MAKING GREEN STEEL WITH HYDROGEN

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SUSTAINABLE SOLUTION: SUSTAINABLE STEEL

A conversation with one of green steel's pioneers Dierk Raabe.

Steel is an undisputed king of materials used in every important industry, from energy to construction to automotive. More than 2 billion tons of steel are produced annually, making it a key alloy in terms of volume and impact. In short, we cannot imagine a world without steel. [1] [2]

At the same time, we are forced to imagine a future in which the primary production of steel is sustainable — fossil-free. Steel no doubt supports sustainability through lightweight design, magnetic devices and efficient turbines, for example. However, its primary production does not. [3]

The current standard for about 70% of steelmaking worldwide involves the smelting of iron ore pellets in blast furnaces where carbon is the reductant. The process generates a staggering 3 billion tons of total direct CO_2 emissions amounting to 7% to 9% of all human-caused greenhouse gas emissions. To meet global energy and climate goals, steelmaking's CO_2 emissions will need to be cut by at least 50% by 2050, with declines towards zero emissions continuing thereafter, according to the World Steel Association (worldsteel). [4]

To accomplish this, current steel technologies must embrace carbon-lean production as a means of achieving a drastic 80% reduction in all CO_2 emissions. This means that the steel industry will need a vast portfolio of breakthrough technologies and a bold call to action for all stakeholder communities, according to worldsteel and the International Energy Agency's Iron and Steel Technology Roadmap. [5] [6]

Green steel

In the R&D community, scientists have been exploring ways to reduce steelmaking's carbon footprint through sustainably produced steel, or "green steel." This involves identifying multiple pathways for decarbonization, namely the direct removal of CO2 at the atomic scale. One highly promising option is the extraction of iron from its ores using hydrogen.

This option replaces carbon with hydrogen or its fossil-free carriers as a reducing agent. The process is known as hydrogen–based direct reduction of iron (H-DRI). Significant progress is being made in understanding the mechanisms of hydrogen-based H-DRI as well as a related alternative, hydrogen-based plasma reduction, according to Professor Dierk Raabe, managing director at the Max Plank Institute for Iron Research in Düsseldorf, Germany.

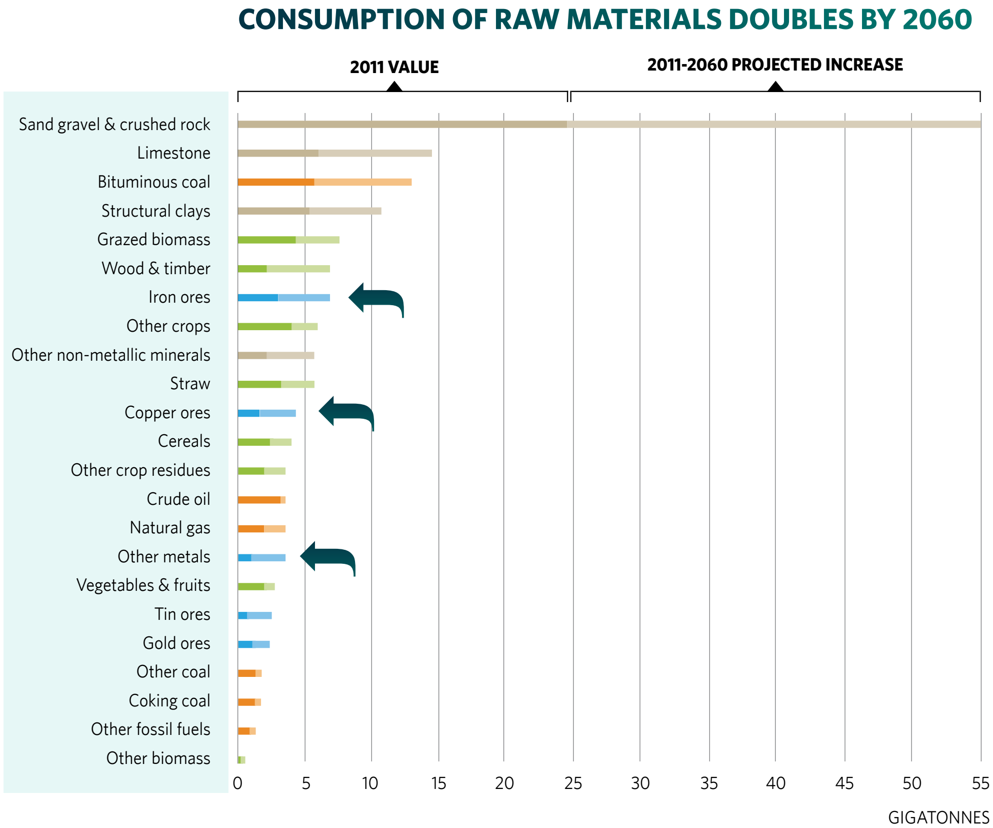
"Both are being explored as a sustainable route to mitigate CO_2 emissions, where the reduction kinetics of the intermediate oxide product Fe_xO (wüstite) into iron is the rate-limiting step of the process," Raabe said. "The total reaction has an endothermic net energy balance. Reduction based on a hydrogen plasma also offers an attractive alternative."

