# Investigation of Variable Manganese and Nickel Content on Ductile Iron Castings Utilizing Ionic Liquids Isolated Iron and Bosch Carbon

#### Blake Stewart Mississippi State University



MATERIALS SCIENCE & TECHNOLOGY Technical Meeting and Exhibition

#### **About the Presenter**

- Blake C. Stewart
  - Graduate Research Assistant
  - Ph.D. candidate
  - B.S. Mechanical Engineering
- Highlights and Interests
  - Steelmaking and cast iron
  - In-situ resource utilization (ISRU)
  - Extraterrestrial manufacturing methods
  - Experience in manufacturing, field engineering, and experimental research



CENTER FOR ADVANCED VEHICULAR SYSTEMS



#### **About the Presenter**

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## **Motivation**

- In-situ resource utilization techniques required for longterm habitation on extraterrestrial surfaces<sup>[1]</sup>
- Various mechanical and structural components needed from resources available in Lunar and Martian environments<sup>[2]</sup>
- Martian regolith is rich in metallic elements but are found as silicate minerals containing bound metal elements

[1] A. Owens, et. al, 2015 [2] Barker, et. al, 1998 [3] NASA JPL, 2019



Artist rendering of humans and habitats on Martian surface<sup>[3]</sup>



#### Overview

- Ductile iron alloys cast with Bosch-sourced carbon (C) and utilizing ionic liquids harvested iron (IL-Fe) composition
  - Four chemistries chosen as combinations of low and high nickel (Ni) and manganese (Mn)
- Produced ingots evaluated to determine effects of additional alloying in Martian environment
  - Dilatometry
  - Characterized microstructure
  - Mechanical properties (hardness)
- Investigation provides viability in using IL-Fe and Bosch C in casting multiple grades of ductile iron with minimal elemental additions



## **Introduction: Martian Environment**

- Martian regolith contains metallic elements bound in silicate compounds that could be used for tools, components, and infrastructure<sup>[4-9]</sup>
- Martian environment rich in CO<sub>2</sub><sup>[10]</sup>

Average Chemical Composition of Martian regolith <sup>[4-9]</sup>				
SiO <sub>2</sub> (n=40)	48 ± 6			
MnO (n=20)	0.3 ± 0.1			
$Fe_xO_x$ (n=40)	15 ± 4			
Ni (n=11)	$0.02 \pm 0.01$			
MgO (n=40)	6 ± 2			
Al <sub>2</sub> O <sub>3</sub> (n=40)	12 ± 5			
CaO (n=40)	8 ± 2			
Cr <sub>2</sub> O <sub>3</sub> (n=14)	$0.2 \pm 0.2$			
	(wt.%) ± st.dev.			



## Introduction: Ionic Liquids Iron Harvesting

- ILs currently studied at MSFC to • extract metallic elements from regolith and meteorites as well as a life support system<sup>[11-14]</sup>
- Current production rate: 1-2 g/day ullet
- IL is regenerated after • harvesting<sup>[15]</sup>

$$2HSO_{4}^{-} + MO \rightarrow 2SO_{4}^{2-} + M^{2+} + H_{2}O$$
$$M^{2+} + 2e^{-} \rightarrow M \parallel 2SO_{4}^{2-} + H_{2} \rightarrow 2HSO_{4}^{-} + 2e^{-}$$

Average Metallic Chemical Composition of IL-Fe (n=3)				
Si	$1.40 \pm 0.3$			
Mn	$0.47 \pm 0.1$			
Fe	$95.4 \pm 0.4$			
Ni	$0.14 \pm 0.02$			
MgO	2.27 ± 0.3			
AI	0.11 ± 0.1			
Са	0.11 ± 0.1			
Со	$0.08 \pm 0$			
Na	$0.04 \pm 0.03$			
	(wt.%) ± st.dev.			

