An analysis of in-situ phase changes occurring in natural hematite exposed to simulated high temperature redox gas cycling encountered in chemical looping

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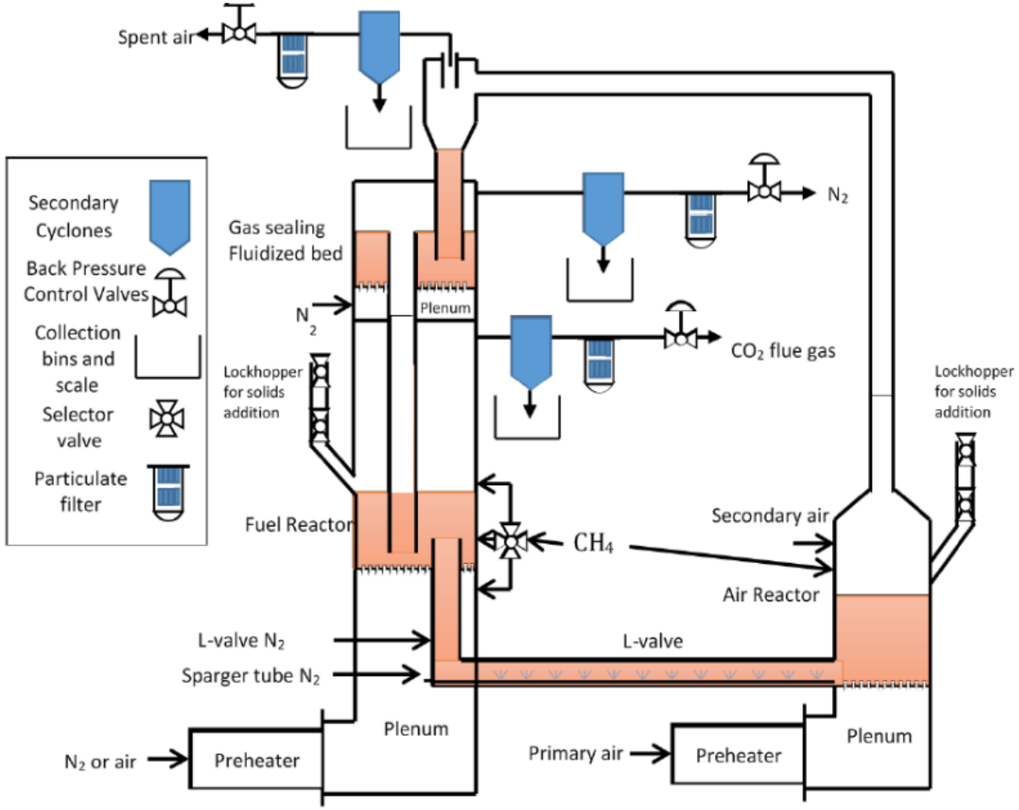
Introduction

Chemical Looping Reactor at NETL Morgantown, West Virginia



Bayham, S., Straub, D., and Weber, J., "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," NETL-PUB-20912; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017.

Technical Issue

Oxygen carriers experience microstructural changes and degradation during CLC, contributing to attrition. Understanding of materials behavior is needed.

Objective of this part of work

Study in-situ microstructural characterization of hematite during oxidation/reduction cycles (no particle mixing).

Experimental *Materials*

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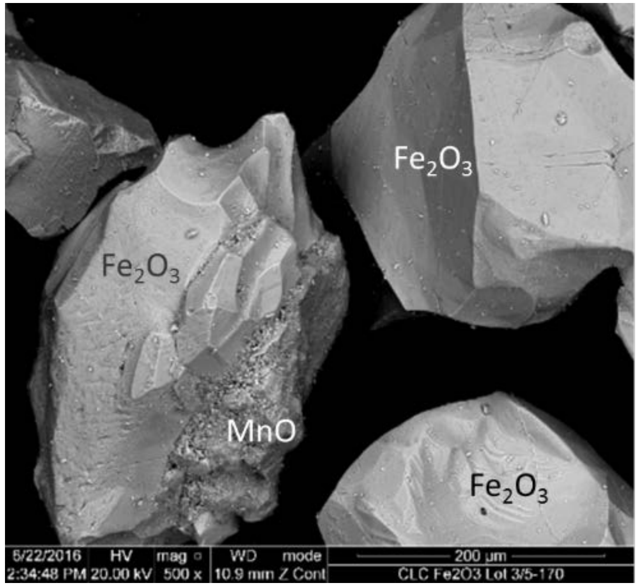
Sample	XRF (mass.%)					XRD
	Fe_2O_3	MnO	SiO_2	Total	ERR%	Identified crystalline phases
Natural hematite	86.27	3.51	10.23	100.0	±0.50	Fe_2O_3 (hematite) SiO_2 (moganite)

Natural hematite

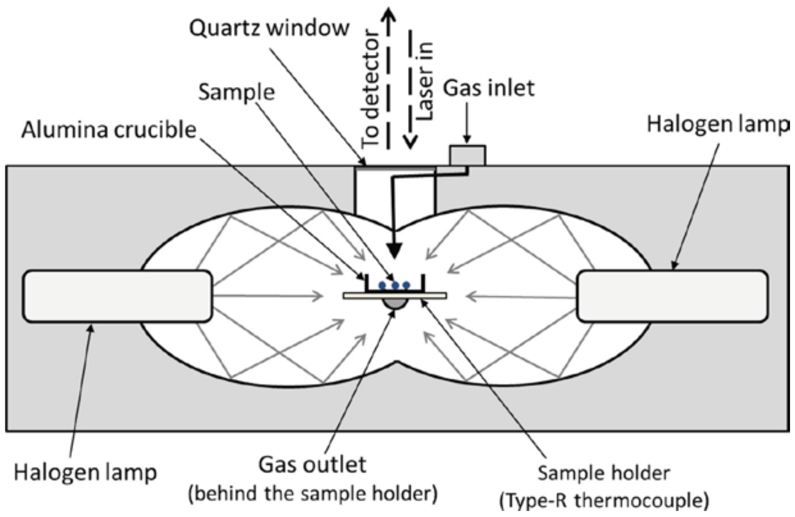
- Primary crystalline phase = hematite.
- Source = Wabush Mine, Newfoundland/Labrador, Canada
- Material crushed, particle size -48 US Mesh.