Q&A with Professor Dierk Raabe

Dierk Raabe (DR) presented at a CAMECA and Nature Research Custom Media webcast in November 2022 on the topic of green steel made with hydrogen. [7] CAMECA caught up with Raabe again to expand on the topic, including the production of green steel by direct reduction and plasma reduction, some of the remaining bottleneck research areas in green steelmaking and more:

Why research green steel?

DR: Much of our greenhouse gas emissions come from the combustion of fossil fuels for energy, from agriculture, manufacturing and construction, the latter of which dominates. We produce about 2 billion tons of steel annually, much more than all the other big ones like aluminum, nickel and titanium combined. Steel is beating them all in quantity, but also in energy consumption and CO_2 emissions.



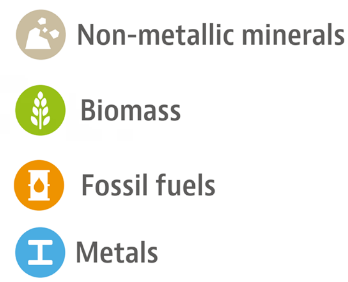


Figure 1: *OECD HIGHLIGHTS. Global Material Resources Outlook to 2060 – Economic Drivers and Environmental Consequence. [8]*

Steel represents the top material class when it comes to sheer volume and environmental impact. This problem is not coming to an end; it actually is growing. A forecast from the OECD shows that by the year of 2060, we will have doubled our consumption of many of the raw materials that lead to immense CO_2 emissions. An example is the consumption of iron ore, which will more than double. *(See Figure 1.)*

What is the role of DRI in green steelmaking?

DR: In primary steel synthesis, iron is reduced from ores by carbon, a process that contributes 30% of global CO_2 emissions from the manufacturing sector and thus qualifies it as the largest single industrial greenhouse gas emission source. The use of hydrogen for iron oxide reduction, also known as direct reduction of iron, or H-DRI, has been explored as a sustainable mitigating route for decades and is an attractive alternative.

However, reduction kinetics in hydrogen metallurgy still are relatively slow and not well understood. Some rate-limiting factors of the underlying reactions are determined by the microstructure and local chemistry of ores, particularly during the final step of the reduction of the oxide wüstite into metallic iron, which is much slower than the preceding reduction of the other oxides (hematite and magnetite). The total reaction has an endothermic

Atom probe tomography: What is it, why use it

Seeing and mapping atoms in complex materials and revealing the associated structure — the composition — and property relationships at this scale presents a great challenge in modern materials science, physics and chemistry. Materials properties emerge from short-range interactions among the atoms they are comprised of as well as their environment.

