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An ab initio driven model for the trapping and diffusion of hydrogen in Fe- Cr-Ni alloys

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AN AB INITIO DRIVEN MODEL FOR THE TRAPPING AND DIFFUSION OF HYDROGEN IN FE-CR-NI ALLOYS

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DALE HITCHCOCK   TIMOTHY KRENTZ
SAVANNAH RIVER NATIONAL LABORATORY

ERICH WIMMER   CLIVE FREEMAN
MATERIALS DESIGN, INC.
Holistic approach to understanding materials manufacturing incorporating theory, computational, and experiments\(^1,\)\(^2\)

Hydrogen Embrittlement is an unknown linkage in the system design chart of many Fe-Cr-Ni systems.

From a manufacturing point of view, fundamental understanding of the underlying chemistry and structure are useful.

Savannah River National Laboratory (Dale Hitchcock and Tim Krentz) performed hydrogen permeation studies tied to microstructural and chemical analysis.

KCNSC and Materials Design, Inc. completed *ab initio* workflows and calculations for determining hydrogen diffusion coefficients.

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How to generate representative atomistic structures?

Employ the Universal Cluster Expansion\(^3\) method to create large scale, thermodynamically stable and energetically minimized atomistic models.

- Monte Carlo heating and cooling temperature schedule.
- Structure selection before phase separation.
- Parse into \(2 \times 2 \times 2\) 32 atom cells.
- SRO matches known electronegativity in Cr.

Section of primitive Fe\(_{0.7}\)Cr\(_{0.2}\)Ni\(_{0.1}\) cell.

\(^3\)D. Lerch et al., “UNCLE: a code for constructing cluster expansions for arbitrary lattices with minimal user-input”, Modelling and Simulation in Materials Science and Engineering 17, 055003 (2009).

P.R. Thomas (KCNSC) NSC-614-5661 dated 09/2023 UUR 09/20/2023 2 / 17
The target chemistry $\text{Fe}_{0.7}\text{Cr}_{0.2}\text{Ni}_{0.1}$ and normal distribution of chemical composition well represented in structure library.

The total energies of the structures have then been analyzed with respect to total chemical variation and Cr:Ni ratio.

<table>
<thead>
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<th>Percentage</th>
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<td>0.2</td>
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<td>0.6</td>
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</tbody>
</table>

![Diagram showing Fe, Cr, and Ni percentages]
Calculations completed in VASP (Vienna ab-initio simulation package). Calculations of parsed atomistic structures show logarithmic total energy as a function of total $E$.

\[ \Delta E_{\text{bind}} = E(\text{Fe}_x, \text{Cr}_y, \text{Ni}_z : H_{\text{int}}) - E(\text{Fe}_x, \text{Cr}_y, \text{Ni}_z) - \frac{1}{2} E(\text{H}_2) \]
Trapping Energy Calculation

Numerically stable method for determining trapping energy in cells.

$$\Delta E_{\text{trap}} = E_{\text{rel}} + E_{H\in\square} - (E_{\square} + E_{H\in\text{int}})$$  \hspace{1cm} (2)

Inherent chemistry dependence of the structures

1. $E_{\text{rel}}$ - Chemistry of the base parsed cell.
2. $E_{H\in\square}$ - Variations of the local chemistry around the three and four fold binding sites in an fcc vacancy.
3. $E_{\square}$ - Chemistry of the element removed from the lattice and the chemistry about the vacancy.
4. $E_{H\in\text{int}}$ - Up to third order nearest neighbor chemistry at the stable octahedral interstitial site.
Performing a topological analysis of the $\rho_{el}$ by searching for minima and saddle points will result in locating the minima and saddle points for a hydrogen atom.

\[ f(\rho) = 10.0 - 20.0\sqrt{\rho} + 30.0 \cdot \rho \] (3)

Applying Nørskov’s theory\textsuperscript{5, 6}, yielded Eq. 3 for both Nickel and FeCrNi systems.


Energetics of the Minima and Transition States
Kinetic Monte Carlo Diffusion Algorithm

The kMC approach is based on a review from Voter\textsuperscript{7} and starting from Einstein\textsuperscript{8} with the corresponding jump rates determined from Eyring’s transition state theory\textsuperscript{9}.