Experimental *Test Procedures*

<u>HT Confocal Scanning Laser Microscope</u> – used to observe isothermal Redox gas cyclic exposures

Heating chamber



- Temperature: 800°C and 1200°C
- Gas switched between synthetic air (oxidation) and 10 vol.% CO-90 vol.% Ar (reduction) at a flow of 50 ml/min
- Repeated 10 cycles -20 gas switches (1 cycle = 7.5 min each for oxidation + 10 min each for reduction)

Natural hematite analysis (800°C)

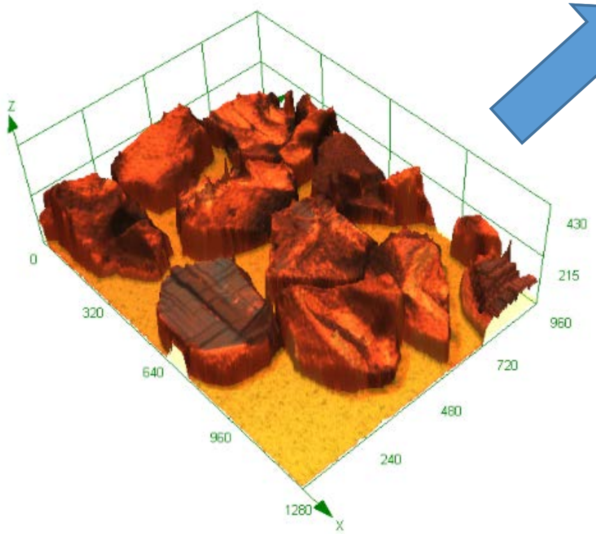
Real time surface morphology change at 800°C

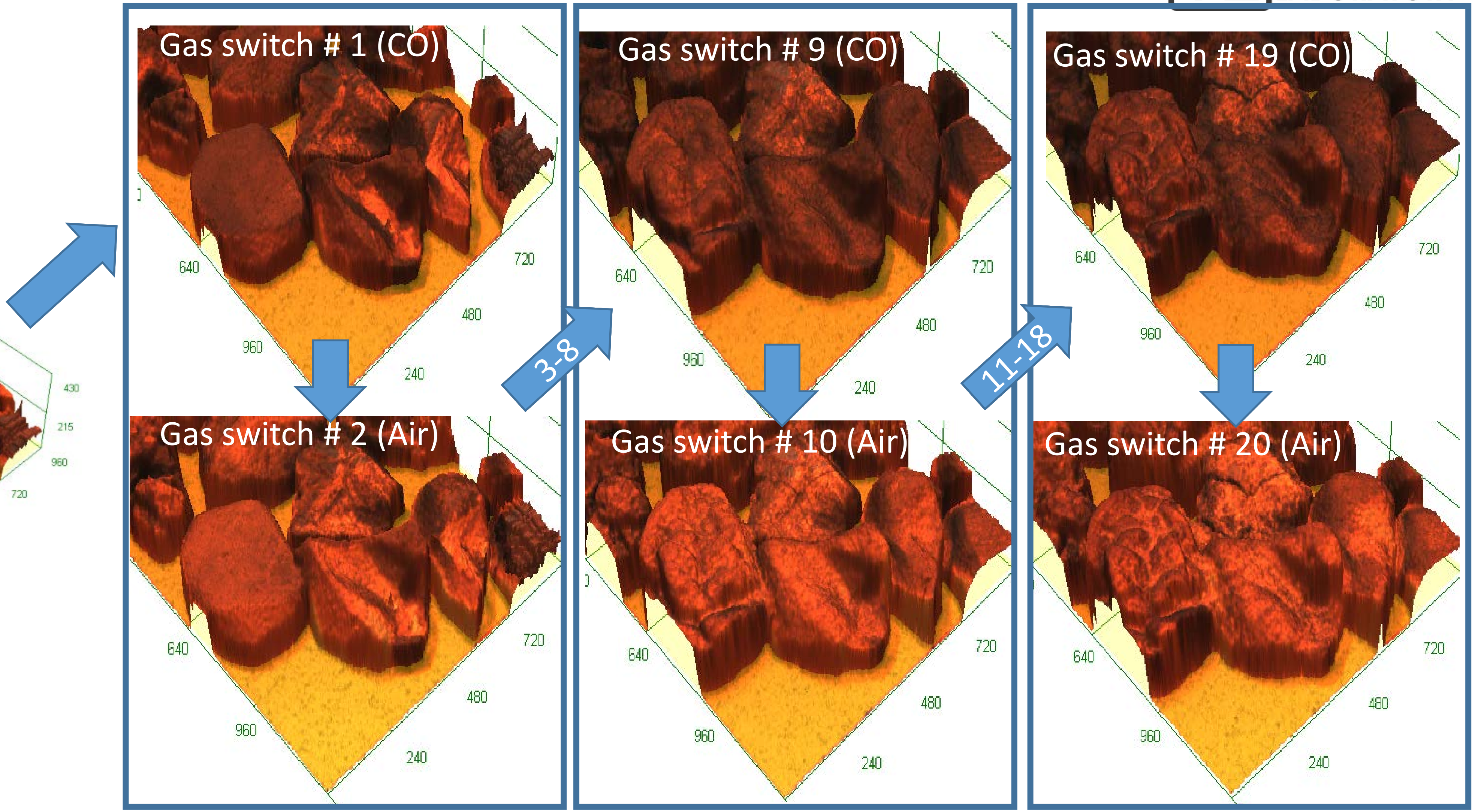
Reduction. Cycle 1: 10CO-Ar

Hematite: Overall change with redox cycles (real color)