A key role of researchers is to obtain correlative information about structure, properties and dynamic behavior of materials at the atomic and electronic scales. At the Max Plank Institute for Iron Research, the atom probe tomography (APT) Local Electrode Atom Probe (LEAP) 3000 and LEAP 5000 tools are used to provide compositional data on a variety of materials systems.

APT's powerful spatial resolution capabilities ($\Delta x \approx \Delta y \approx 0.2$ nm and $\Delta z \approx 0.1$ nm) and detection sensitivity (element concentrations down to a few ppm detected regardless of elemental mass), provide information essential to understanding the structure-property relationships of complex materials. Similarly, APT allows advanced knowledge of atomic-scale phenomena such as solute segregation and clustering.

Through establishing the close atomic-scale relationship between structure and properties, scientists can work out the minutiae of material processes and further advance the development of next-generation materials. Despite the impressive performance of current analytical techniques, we still are far from reaching the ultimate resolution limit — i.e., obtaining the information we need to fully understand materials at 3D atomic and electronic scales. [10]

CONSUMPTION OF RAW MATERIALS DOUBLES BY 2060

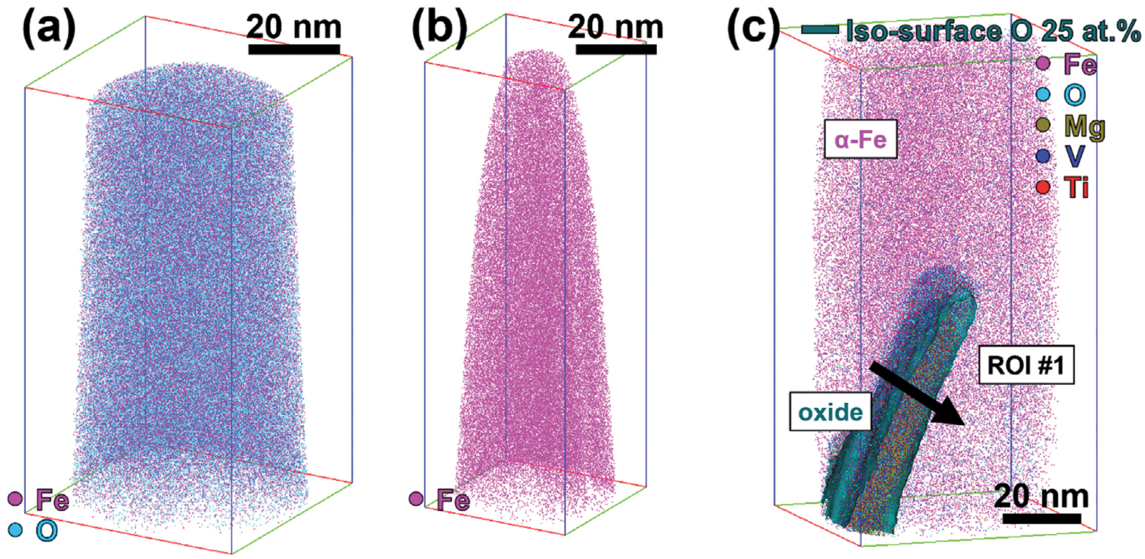


Figure 2: *3D atom probe maps of (a) before and (b) after the direct reduction of as-received hematite iron ore (hematite), from a region about 1 mm below the pellet surface. Pink and cyan dots in the 3D reconstructions represent individual Fe and O atoms, respectively. (c) A reconstructed 3D atom map acquired from as-reduced ore. Iso-surface of O at 25 at.% (cyan) represents the interface between α-Fe and the wüstite oxide. The inset is a 3D atom probe map of a 5 nm thin slice. [3]*

net energy balance, and it will require much more research to understand these processes. This includes continuing the study of the microstructures and composition at the atomic scale. *(See Figure 2.)*

There are macroscopic studies on the reduction of iron oxide exposed to gas mixtures that include hydrogen. Again, key aspects that influence reduction kinetics — microstructure, nano-chemistry, porosity, pressure conditions, reductant mixtures and more — require further research. We know that all of these lesser-known parameters and mechanisms act on micro- and even near-atomic length scales, with significant influence on transport and reaction kinetics. Thus, the next level of insight requires direct observations at these small scales, probing both structure and chemistry. [3]

Why is hydrogen plasma reduction (HPR) a viable hybrid method?