[11] B. R. Brown, et. al, 2017 [13] L. J. Karr, et. al, 2018

[12] B. R. Brown, et. al, 2018 [14] A. Asiaee, et. al, 2020

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[15] E. T. Fox, 2019



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## Introduction: Bosch Carbon

- Bosch process studied at MSFC as an oxygen (O<sub>2</sub>) regeneration system producing a by-product C<sup>[16-18]</sup>
- Bosch C previously studied in alloying for low C steel, gray iron, and ductile iron<sup>[19-21]</sup>
- Current production rate: 8-10 g/hr

 $CO_2 + H_2 \leftrightarrow H_2O + CO$ 

$$CO + H_2 \leftrightarrow H_2O + C(s) \longrightarrow CO_2 + H_2 \leftrightarrow 2H_2O + C(s)$$

$$2C0 \leftrightarrow CO_2 + C(s) \_$$

[16] M. B. Abney and J. M. Mansell, 2011[19] B. C. Stewart, 2019

[17] M. B. Abney, et. al, 2013 [20] B. C. Stewart, 2021



**Series-Bosch catalyst** 

test stand<sup>[16]</sup>





Bosch C morphology<sup>[20]</sup>

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#### **Experimental Evaluations**





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## **Chemical Composition**

- Composition measured with optical emission spectrometer (OES) w/ C ulletverified with C/S analyzer
- Ni values targeted: Low (L-Ni): 0.14 wt.% and high (H-Ni): 4 wt.%<sup>[22]</sup> •
- Mn values targeted: Low (L-Mn): 0.41 wt.% and high (H-Mn): 1 wt.%<sup>[23]</sup> •

Chemical composition of Cast Ingots (n=10)									
	С	Si	Mn	Ni	Al	Со	Ca	Mg	Fe
L-Ni /	3.53^	<b>1.43</b>	0.497	0.150	0.053	0.081	0.004	0.046	bal
L-Mn	± 0.02	± 0.02	± 0.003	± 0.004	±0.002	± 0.003	± 0.003	± 0.004	
H-Ni /	3.37^	<b>1.44</b>	0.51	<b>4.25</b>	0.07	0.084	0.002	0.042	"
L-Mn	± 0.05	± 0.01	± 0.005	± 0.02	± 0.001	±0.002	± 0.0003	± 0.003	
L-Ni /	3.59^	<b>1.36</b>	<b>1.01</b>	0.156	0.056	0.062	0.002	0.044	"
H-Mn	± 0.02	± 0.03	± 0.01	± 0.002	± 0.001	± 0.002	±0.001	± 0.004	
H-Ni /	3.54^	<b>1.46</b>	1.04	4.38	0.067	0.088	0.003	0.055	"
H-Mn	± 0.04	± 0.02	± 0.01	± 0.02	± 0.002	±0.002	±0.002	± 0.005	
^n=3 from C/S analyzer (wt.%)						wt.%) ± st.dev.			

[20] C. Hsu, 2007 [21] DIS, 2001

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#### Dilatometry

- 6 mm OD x 22 mm L samples heated at 5°C/s to 900°C, held for 30 min, and cooled at prescribed cooling rate<sup>[24]</sup>
- Contact dilatometer used to measure change throughout testing
- Cooling rates performed: 1 and 10°C/s



Dilation vs Temperature Cooling at 10°C/s



#### [22] Samuel and Viswanathan, 2008



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#### **Transformation Temperatures**

- Transformation temperatures show similarities with H-Ni and L-Ni in separate "classes"
- H-Ni materials readily obtain martensite even at a relatively slow rate
- Mn does not seem to drastically affect material performance despite also encouraging austenite stability

Transformation Temperatures								
°C/s	Mat'l	$F_{S}$	$F_F,P_S$	$P_F,B_S$	B <sub>F</sub>	$M_{S}$		
1	L-Ni / L-Mn	755	627	563	-	-		
	H-Ni / L-Mn	-	-	546	365	162		
	L-Ni / H-Mn	817	613	547	-	-		
	H-Ni / H-Mn	-	-	517	335	175		
10	L-Ni / L-Mn	-	-	580	348	162		
	H-Ni / L-Mn	-	-	542	376	138		
	L-Ni / H-Mn	-	-	553	366	186		
	H-Ni / H-Mn	-	-	513	370	142		
						(°C)		