800°C

Before redox cycles





Hematite: Overall change with redox cycles (topology map)

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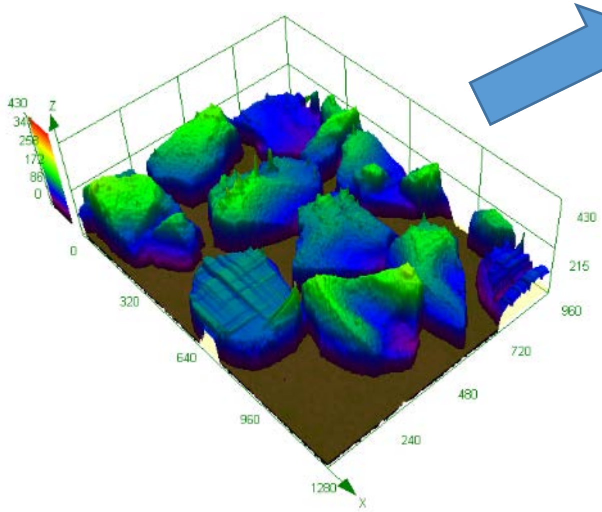
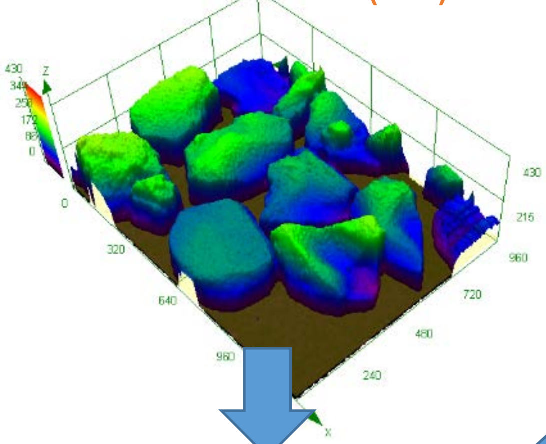
800°C

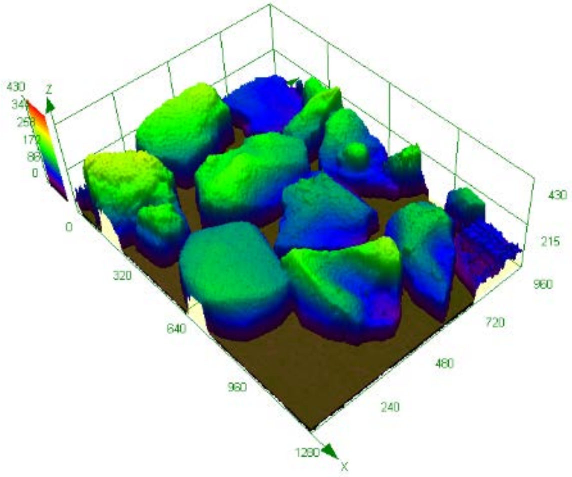
Before redox cycles



Gas switch # 1 (CO)



Gas switch # 2 (Air)



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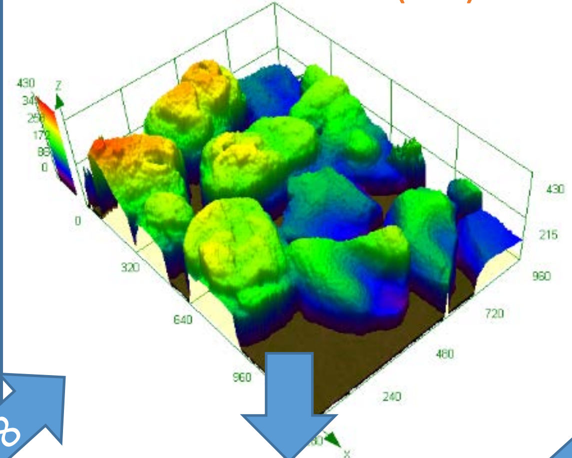
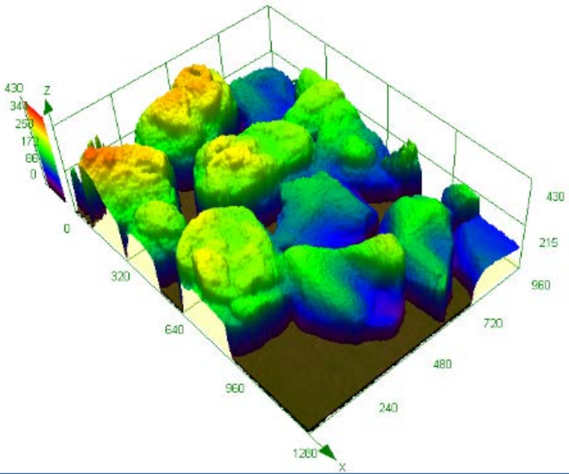
Gas switch # 9 (CO)