DR: In direct reduction with hydrogen, the reduction kinetics of wüstite, the intermediate oxide product, into iron is the rate-limiting step. Reduction of hematite using a hydrogen-containing plasma is another attractive option. Researchers have studied the evolution of chemical composition and phase transformations in several intermediate states. The key is an optimized input mass-arc power ratio, which must be carefully controlled during exposure of the molten oxide to hydrogen plasma.

In hydrogen-plasma based reduction the micro- and nanoscale chemical and microstructure analysis has shown that gangue elements partition into the remaining oxide regions. They are probed in part by energy dispersive spectroscopy and atom probe tomography (APT).

ATOM PROBE TOMOGRAPHY ANALYSIS OF THE WÜSTITE-IRON INTERFACE

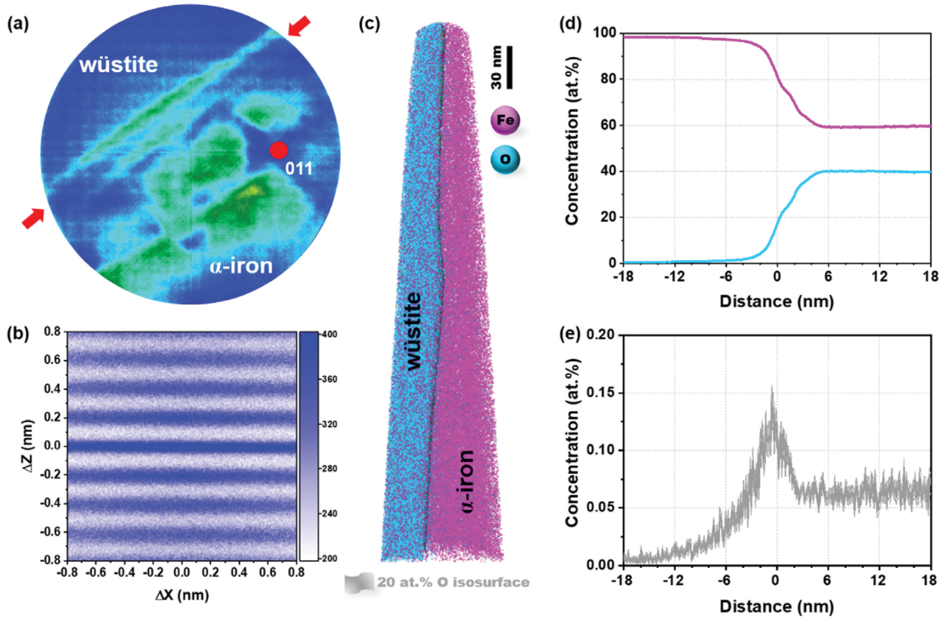


Figure 3: *Atom probe tomography (APT) analysis of the wüstite-iron interface in the partially hydrogen plasma-reduced sample after 5 min exposure time. (a) Cumulative field evaporation histogram with the (011) pole of the reduced iron (the arrows indicate the position of the interface); (b) spatial distribution map analysis showing the {011} lattice plane of the reduced iron; (c) three-dimensional atom probe tomography maps of iron and oxygen, and the wüstite-iron interface is marked by a 20 at.% oxygen isoconcentration surface; concentration profiles of (d) iron and oxygen, as well as (e) silicon relative to the position of the wüstite-iron interface. [5] [8]*

The APT (Local Electrode Atom Probe, or LEAP) specimens were prepared using the site-specific lift-out method at the wüstite-iron interface in a sample partially reduced for five minutes. The laser-pulsing mode of the instrument was used at a wavelength of 355nm, laser energy of 40pJ, and a laser pulse frequency of 200kHz. Findings are reconstructed into 3D atom maps and data analysis. [5] *(See Figure 3.)*

What next?