The diffusion coefficient can be calculated as:

\[ D = \frac{1}{2\alpha t} \langle |D\mathbf{r}(t)|^2 \rangle \]  \hspace{1cm} (4)

and the corresponding jump rates of hydrogen as:

\[ \Gamma = \frac{kT}{h} \prod_{i=1}^{3N-7} \left[ 2\sinh \left( \frac{h\nu_i T}{2kT} \right) \right]^{-1} e^{-\frac{\Delta E_{el}}{kT}} \]

\[ \prod_{i=1}^{3N-6} \left[ 2\sinh \left( \frac{h\nu_i^0}{2kT} \right) \right]^{-1} e^{-\Delta E_{el}/kT} \]  \hspace{1cm} (5)

---


\textsuperscript{8} A. Einstein, “¨Uber die von der molekularkinetischen theorie der w¨ arme geforderte bewegung von in ruhenden fl¨ ussigkeiten suspendierten teilchen”, Annalen der physik 4 (1905).

Exemplar System: Nickel Diffusion Coefficients

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$D$</th>
<th>$D_x$</th>
<th>$D_y$</th>
<th>$D_z$</th>
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</thead>
<tbody>
<tr>
<td>298.0</td>
<td>2.15998E-14</td>
<td>2.15442E-14</td>
<td>2.15425E-14</td>
<td>2.17129E-14</td>
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<td>500.0</td>
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<td>2.97662E-11</td>
<td>3.03133E-11</td>
<td>2.99680E-11</td>
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<tr>
<td>1000.0</td>
<td>7.51698E-09</td>
<td>7.58479E-09</td>
<td>7.54248E-09</td>
<td>7.42369E-09</td>
</tr>
</tbody>
</table>
Diffusion Coefficient Comparison

![Graph showing comparison of diffusion coefficients for different materials. The graph plots log(D, D in m^2/s) against 1000/T (1/K). The lines represent different materials: H in Fe-Ni-Cr, H in pure Ni, and H in Ni (2008).]
Interatomic Potential for A-F Interfaces

- New interatomic potential based on the embedded atom method (EAM).
- Includes the Ziegler-Biersack-Littmark (ZBL) short-range repulsive potential for simulations of collisions with high energy particles, e.g., neutrons.
- Flexible embedding function designed to represent the dominant attractive and repulsive terms.
- Set of floating Gaussians to capture additional features of the local environment around each atom.

\[
V_{ij}(r) = \{V_{ZBL}(r) f_{cut,\text{in}}(r) G(r) [1 - f_{cut,\text{in}}(r)]\} f_{cut,\text{out}}(r)
\]

(6)

\[
G(r) = \left[ \sum_{m=1}^{M} A_m e^{-\alpha_m r} + \sum_{n=1}^{N} c_n e^{-\gamma_n (r-r_n)^2} \right]
\]

(7)

\[
V_{ZBL}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} \phi \left( \frac{r_{ij}}{a} \right)
\]

(8)
Acknowledgements


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- Calculations completed with MedeA 3.7; MedeA is a registered trademark of Materials Design, Inc., San Diego, USA.¹⁰

- Special Thank You to KCNSC HPC Administrators: Ryan Simmons, Sam Adams, Lee Stoppelman!

¹⁰ M. Design, Medea 3.7 (materials exploration and design analysis), 12121 Scripps Summit Drive, Ste 160 San Diego, CA 92131, 2023.
Conclusions

- A model and workflow for accurate determination of atomistic models and high-throughput transition state calculations has been leveraged to create inputs to a kinetic Monte Carlo algorithm capable of determining diffusion coefficients as a function of temperature.
- A classical EAM-ZBL-FG potential has been created specifically to probe the hydrogen diffusion rates at known austenite-ferrite boundaries.
- A more rigorous analysis is included in the publication draft relating the first-principles work to the experimental values.
Experimental Validation Data

Courtesy of Savannah River National Laboratory
Experimental Validation Data

Courtesy of Savannah River National Laboratory