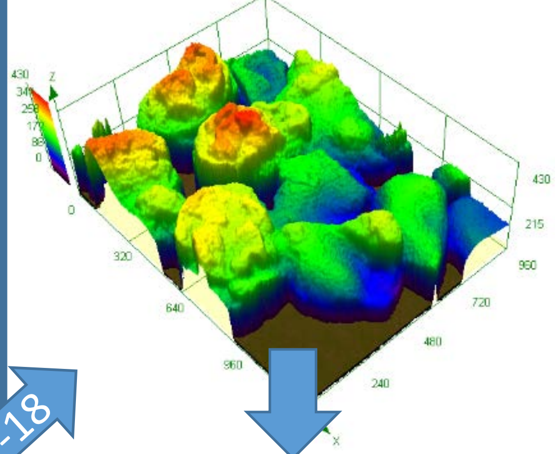


Gas switch # 10 (Air)

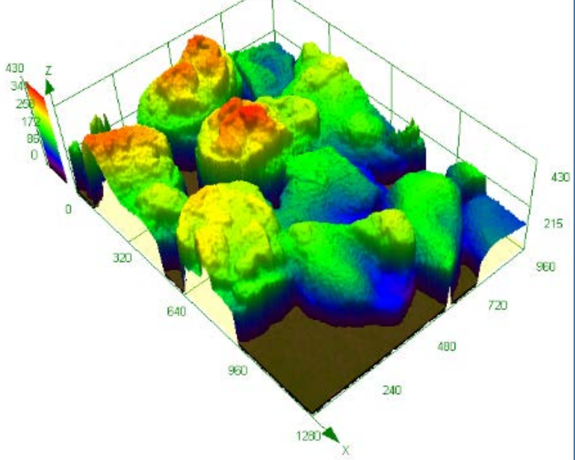


11-18

Gas switch # 19 (CO)



Gas switch # 20 (Air)