DR: A growing number of academic and R&D professionals are recognizing that future steelmaking will use approaches where hydrogen is used as reductant for iron ores. Hydrogen using renewable energy will remain a bottleneck in research for a couple of decades, or so. Fundamental to taking a sustainable approach is the use of green hydrogen, generated by renewable energy or from low-carbon power. [9]

"A GROWING NUMBER OF ACADEMIC AND R&D PROFESSIONALS ARE RECOGNIZING THAT FUTURE STEELMAKING WILL USE APPROACHES WHERE HYDROGEN IS USED AS REDUCTANT FOR IRON ORES."

We must continue pursuing a hybrid approach that allows researchers to take advantage of the characteristics and kinetically beneficial aspects of both DR and HPR. Remember: Iron- and steelmaking produce 7% to 9% of humanity's hazardous emissions due to the use of carbon for the reduction of iron ores. I and my colleagues urge researchers and the broader community to take advantage of the small window of opportunity that we have.

***Dierk Raabe**, managing director at the Max Plank Institute for Iron Research (Düsseldorf, Germany), studied music (conservatorium Wuppertal), and metallurgy and metal physics (RWTH Aachen). After earning a doctorate in 1992 and habilitation in 1997 (RWTH Aachen), he worked at Carnegie Mellon University (Pittsburgh) and at the National High Magnet Field Lab (Tallahassee). He joined the Max Planck Institute in 1999.*

Raabe's interests include phase transformation, alloy and segregation design, hydrogen, sustainable metallurgy, computational materials science, and atom probe tomography. He received the Leibniz Prize (highest German Science award) and two ERC Advanced Grants. The Max Plank Institute uses CAMECA's LEAP 3000 and LEAP 5000 instruments to generate compositional data on a variety of materials systems. This use does not constitute an endorsement of CAMECA or its instrumentation.

ENDNOTES

[1] Statistica, Statista Research Department, "Crude steel production worldwide 2012-2021," April 2022.

[2] YouTube, Metallurgy Guru – Sustainability Materials Science, "Sustainable Metallurgy and Green Metals," June 2020, via University of Groningen, "Green steel made with hydrogen as reductant Prof. Dierk Raabe, Max-Planck Institut für Eisenforschung, Düsseldorf, Germany," April 2022.

[3] Se-Ho Kim et al., "Influence of microstructure and atomic-scale chemistry on the direct reduction of iron ore with hydrogen at 700°C," *Acta Materialia*, June 2021.

[4] World Steel Association, "Climate change and the production of iron and steel," p. 3, 2021.

[5] I.R. Souza Filho et al, "Sustainable steel through hydrogen plasma reduction of iron ores: process, kinetics, microstructure, chemistry," *Acta Materialia*, July 2021.

[6] International Energy Agency, "Iron and Steel Technology Roadmap," p. 13, 2020.

[7] CAMECA-Nature Research Custom Media webcast, "Advancements in the development of green steel — making green steel with hydrogen," with Professor Dierk Raabe, Max-Planck Institut für Eisenforschung, Düsseldorf, Germany, November 2022.

[8] The Organisation for Economic Co-operation and Development (OECD), "OECD HIGHLIGHTS: Global Material Resources Outlook to 2060 – Economic Drivers and Environmental Consequence," p. 15, October 2018.

[9] I.R. Souza Filho et al, "Green steel at its crossroads: hybrid hydrogen-based reduction or iron ores," *Journal of Cleaner Production*, March 2022.

[10] Based largely on website content by Dierk Raabe, professor at the Max Plank Institute for Iron Research, "Atom Probe Tomography."

***CAMECA** is a global supplier of microanalytical and metrology instrumentation for research and process control. CAMECA, a business unit of AMETEK, provides a diverse range of advanced characterization technologies that measure elemental and isotropic composition in materials down to atomic resolution, and equip government, academic and high-tech industry labs around the world.*

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