Computational Metallurgy

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It is fitting that steel, one of the oldest of man-made materials, is now the focus of a program aimed at changing the way new and improved materials are developed. This approach exploits the ever-growing power of computers and computational methods in an area of interdisciplinary research that has become known as computational materials science. Whereas computer-aided design and development have proved extremely useful in many areas of science and engineering, the use of computational methods in the design of materials has not progressed as rapidly. The reasons for this slow progress are related to the fact that materials properties cannot be attributed to a single phenomenon. Rather, these properties result from phenomena occurring at many different scales of length and energy. Consequently, the successful incorporation of computational methods in the materials development process has required a long waiting period, while models and methods capable of treating each of these phenomena independently were perfected. Only then could all the models and methods be incorporated into a single program of materials development. Now, after more than a decade of work by researchers around the world, the tools that will allow for the computationally assisted design of structural metals are coming together. As reported on page 376 of this issue, researchers of the Steel Research Group at Northwestern University are taking up these tools in an attempt to design new structural steels (*1*).

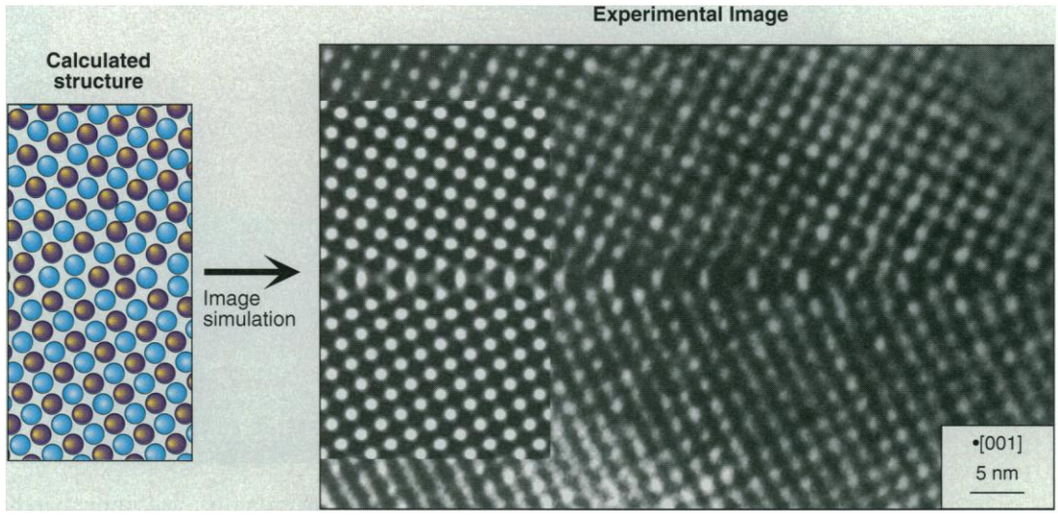
Steels consist mainly of iron atoms. The iron atoms combine with other elements to form various crystal phases and arrangements, which constitute the many different types and conditions of steel. In the last half century, steel development has benefited from a more fundamental understanding of alloying, solidification, phase transformations, deformation, and fracture mechanisms. In the pursuit of improved structural steels, all of these phenomena are being investigated through combined programs of computation and experimentation. However, particular emphasis is being placed on the use of computational methods to uncover mechanisms by which strength can be increased without the introduction of undesirable failure modes.

For centuries it has been known that under certain conditions steels will fail in a brittle fashion. It has also been observed that as the strength of a steel is increased, its susceptibility to brittle failure also increases. The origins of this behavior have been traced to the presence of impurities whose concentrations are so low, less than a few parts per million, that they cannot be removed cost effectively from the alloys. Yet, given the right thermal conditions, these impurities will segregate to internal boundaries, where they will degrade the cohesive properties across these boundaries. Elements that degrade cohesive properties are referred to as embrittling elements. On the other hand, there are elements that similarly segregate to internal boundaries yet have the opposite effect in that they tend to improve the cohesive properties of these boundaries. Such elements are called cohesive enhancers.