#### **1°C/s Microstructures**





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#### **10°C/s Microstructures**





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## Ni vs Mn Additions on IL DI

#### <u>Nickel</u>

- H-Ni content promotes more austenite stability in IL DI with retained austenite easily attainable
  - Retained austenite likely to transform in Martian application due to reduced atmospheric temperature
- Significant hardness benefits
- Readily available from meteorites, asteroids, etc.

#### <u>Manganese</u>

- H-Mn does not give significant variation in property
  - Small window from L-Mn to H-Mn value due to Mn composition limits
- Slight hardness increases
- Little microstructural change
  - Baseline L-Mn seems sufficient, but additions could be made depending on desired properties
- May be available in some areas for additions to IL composition



## Summary

- Dilatometry showed similar phase transitions with significant grouping of H-Ni materials for property variation
  - Additional Mn may not be worthwhile due to minimal effects from baseline L-Mn
- Hardness and microstructure showed IL DI responds well to heat treatment
  - With Ni additive, increased cooling rates will result in significant retained austenite
  - Likely that Martian/Lunar surface temperatures are cool enough to allow complete martensite transition
- The use of IL-Fe and Bosch C as casting feedstock could produce numerous ductile iron grades with minimal additions and some cooling rate control or post processing
- In summary, the use of Bosch C with IL-Fe is likely a viable option to manufacture ductile iron on the Lunar or Martian surfaces, with some limitations



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[1] Andrew Ow ens, Sydney Do, Andrew Kurtz, and Olivier de Weck, "Benefits of Additive Manufacturing for Human Exploration of Mars," presented at the International Conference on Environmental Systems, Bellevue, Washington, Jul. 2015. [Online]. Available: https://ttu-ir.tdl.org/bitstream/handle/2346/64526/ICES\_2015\_submission\_287.pdf?sequence=1&isAllow ed=y

[2] Donald Barker, Gregory Chamitoff, and George James, "Resource Utilization and Site Selection for a Self-Sufficient Martian Outpost," Johnson Space Center, Technical Memorandum (TM) 19980147990, Apr. 1998. [Online]. Available: https://ntrs.nasa.gov/citations/19980147990

[3] NASA, "First Humans on Mars (Artist's Concept)," Jun. 12, 2019. https://www.jpl.nasa.gov/images/first-humans-on-mars-artists-concept

[4] A. Yen et al., "Evidence for a Global Martian Soil Composition Extends to Gale Crater," presented at the Lunar and Planetary Science Conference, The Woodlands, TX, Jan. 2013. [Online]. Available: https://ntrs.nasa.gov/citations/20130009717
[5] R. V. Morris et al., "Update on the chemical composition of crystalline, smectite, and amorphous components for rocknest soil and John Klein and Cumberland mudstone drill fines at Gale Crater Mars," presented at the Lunar and Planetary Science Conference, The Woodlands, TX, Mar. 2015. [Online]. Available: https://ntrs.nasa.gov/citations/20150001942

[6] M. J. Rutherford, M. Minitti, and C. M. Weitz, "Compositions of mars rocks: SNC meteorites, differentiates, and soils," Jan. 1999, pp. 92–93. [Online]. Available: https://ntrs.nasa.gov/citations/20000012732

[7] Gregory H. Peters et al., "Mojave Mars simulant - Characterization of a new geologic Mars analog," lcarus, vol. 197, no. 2, pp. 470-479, Oct. 2008, doi: 10.1016/j.icarus.2008.05.004.

[8] Carlton C. Allen, Karen M. Jager, Richard V. Morris, David J. Lindstrom, and John P. Lockwood, "Martian Soil simulant Available for Scientific, Educational Study," EOS Trans. Am. Geophys. Union, vol. 79, no. 34, pp. 405-412, Aug. 1998.

