Post Sinter Sensitivity to the Stability of Manganese Sulfide as a Machine Additive for Powder Metal Components

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Machinability of PM

Machinability can be measured in 3 ways, the life of the cutting tool, the power required for cutting, and the surface quality of the machined product

In General:

- PM has a relatively poor measure of machinability when compared to wrought or cast irons due to residual porosity and other unique features
- Even though a near net shape, many parts require secondary machining for tight tolerance, surface finish, through holes etc.

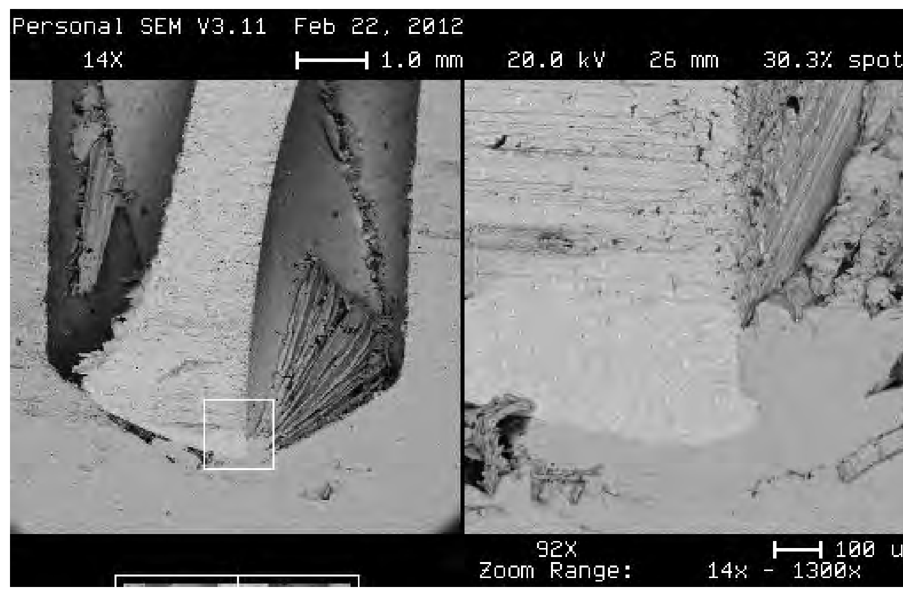
But! We can add "*magical*" machine enhancers to improve machinability performance

- A number of new proprietary additives for drilling and/or turning
- MnS still widely accepted and used

MnS Machinability additive

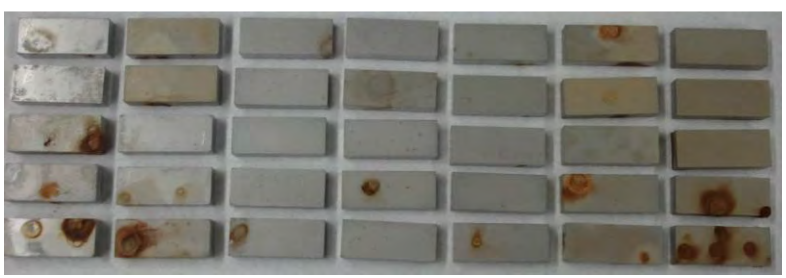
The advantages:

- Mainly to provide lubrication between cutting tool and work pieces by depositing on the wear surface
- Reduce tool wear
- Limited effect on mechanical properties
- Small impact on dimensional changes
- MnS inclusions can act as stress concentrations in the machining shear zone that initiate cracks that lead to the fracture of the chip



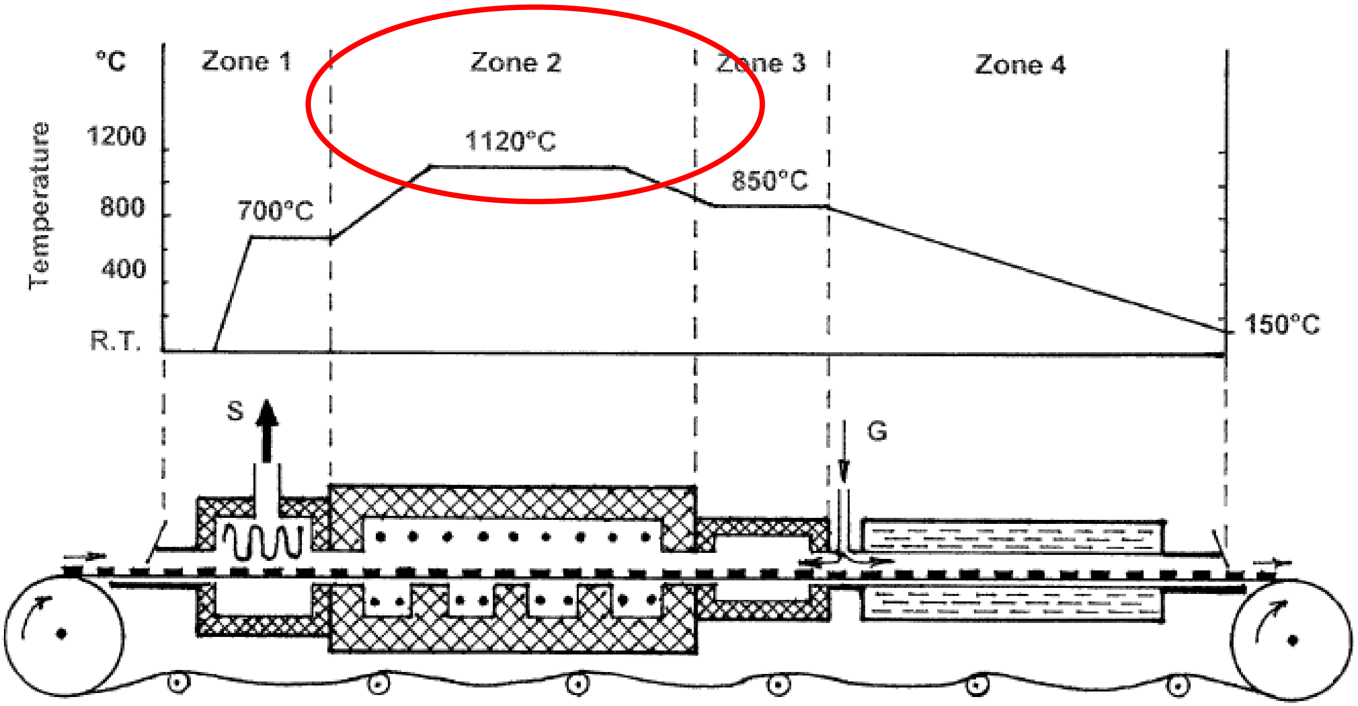
The disadvantages:

- Easy oxidation in a humid atmosphere
  (Increase corrosion of parts)
- Less effective as alloy content increases



Furnace Thermal Profile

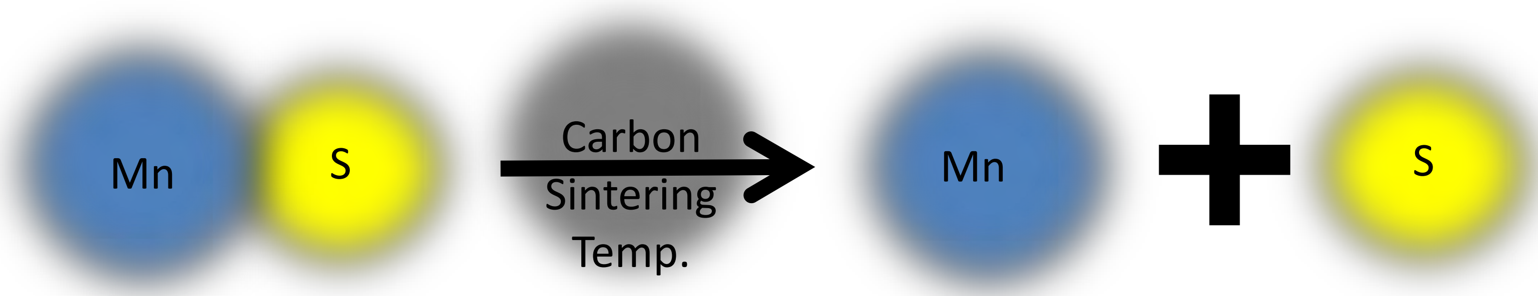
Several Key aspects to the stability of MnS through the temperature profile

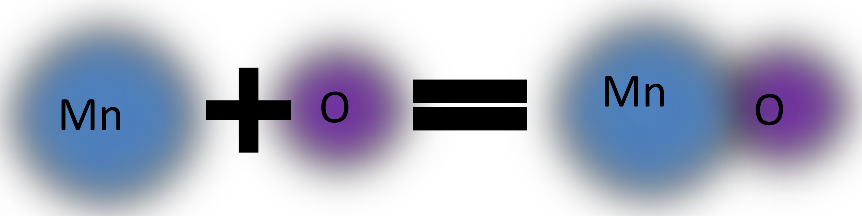


Zone 1 = Burning-off lubricants, 2 = Sintering, 3 = Re-carbonizing, 4 = Cooling
G = Gas inlet, S = Smoke and gas outlet

High Temperature Thermal Stability of MnS

- MnS is stable to sintering temperature for most ferrous alloys with very little to no interactions detected with the matrix materials
- However, a small drop in sulfur content is observed if carbon content is above 0.6% C [1]
- Small portion of the MnS is decomposed to Mn +S [2]
    - Mn can be dissolved into Fe matrix
    - Mn can form MnO (or other Mn oxides) if oxygen present in sintering atmosphere





[1] K.Y. Lee, D.K. Park, and H.B. Kim, "Enhanced Stability and Machinability of PM Steels Using Modified MnS Additions," *Adv. 2002 World Congress on Powder Metall. And Part. Mat.* Orlando, MPIF, Part 12, 2002, p. 72

[2] A. Salak, "Evaluation of Structural Activity of Iron Powder By Tensile Strength of Manganese Steel Sintered in a-iron Region," *Poroshkovaya Metalurgiya,* 1984, No. 8, p 58

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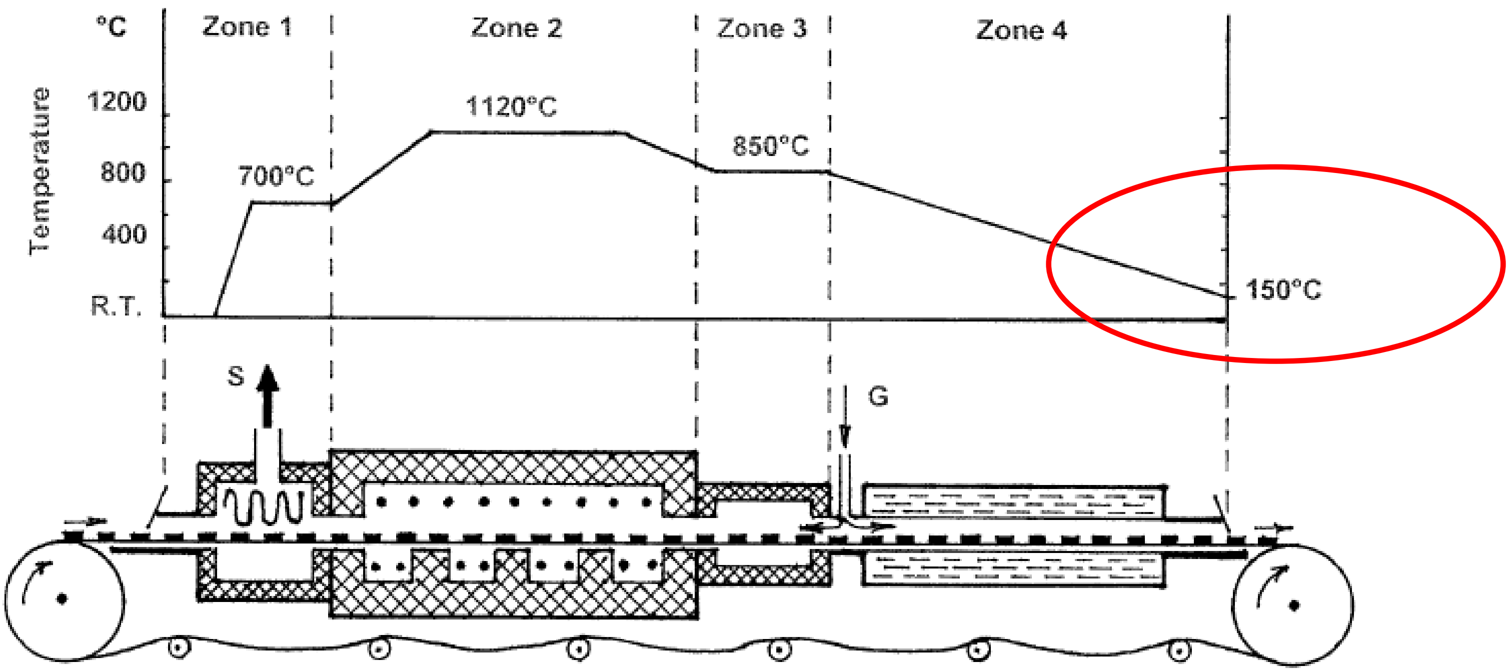