The improvement of structural steels is intimately tied to our ability to counter or eliminate the effects of embrittling elements. Yet only 15 years ago, the mechanisms by which these elements embrittled a boundary were not well understood. The prospects for uncovering these mechanisms through traditional experimental investigations were not promising, as the embrittled boundaries are internal and so hidden from direct observation. This led two investigators at General Electric Research Center to begin a pioneering computational study of embrittlement. Using quantum mechanical methods, Messmer and Briant (*2*) modeled metal clusters coordinating known embrittling elements. They searched for characteristics of the calculated electronic structure that could be identified as the fingerprint of embrittlement. Although this investigation did result in new theories of embrittlement, its more long-lasting contribution was to make an explanation of this phenomenon a benchmark in the development of computational materials science. For many materials modelers working at the atomic level, the challenge of explaining embrittlement was seen as the acid test for the tools and methods they were developing.

The sudden interest in the application of quantum mechanical methods to the study of embrittlement phenomena had the effect of producing collaborations between metallurgists, chemists, and solid-state physicists. At the outset, it was realized that if these collaborations were to be successful at explaining embrittlement, rather than simply correlating its occurrence with features of the electronic structure, it was necessary to associate some calculable quantity with its occurrence. Several such quantities were suggested.

Rice and Wang (*3*), reasoning from a thermodynamic point of view, argued that the difference in segregation energy for an



Calculated model (left) and high resolution microscope image (right) of the symmetric tilt grain boundary with [001] tilt axes, which forms a twin about the (310) plane, viewed parallel to tilt axes. Inserted in the micrographs are simulated images obtained with the calculated grain boundary structure.

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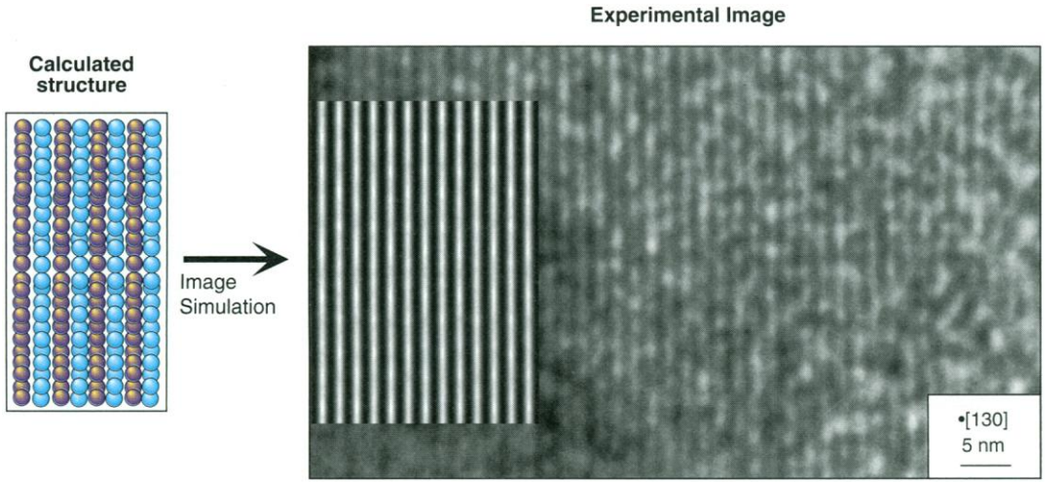
impurity atom at a grain boundary and free surface provided a measure of that element's embrittling potency; the more positive this value, the more potent an embrittler. The difficulty at the time was that quantum mechanical methods had not demonstrated sufficient accuracy to calculate these quantities. Vvedensky and I adopted an alternative view of embrittlement (*4*), one consistent with what was then calculable. In our view, the fracture of a boundary is best seen as a chemical reaction, with the grain boundary being the reactant and the free surfaces resulting from fracture, the products. Embrittling elements were then seen as catalyzing or promoting the reaction, whereas cohesive enhancers acted as poisons to the reaction. The calculable quantity in this model was the energy and symmetry of the one-electron states that would be involved in charge transfer during a chemical reaction. These are important quantities in the well-established quantum mechanical theories of reaction kinetics. Painter and Avrill (*5*) adopted a third view. Reasoning that grain boundary strength was tied to the forces necessary to distort metal clusters representative of the grain boundary environment, they calculated these forces for metal clusters and clusters coordinating impurity elements.