Agglomeration at 800°C

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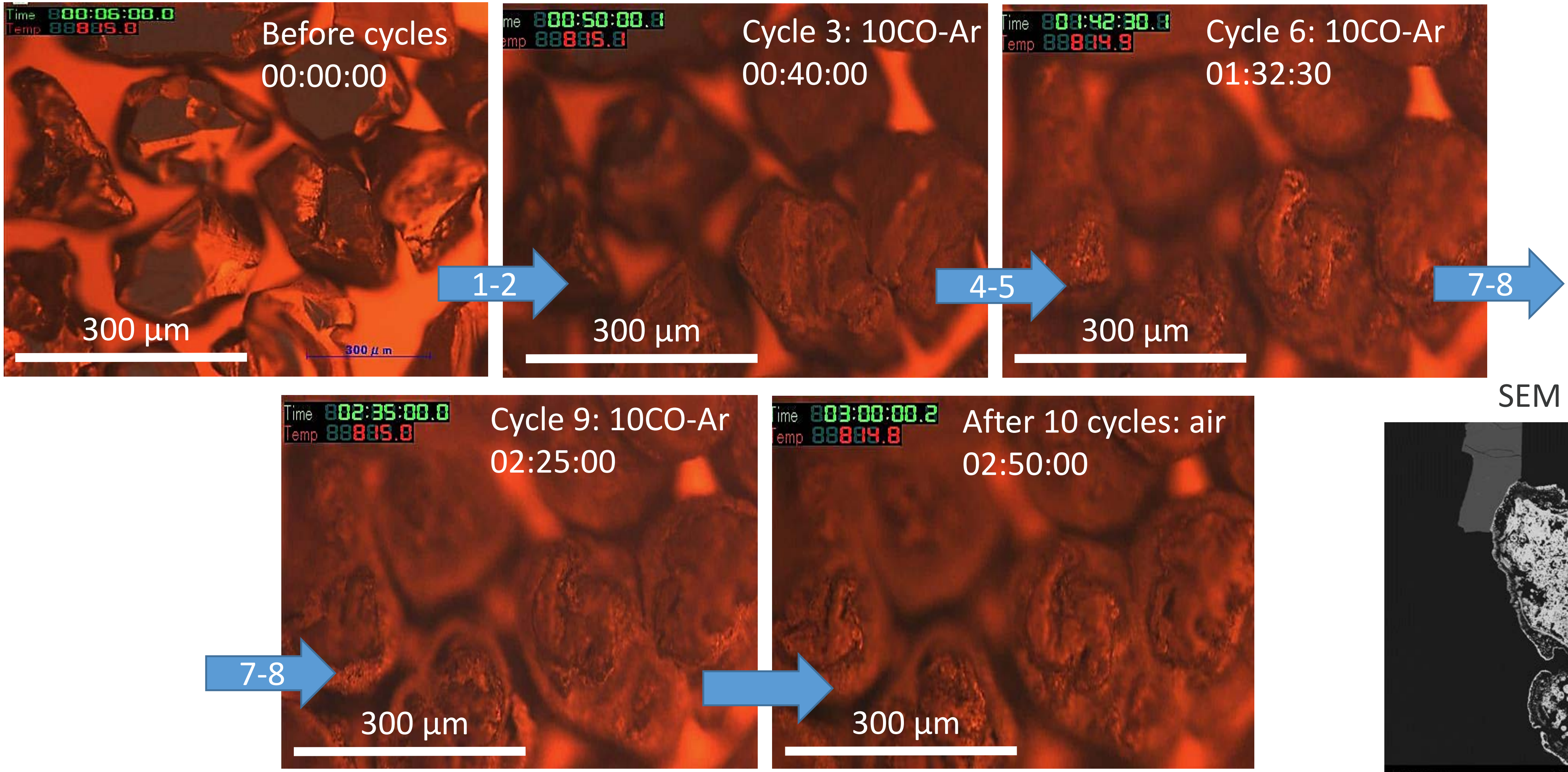
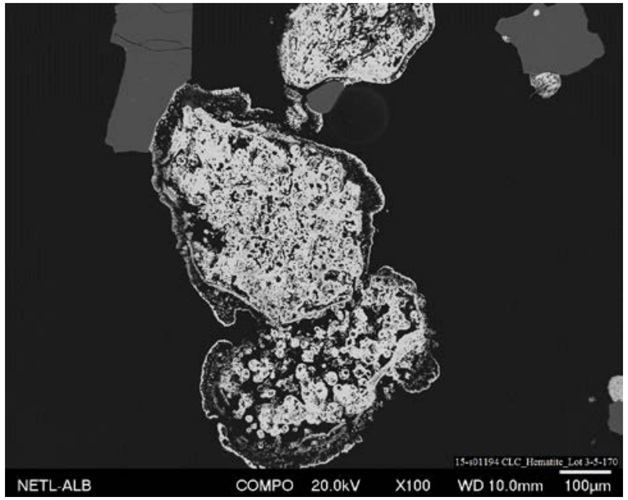
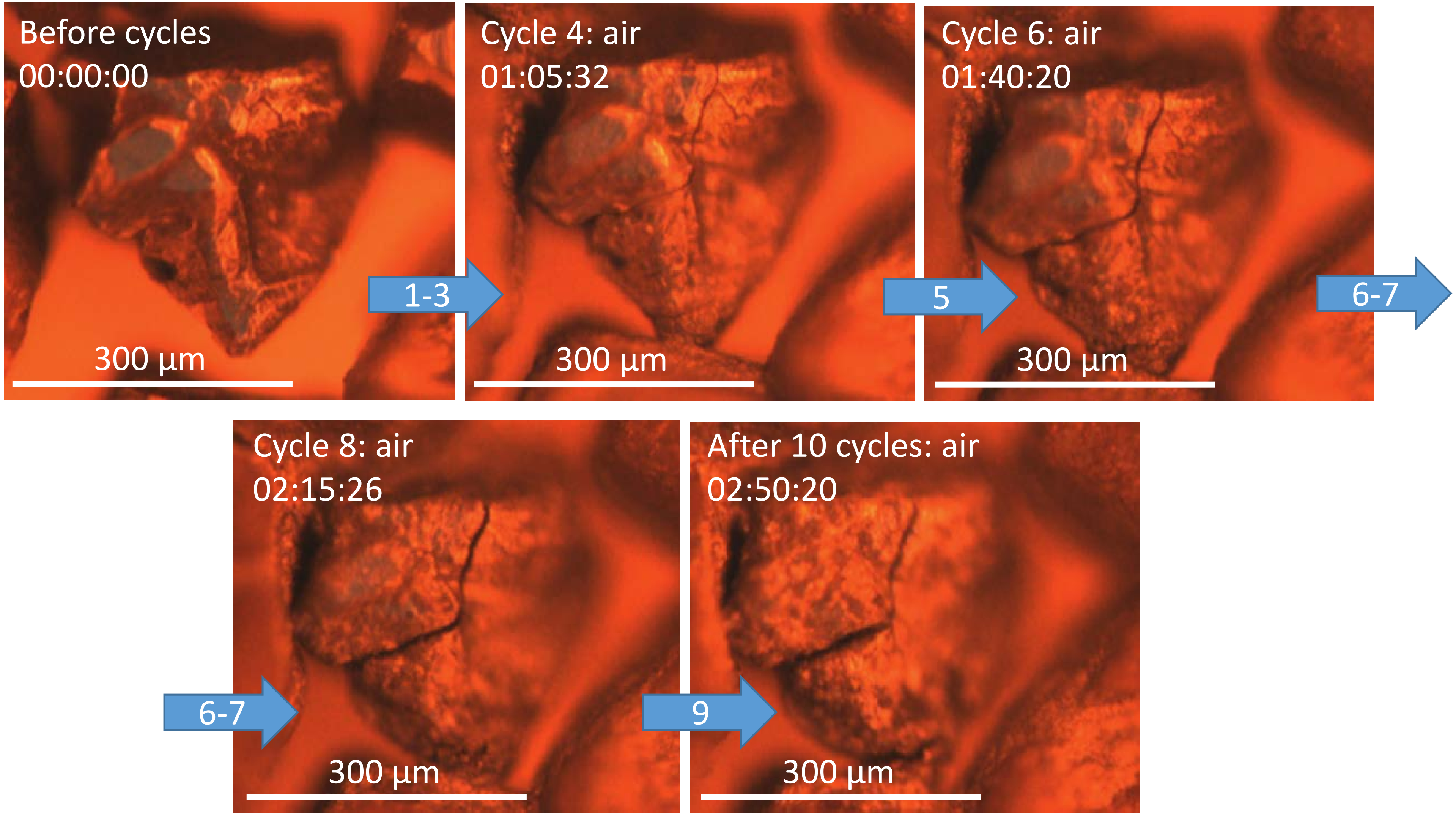


SEM (cross-section)