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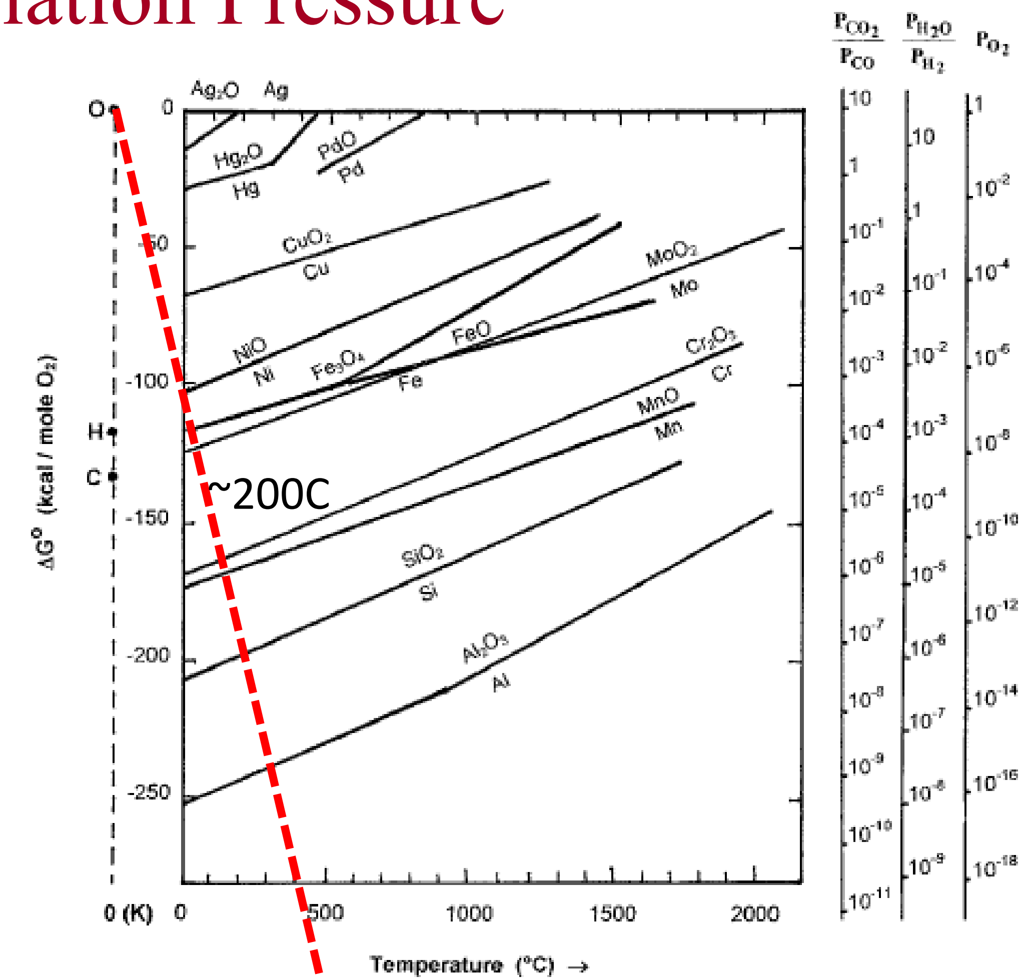
Equilibrium Dissociation Pressure

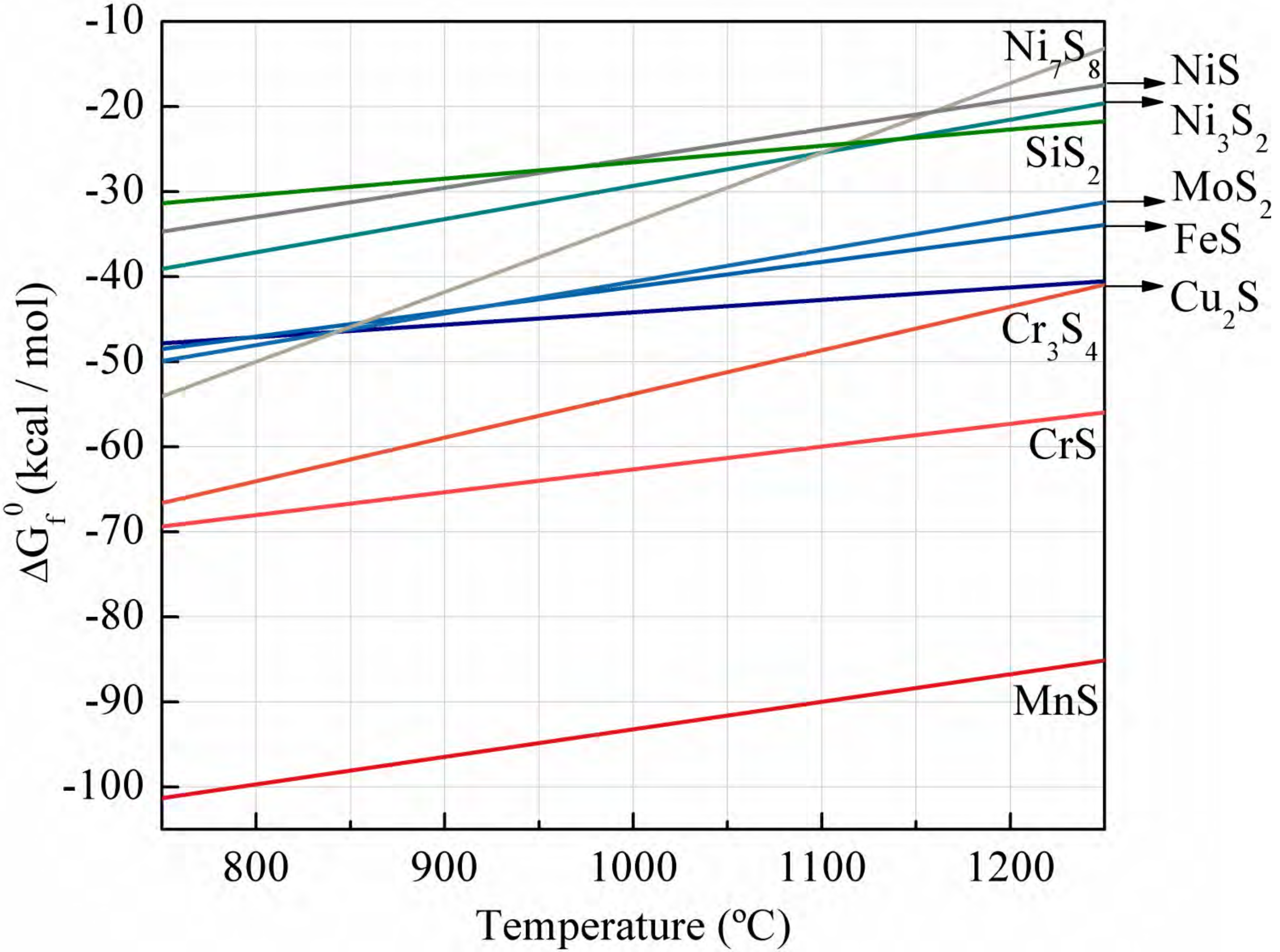
- At any given temperature, a metal and its oxide are in equilibrium with a particular partial pressure of oxygen Po_2
- Above this pressure the metal oxidizes, below this pressure the oxide dissociates into metal and gaseous oxygen

