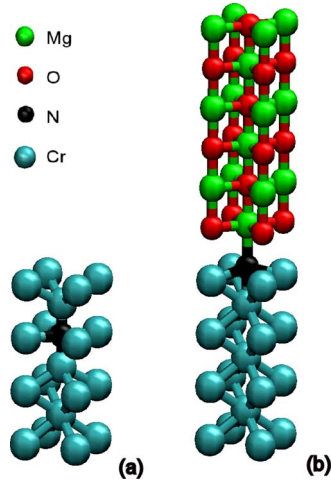


FIG. 1. (Color online) The schemes of the simulated systems: (a) a  $1 \times 1 \times 3$  Cr or Mo supercell containing a nitrogen or oxygen impurity at the center and (b) a  $1 \times 1 \times 3$  Cr or Mo supercell (bottom) interfaced with six stacks of MgO layers on top, with nitrogen or oxygen impurity near the interface.

states within 0.1 Ryd near the Fermi level. These states belong to chromium's  $3d$  and  $4s$  bands, as magnesium and oxygen's energy bands are much farther away from the Fermi level. The spatial extent of these states is therefore mostly confined to the Cr side in system 1(b) and includes all space in system 1(a). Around 14% of charge in these states is found in the interstitial region for the impurity embrittled system. In ductility enhanced system this proportion is found to be 16% (about 14% increase similar in range found in experiments<sup>12</sup>), indicating a higher concentration of interstitial charge or a more delocalized distribution. We also calculated the variance of MT charge distributions for these states for the impurity embrittled system  $\sigma^2=0.014e^2$  and for the MgO dispersed system  $\sigma^2=0.012e^2$ . A lower variance represents more evenly spread (or delocalized) MT charge distribution. The higher proportion of interstitial charge and more uniformly distributed MT charge together contribute to stabilize the stacking fault configuration. Therefore, the extent of charge delocalization can be used as a criterion for ductility.

The electron charge can also be projected into different angular momentum channels within each MT. For transition metal Cr, the valence electrons occupy  $4s$  and  $3d$  orbitals. Chemical bonds formed by  $s$  orbitals are more flexible than those formed by  $d$  orbitals. This is because the spatial distribution of  $s$  orbital is isotropic. Correspondingly, the characteristics of the chemical bonds are more metallic, having no directional preferences, and are easier to adapt to unstable stacking configurations. In contrast, chemical bonds formed by  $d$  orbitals are highly directional, behave more covalent-like, and cost more energy to bend. The average angular momentum projected occupations are calculated to be  $0.22e$  in  $s$  orbital and  $3.75e$  in  $d$  orbital, respectively, for a Cr in the impurity embrittled system; while for a Cr in the MgO dispersed system, the average occupations are slight higher:  $0.27e$  in  $s$  orbital and  $3.96e$  in  $d$  orbital. Evidentially, the Cr–Cr bonds are strengthened in the latter case. When the partition ratios are compared, the brittle system has about 5.5% electrons in  $s$  orbital, while the ductile system has 6.4% (about 16% increase). The increase in  $s$  channel partition ratio leads to an increase in the metallic bond behavior. The

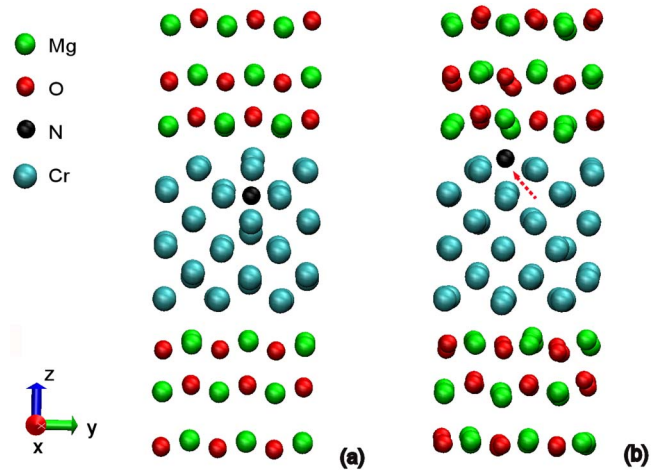


FIG. 2. (Color online) The diffusion of N in Cr/MgO system (109 atoms) obtained using FIREBALL molecular dynamics package. The temperature is 600 K. Shown on the left is the initial system configuration, where the nitrogen impurity is placed inside the Cr matrix. The final system configuration after 1000 simulation steps (1 ps) is shown on the right. The diffusion length is about 0.2 nm.

fact that metallic bonds render ductility and covalent bonds cause brittleness can be understood through Rice's criterion as well. In systems where metallic bonds dominate, the uniformly shared electrons are more tolerant with stacking faults; whereas in covalent materials, the stretching and reconnection of bonds associated with dislocation flow usually encounter significant higher energy barrier. Assuming an equal energy cost to create new surfaces by cleavage, the Rice ratio  $\gamma_{us}/\gamma_0$  will be higher in metallic systems than in covalent systems. Therefore, the partition ratio of  $s$  and  $d$  channels may serve as an indicative of material's mechanical properties.