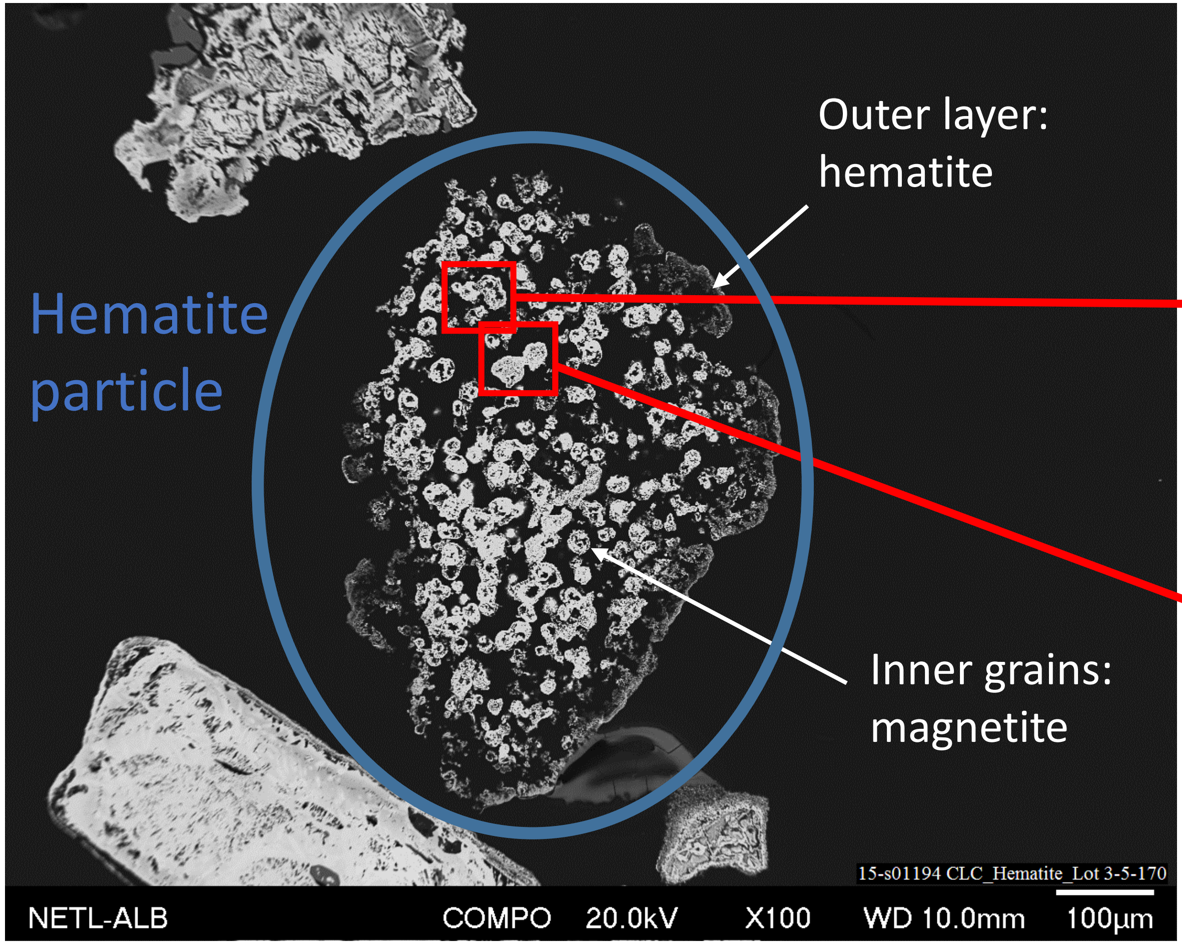


Crack formation at 800°C

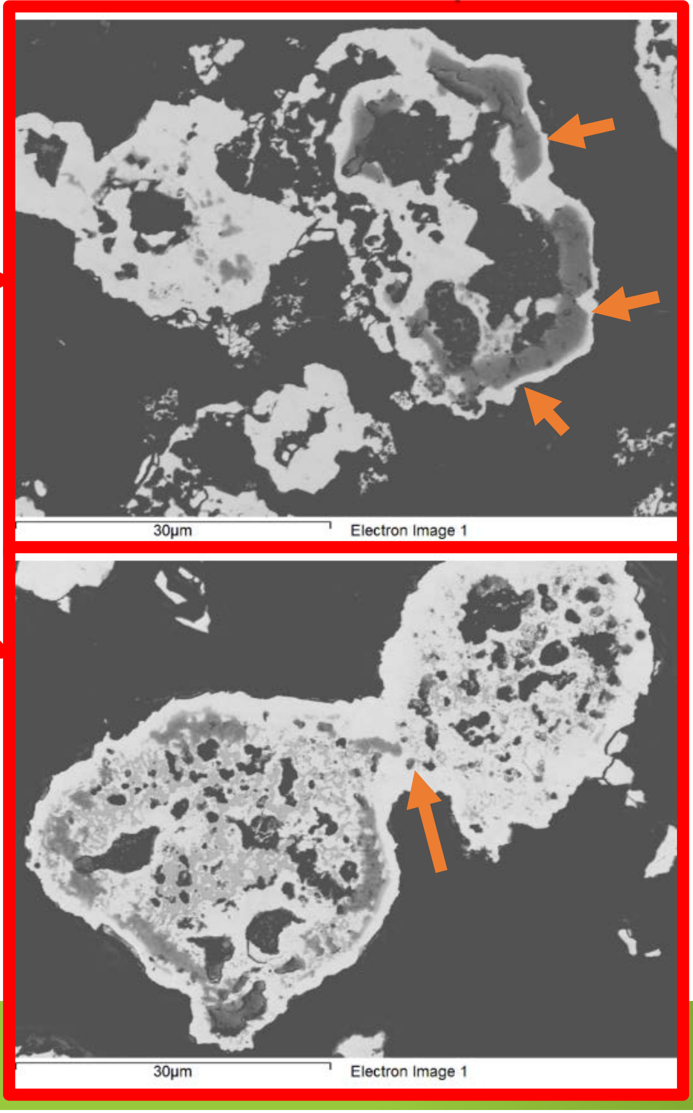


Inner grains in each particle After 10 redox cycles at 800°C

SEM-WDS analysis: cross-section



Grains inside the particle

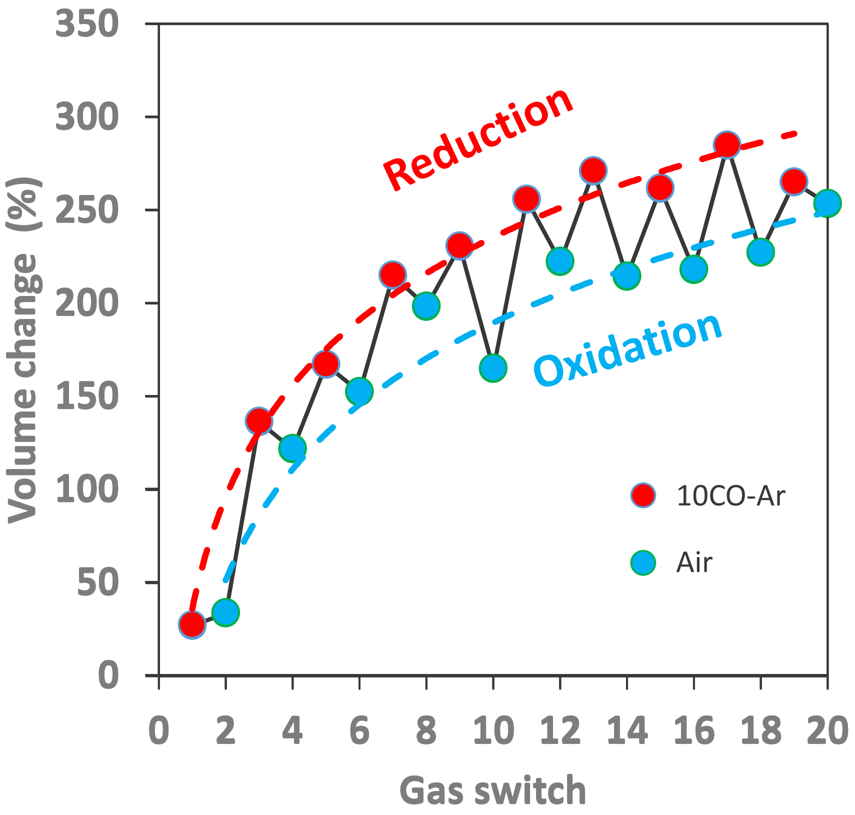


Outer layer formation around individual inner grains

Sintering of inner grains inside the particle