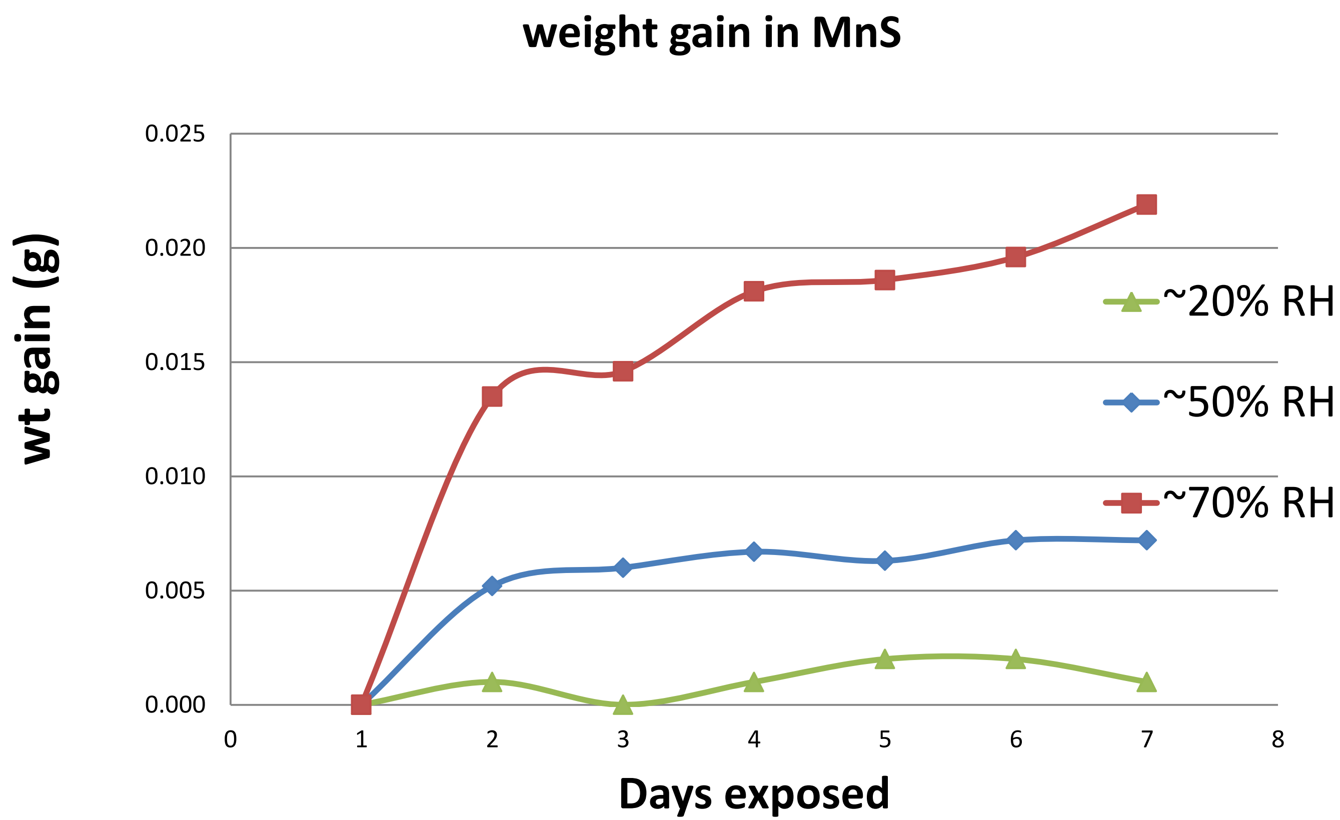


Ellingham-Richardson Diagram

Mn wants to oxidize in the presence of air/water

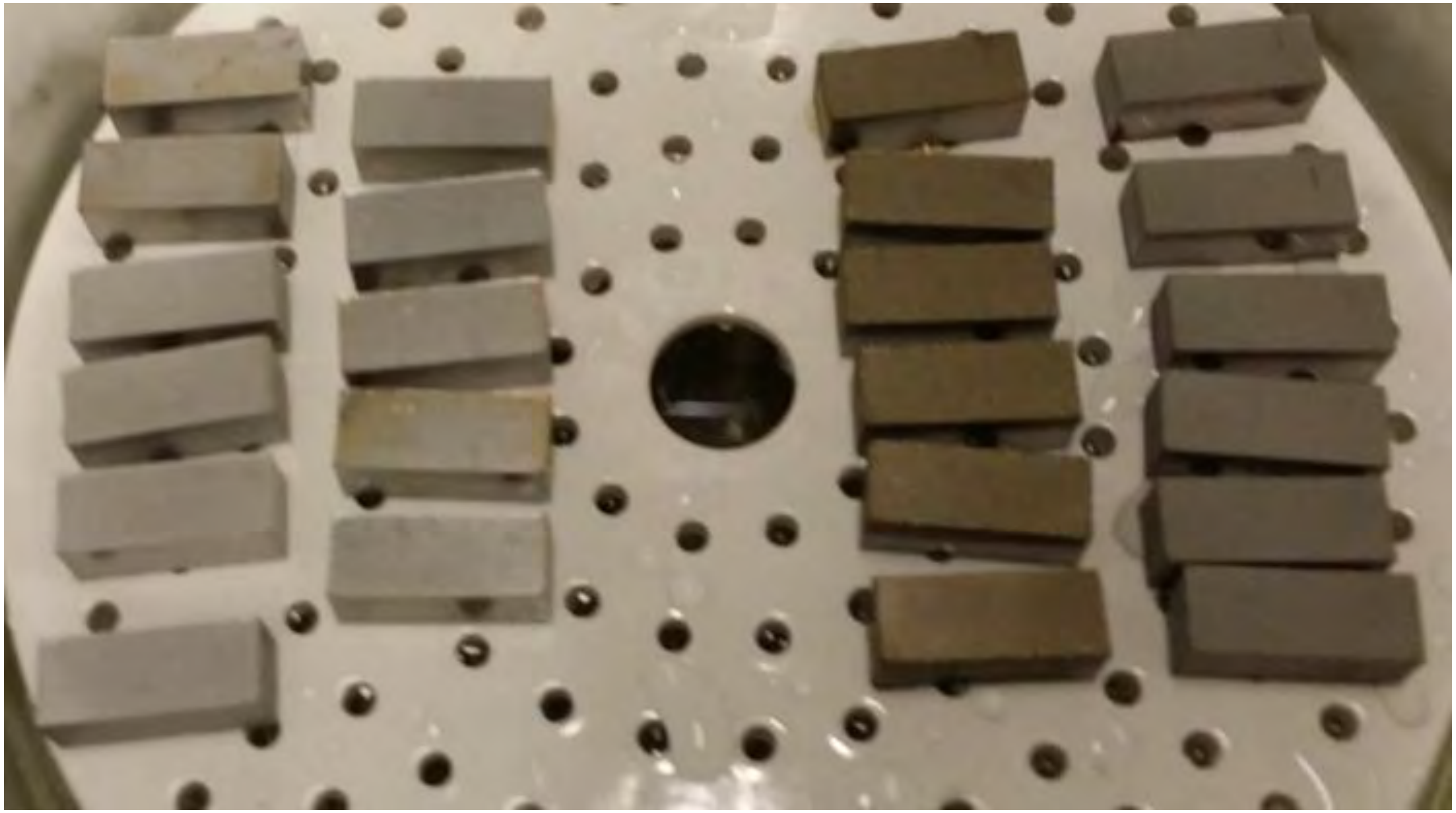
Ellingham Diagram for Sulphides