Finally, using FIREBALL package, we were able to extend the model system to a larger scale and to carry out the molecular dynamics simulations. At a constant temperature of 600 K, a nitrogen impurity was initially placed within the center of a  $3 \times 3 \times 3$  Cr supercell that is interfaced with six stacks of MgO. During the simulation period of 1 ps (1000 simulation steps), the nitrogen impurity was found to diffuse to the Cr/MgO interfacial boundaries (see Fig. 2), which is consistent with the experiments of Brady *et al.*<sup>12</sup> To understand how the position of the nitrogen impurity affects the system's mechanic properties, we carried out the electronic structure analyses for both the initial and final configurations. To compare the extent of delocalization for a given electronic state, we evaluate the entropy of the state defined as  $S = -\sum n_i \log n_i$ , where  $n_i$  is the partition of the charge on the  $i$ th atomic site, and the summation goes over all atomic sites. States with larger entropy are more delocalized. Within 1 eV around the Fermi level, the total number of states is found to increase from 73 to 76 as the impurity diffused from the center of Cr matrix to the Cr/MgO boundary. The average entropy for these states has also increased from 81.4 to 83.9. The MgO induced diffusion of nitrogen indeed promotes both the mobility and delocalization of the electronic charge within the system. Our proposed criteria therefore explain the ductility enhancement.

To summarize, we obtained and compared the electronic structures of selected Cr systems containing N 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 and the angular momentum projected occupations. These criteria are shown to be in consistency with the Rice's criterion derived from energetic arguments. Based on these criteria, we explained the impurity embrittlement and ductility enhancement effects due to N and MgO.

This work is supported by DOE/NETL Fossil Energy advanced research material program under Subcontract No. 6400005286 and DOE/NETL UCR program under Contract No. DE-FG26-05NT42526.

- <sup>1</sup>M. K. Meyer, M. J. Kramer, and M. Akinc, *Intermetallics* **4**, 273 (1996); M. K. Meyer and M. J. Akinc, *J. Am. Ceram. Soc.* **79**, 2763 (1996).
- <sup>2</sup>D. M. Berczik, U.S. Patent No. 5,595,616 and 5,693,156 (1997).
- <sup>3</sup>J. H. Schneibel, C. T. Liu, L. Heatherly, and M. J. Kramer, *Scr. Mater.* **38**, 1169 (1998).
- <sup>4</sup>M. Akinc, M. K. Meyer, M. J. Kramer, A. J. Thom, J. J. Heusch, and B. Cook, *Mater. Sci. Eng., A* **261**, 16 (1999); M. K. Meyer, A. J. Thom, and M. Akinc, *Intermetallics* **7**, 153 (1999).
- <sup>5</sup>K. Natesan and S. C. Deevi, *Intermetallics* **8**, 1147 (2000).
- <sup>6</sup>J. H. Schneibel, M. J. Kramer, O. Unal, and R. N. Wright, *Intermetallics* **9**, 25 (2001); H. Choe, D. Chen, J. H. Schneibel, and R. O. Ritchie, *ibid.* **9**, 319 (2001).
- <sup>7</sup>J. H. Schneibel, M. J. Kramer, and D. S. Easton, *Scr. Mater.* **46**, 217 (2002).
- <sup>8</sup>H. Choe, J. H. Schneibel, and R. O. Ritchie, *Metall. Mater. Trans. A* **34**, 225 (2003).
- <sup>9</sup>J. H. Schneibel, J. J. Kruzic, and R. O. Ritchie, Proceedings of the 17th Annual Conference on Fossil Energy Materials, Baltimore, MD, 22–44 April 2003 (unpublished).
- <sup>10</sup>V. Supatarawanich, D. R. Johnson, and C. T. Liu, *Mater. Sci. Eng., A* **344**, 328 (2003).
- <sup>11</sup>J. J. Kruzic, J. H. Schneibel, and R. O. Ritchie, *Scr. Mater.* **50**, 459 (2004).
- <sup>12</sup>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, and C. A. Walls, *Mater. Sci. Eng., A* **358**, 243 (2003).
- <sup>13</sup>A. A. Griffith, "The theory of rupture," in *Proceedings of the First International Congress of Applied Mechanics* (Delft, The Netherlands, 1924), pp. 55–63.
- <sup>14</sup>J. R. Rice, *J. Mech. Phys. Solids* **40**, 239 (1992).
- <sup>15</sup>D. L. Price and B. R. Cooper, *Phys. Rev. B* **39**, 4945 (1989); D. L. Price, J. M. Wills, and B. R. Cooper, *ibid.* **46**, 11368 (1992).
- <sup>16</sup>J. P. Lewis, K. R. Glaesemann, G. A. Voth, J. Fritsch, A. A. Demkov, J. Ortega, and O. F. Sankey, *Phys. Rev. B* **64**, 195103 (2001).