[9] Carlton C. Allen, Richard V. Morris, David J. Lindstrom, Marilyn M. Lindstrom, and John P. Lockwood, "JSC Mars-1: Martian Soil Simulant," presented at the Lunar and Planetary Science XXVII, 1997.

[10] P. Mahaffy et al., "Abundance and Isotopic Composition of Gases in the Martian Atmosphere from the Curiosity Rover," Science, vol. 341, no. 1, pp. 263–266, 2013, doi: 10.1126/science.1237966.

[11] Brittany R. Brown, Morgan B. Abney, Laurel J. Karr, Christine M. Stanley, Dave N. Donovan, and Mark S. Paley, "lonic Liquids Enabling Revolutionary Closed-Loop Life Support," presented at the International Conference on Environmental Systems, Charleston, SC, Jul. 2017.

[12] Brittany R. Brown et al., "Utilizing lonic Liquids to Enable the Future of Closed Closed Loop Life Support Technology," presented at the International Conference on Environmental Systems, Albuquerque, NM, Jul. 2018.

[13] L. J. Karr et al., "Ionic Liquid Facilitated Recovery of Metals and Oxygen from Regolith," presented at the AIAA Space Forum, Orlando, FL, Sep. 2018. Accessed: Jul. 21, 2021. [Online]. Available: https://ntrs.nasa.gov/citations/20180006392

[14] A. Asiaee et al., "On the potential of ionic liquids to recover metals from the Martian regolith: Computational insights into interfacial interactions," J. Mol. Liq., vol. 319, p. 114208, Dec. 2020, doi: 10.1016/j.molliq.2020.114208.

[15] Eric T. Fox, "Ionic Liquid and In Situ Resource Utilization," presented at the Astronomy on Tap, Huntdell, AL, May 2019. [Online]. Available: https://ntrs.nasa.gov/citations/20190027398

[16] M. Abney and J. M. Mansell, "Evaluation of Bosch-Based Systems Using Non-Traditional Catalysts at Reduced Temperatures," Jul. 2011. doi: 10.2514/6.2011-5059.

[17] M. B. Abney, J. M. Mansell, S. DuMez, J. Thomas, C. Cooper, and D. Long, "Ongoing Development of a Series Bosch Reactor System," Jul. 2013. doi: 10.2514/6.2013-3512.

[18] Morgan B. Abney et al., "Series-Bosch Technology For Oxygen Recovery During Lunar or Martian Surface Missions," presented at the 44th International Conference on Environmental Systems, Tucson, AZ, Jul. 2014.

[19] Blake C. Stewart, "A Study of an Alternative Carbon Source to Improve Environmental Sustainability in Steel Production," presented at the MS&T, Portland, OR, Oct. 2019.

[20] Blake C. Stewart, "Investigation of Ionic Liquid Isolated Iron for Ductile Iron Castings," presented at the TMS, Online, Mar. 2021.

[21] Blake C. Stewart, Haley R. Doude, Terry L. Taylor, Morgan B. Abney, and Hongjoo Rhee, "Evaluation of Bosch Process-Sourced Carbon in Low Carbon Steel and Gray Iron Casting for Martian Surface Manufacturing," J. Aerosp. Eng., (in Review).

[22] C.-H. Hsu, M.-L. Chen, and C.-J. Hu, "Microstructure and mechanical properties of 4% cobalt and nickel alloyed ductile irons," Mater. Sci. Eng. A, vol. 444, no. 1–2, pp. 339–346, Jan. 2007, doi: 10.1016/j.msea.2006.09.027. [23] "Manganese and its Effects on Ductile Iron," Ductile Iron Society, 2001.

[24] C. Samuel and S. Visw anathan, "Transformation Kinetics and Ferrite-Pearlite Ratios in a 65-45-12 Ductile Iron," Int. J. Met., vol. 2, no. 4, pp. 55-65, Oct. 2008, doi: 10.1007/BF03355436.