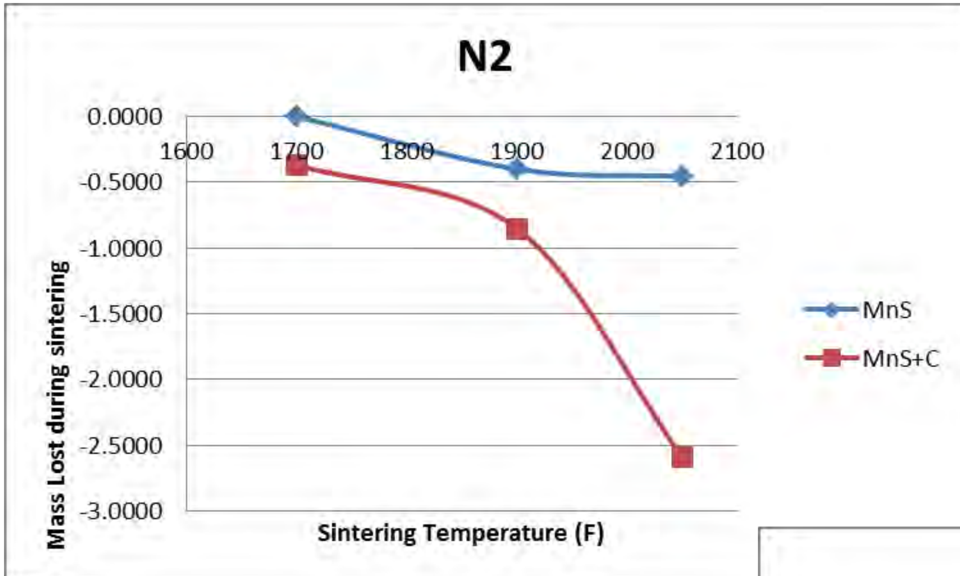


Weight pickup from powder sitting out in exposed environment
Cannot bring back into weight, once exposed the MnS keeps H2O