At the same time that scientific rationales for embrittlement were being proposed and tested, new methods of quantum mechanical calculations were being devised and existing methods improved. The impetus for the development of some of these techniques could be traced directly to the desire to better describe the electronic structure of grain boundaries and surfaces and the effect of impurities on these boundaries. The Layer-Korringa-Kohn-Rostoker (LKKR) technique (*6*) was developed as a method capable of treating an isolated interface or surface and was first used to model the embrittling effects of sulfur on nickel grain boundaries. The desire to apply these methods to calculate the energy difference proposed by Rice as an indicator of embrittling potency required first a demonstration that known interfacial energies could be accurately determined. This motivated a series of studies (*7*) aimed at calculating fault energies and the effects of impurities on these energies. These studies convincingly demonstrated that modern quantum mechanical techniques are sufficiently accurate to determine the values of the interfacial energies that are important to a complete understanding of embrittlement. All of these investigations have now culminated with the paper by Wu, Freeman, and Olson (*1*), which reports the results of investigations that made use of the highly accurate FLAPW technique to determine the difference in interfacial energies associated with embrittling potency.

Fifteen years after Messmer and Briant's quantum mechanical investigation of embrittlement, after extensive improvements to techniques, after numerous investigations seeking to confirm different rationales for embrittling behavior, can the origins of embrittlement now be explained? With cautious optimism, the answer is yes. All of the calculations, whether seeking a chemical, energetic, or force basis to explain embrittlement, show characteristic similarities that are alternatively evoked as justification for the magnitude of the quantities calculated. Vvedensky and I (*4*) noted that cohesive enhancers must necessarily give rise to delocalized grain boundary states. In turn, embrittling elements must give rise to localized "atom-like" states at a grain boundary. We further noted that there must be certain relations between the energies and number of electrons on the impurity atom and the energies of the electrons in the host metal in order to promote cohesive enhancement or embrittlement. These same characteristics are noted by Wu, Freeman, and Olson (*1*) and are convincingly argued to be the origins of the trends in the grain boundary and surface energies that they compute for phosphorus and boron in an iron host. Now, using the traits identified as being responsible for embrittlement phenomena, researchers of the Steel Research Group at Northwestern are using computational methods in a search for new alloying elements for structural steels. It is hoped that these will reduce or eliminate the effects of embrittling elements. If successful in this effort, quantum mechanical methods will have demonstrated their utility in the growing field of computational materials science.



Calculated model (left) and microscope image (right) of the same grain boundary, viewed perpendicular to tilt axes. It is at boundaries like these that segregants produce their embrittling or cohesive enhancing effects. [Figures courtesy of G. Campbell and W. King, Lawrence Livermore National Laboratory]

For the broad area of computational materials science, the experience gained in the development of a theory of embrittlement offers a number of valuable lessons. First among these is the level of expectation that one should place in computational methods. Progress from the identification of the problem, to the development of the appropriate computational tools, through the theoretical investigations, and ending with a consensus as to the origins of embrittlement has required more than 15 years. By today's standards, this is an extremely long time from the inception of a research program to payoff. Unless expectations can be held to time scales of this sort, there will be inevitable disappointments when computational methods do not produce short-term results. However, if programs are begun with reasonable expectations and as experience is gained in the use of computational methods in the materials development process, these methods will offer the ability to explore materials properties at a level unavailable through the use of experimental techniques alone.

References

1. R. Wu, A. J. Freeman, G. B. Olson, *Science* **265**, 376 (1994).
2. R. P. Messmer and C. L. Briant, *Acta. Metall.* **30**, 457 (1982).
3. J. R. Rice and J. S. Wang, *Mater. Sci. Eng.* **1**, 251 (1989).
4. M. E. Eberhart and D. D. Vvedensky, *Scr. Metall.* **22**, 183 (1988).
5. G. S. Painter and F. W. Avrill, *Phys. Rev. Lett.* **58**, 234 (1987).
6. J. M. MacLaren, S. Crampin, D. D. Vvedensky, J. B. Pendry, *Phys. Rev. B* **40**, 12164 (1989).
7. J. M. MacLaren, S. Crampin, D. D. Vvedensky, M. E. Eberhart, *Phys. Rev. Lett.* **63**, 2586 (1989).