Note: Dark grey area is remaining silica-based polishing/epoxy

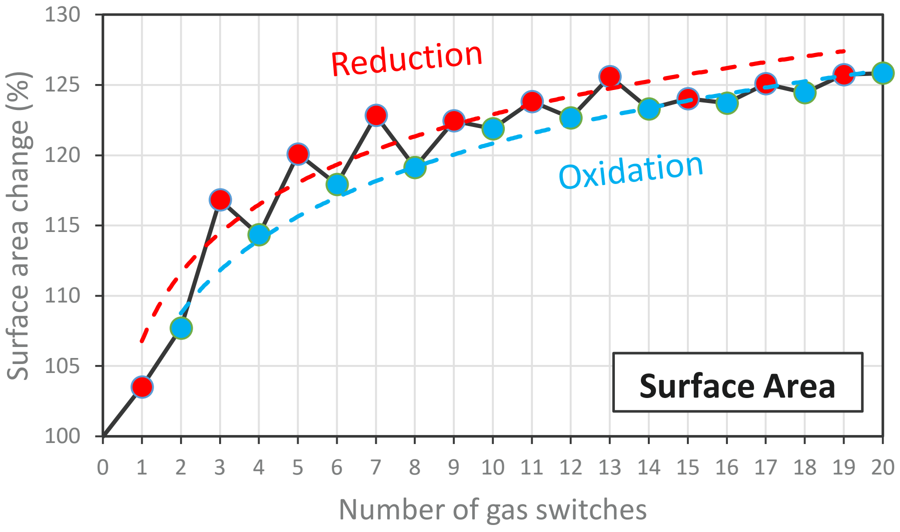
Volume change at 800°C

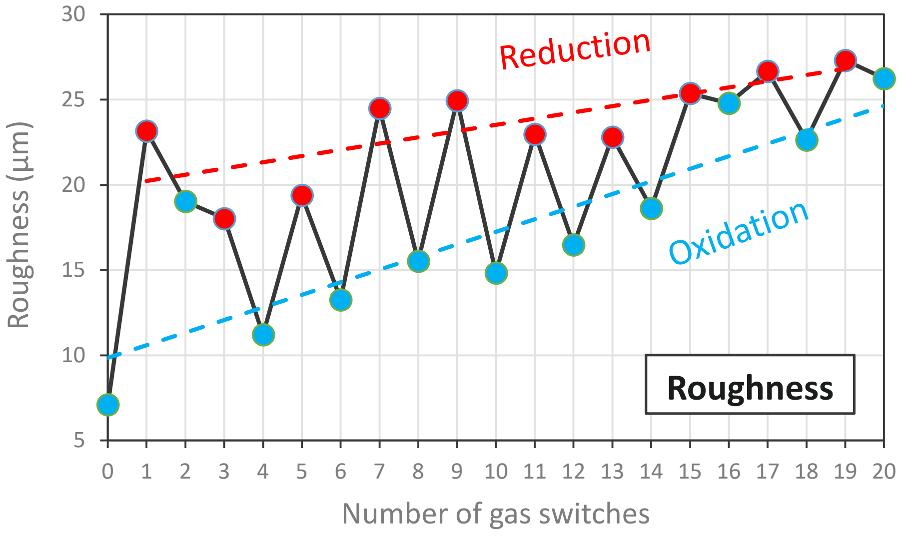


- Zig-zag volume change: decreases from reduction to oxidation, increases from oxidation to reduction – mainly due to **hematite ↔ magnetite** transitions (magnetite lattice > hematite lattice).
- Overall volume increase due to **void formation**.