Corrosion



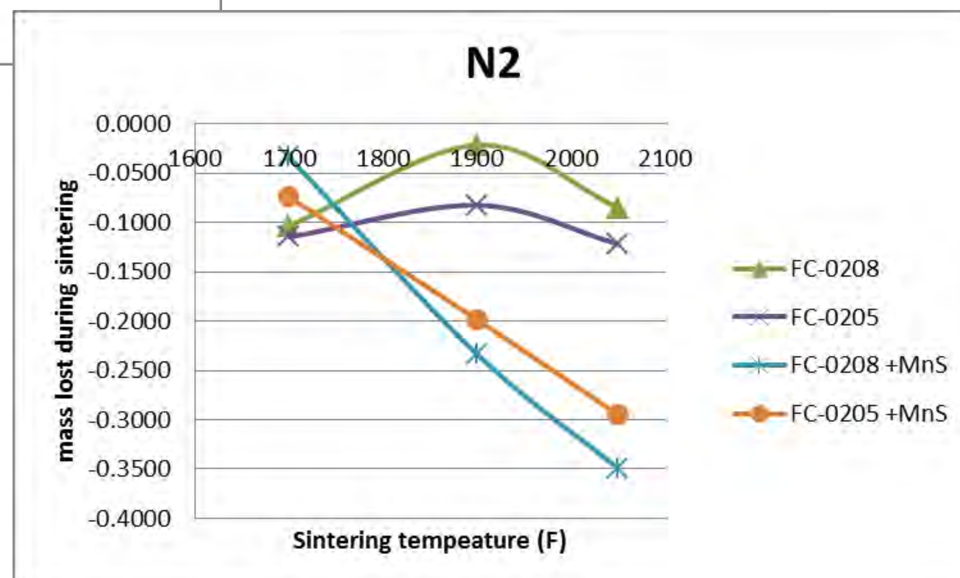
MnS Green　　MnS Sintered

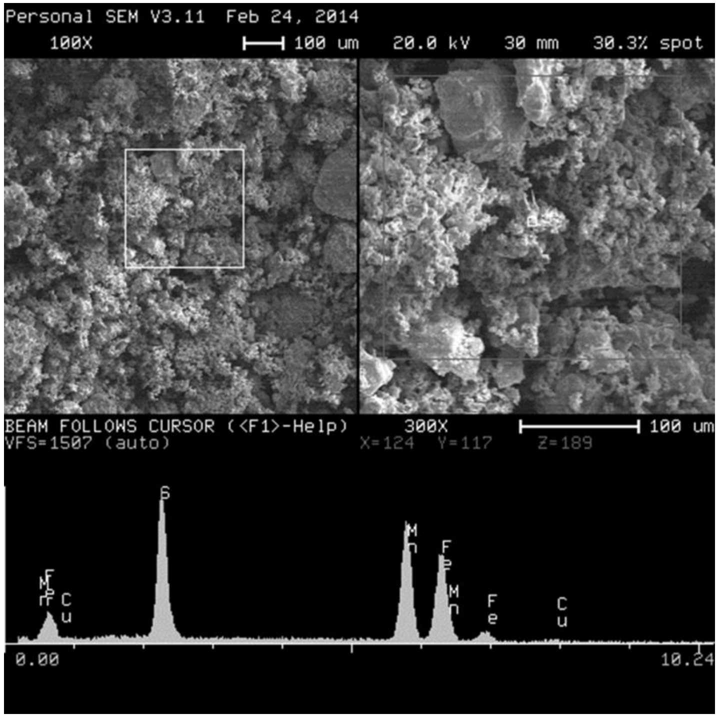


Wt loss from powder crucibules sintered at 1700, 1900, 2050 in air, N2, N2H2

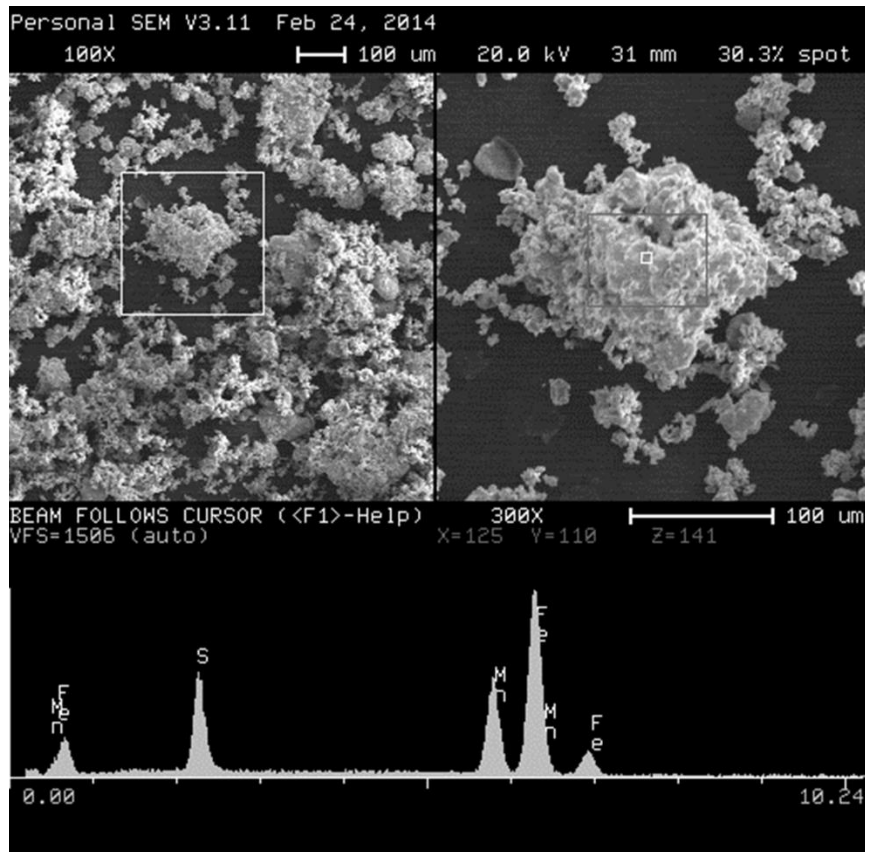
- Pretty evident MnS in influencing wt loss in material and it appears carbon has an additional impact

- Carbon has huge impact on MnS stability

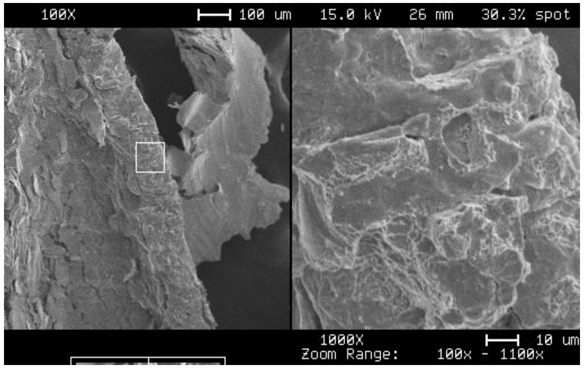




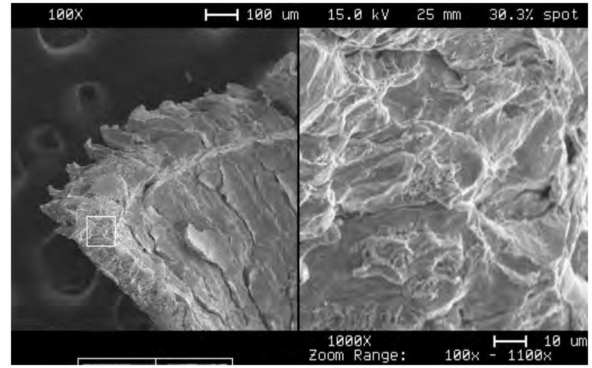
EDS looking at Mn, Fe, and S relative peak height
- Putting this together now to see chemistry change that occurs during sintering at different atmospheres/temperarures



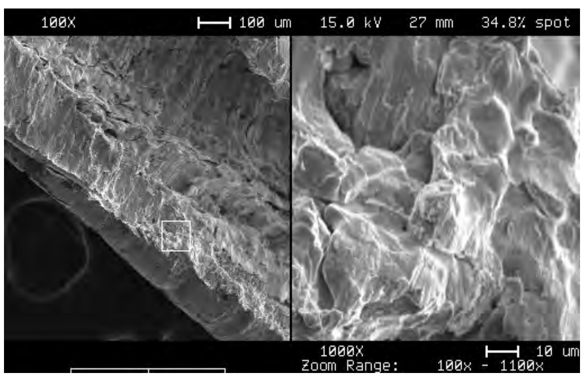
Chip analysis for post sinter conditions



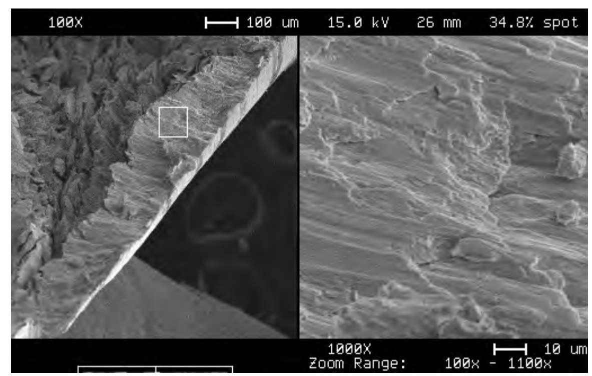
Liquid N_2



Furnace cooled to ~150F

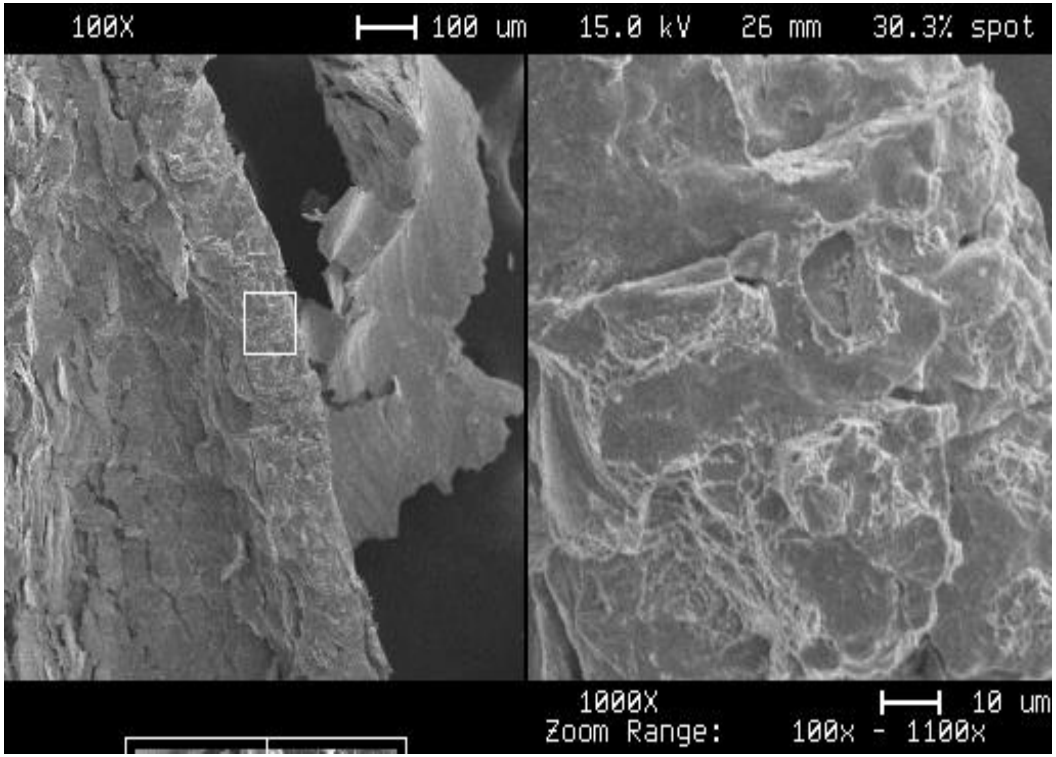


Furnace cooled to ~200F



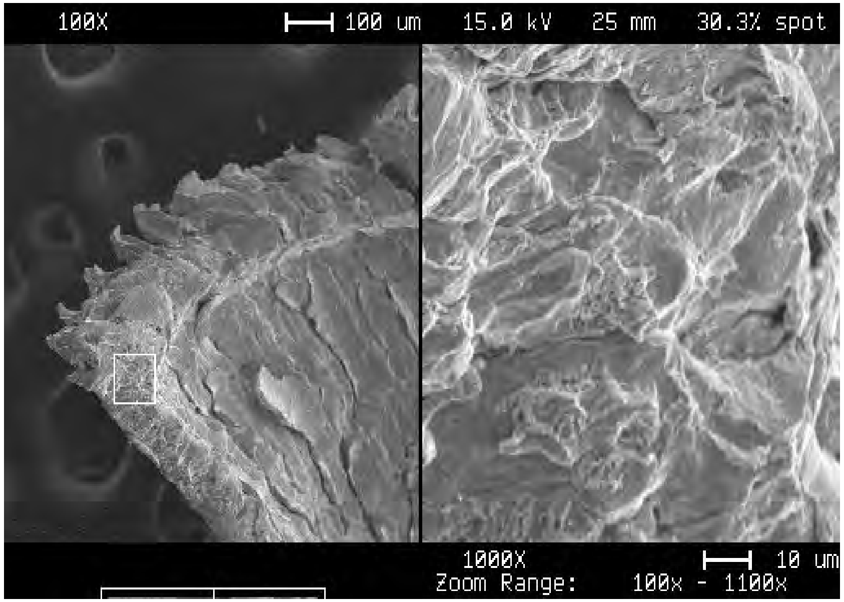
Furnace cooled to ~200F reheated in water vapor for 1 hr at 200F

Liquid N_2 cooled samples

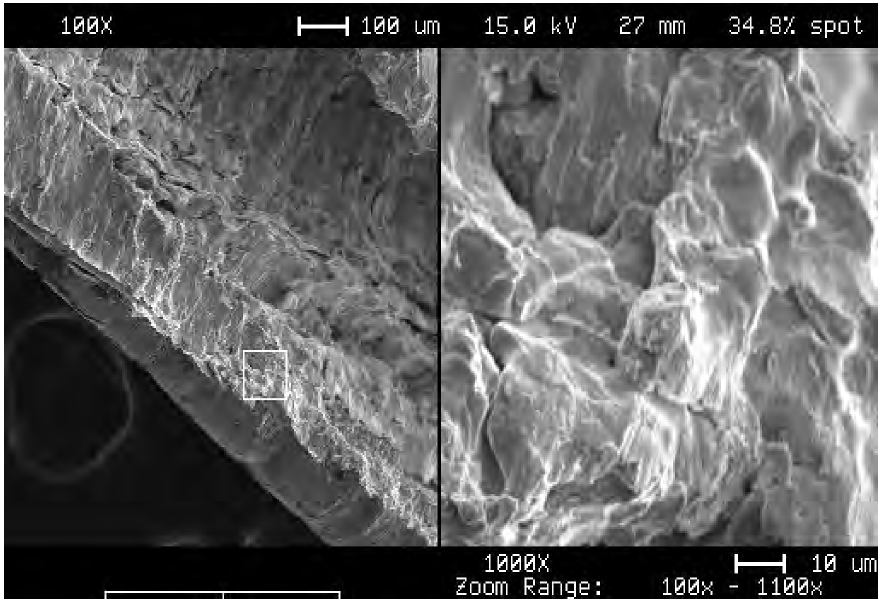


- Broken chip from fracture concentrations created by MnS
- Many crack origins observed throughout chip cross section
- MnS inclusions highly sheared
- Small amount of oxide observed

150F and 200F furnace cooled samples



150 F cooled



200 F cooled

- Still can see broken chip from fracture concentrations created by MnS
- fewer crack origins observed throughout chip cross section
- Highly sheared MnS inclusions not observed
- oxide observed throughout chip cross section

ATLAS PRESSED METALS

Furnace cooled to ~200F reheated in water vapor for 1 hr at 200F

- Observed smearing across chip cross section
- No highly sheared MnS inclusions observed

Formation of Sulfuric Acid

Some history:

1746 John Roebuck produced sulfuric acid by dry distilling iron disulfide (FeS_2)

$$FeS_2 \xrightarrow[\text{Heated in air}]{} FeSO_4 \xrightarrow[\text{Further Heated in air}]{} Fe_2(SO_4)_3 \xrightarrow[\text{Heated in air}]{H_2O} Fe_2O_3 + H_2SO_4$$

H_2SO_4 → Any concentration

Can we see the same reaction in our ferrous parts?

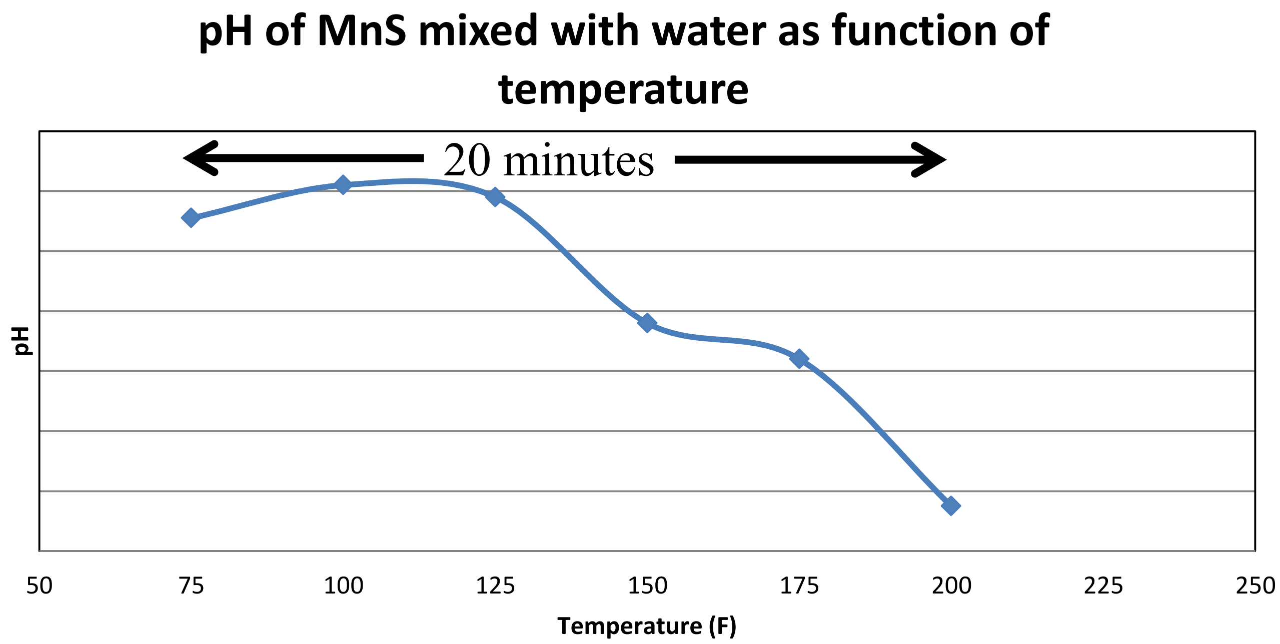
- High carbon parts → free sulfur from decomposition of MnS
- Can also get a small contribution from MnS directly

$$MnS \xrightarrow[\text{Heated in air}]{} MnSO_4 \xrightarrow[\text{Heated in air}]{H_2O} MnO + H_2SO_4$$

- The formation of sulfuric acid may help explain the presence of smearing across chips exposed to water vapor at 200F
- Can this happen at temperatures below that of which a part is exposed to the ambient?

Formation of Sulfuric Acid

Powder of MnS mixed with water to form a slurry and heated on a hotplate



- At 125F slurry starts to go from a green to a brown in color and rotten egg smell appears
- At 150F a significant drop in pH is measured (formation of an acid)

Conclusions

- MnS stability in carbon >0.6% critical
- MnO formation at temperatures at 200F or lower is a dominant reaction
- Formation of sulfuric acid from free sulfur at temperatures of >125F can degrade machinability performance and assist in part corrosion
- Chip formation and machinability can be influenced by post sinter handling

Thank you for your attention

Questions