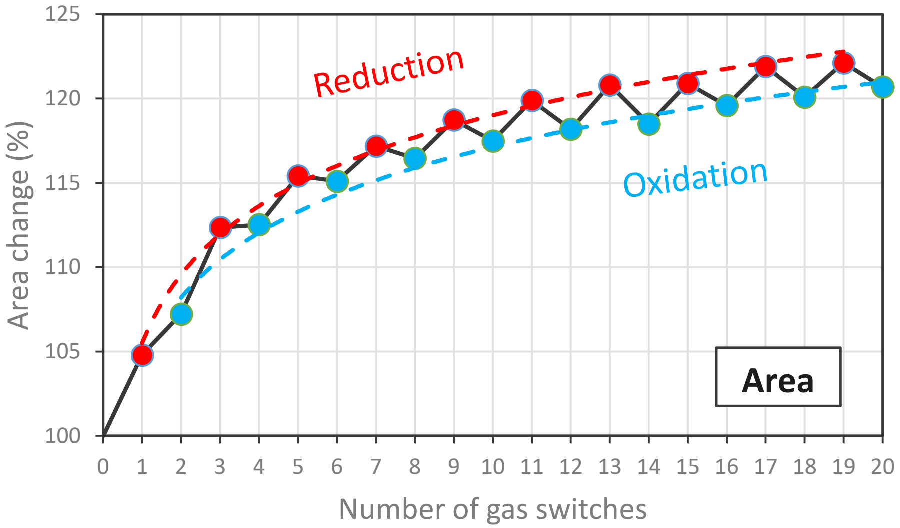
Note: 3D scan in Air at 800°C was used as a reference 100% volume.

Surface area, Area, and Roughness Changes at 800°C





- **Surface area** = topography area (including bumps and dents – 3 D).
- **Area** = overall area without bumps and dents – 2 D.
- **Roughness** = difference in max. heights and pits over surface

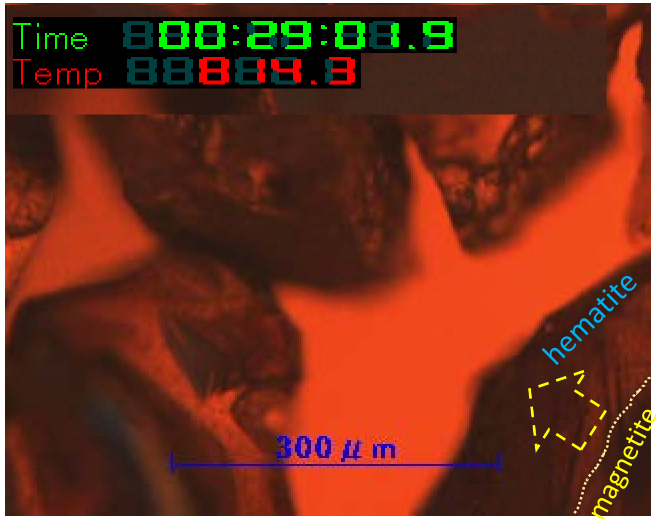


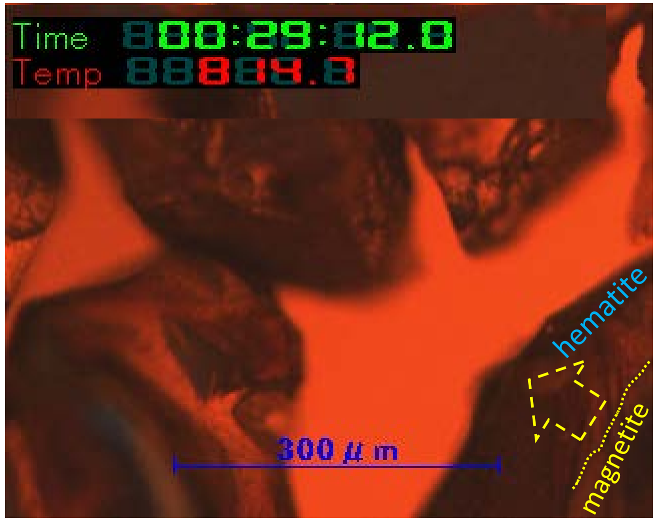
- Increasing zig-zag trend with cycles
- Surface area increase (25%) > area increase (21%) → due to the formation of **surface bumps and dents**.
- Overall roughness increase → due to **structural breakdown/void formation**.

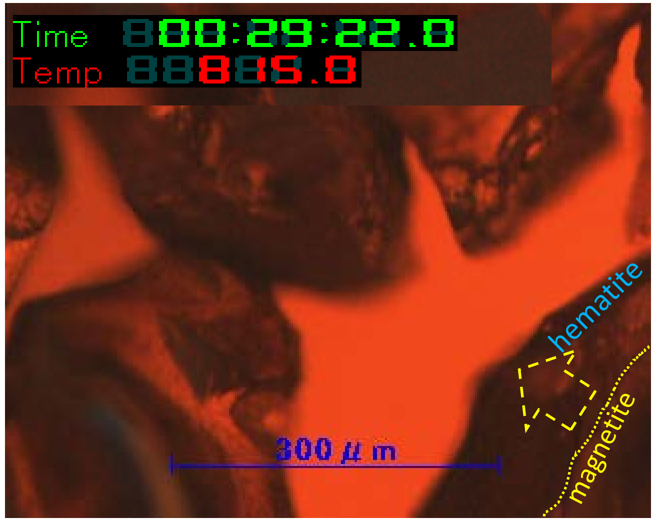
Note: 3D scan in air at room temperature before redox exposure was used as a reference for surface area and area.

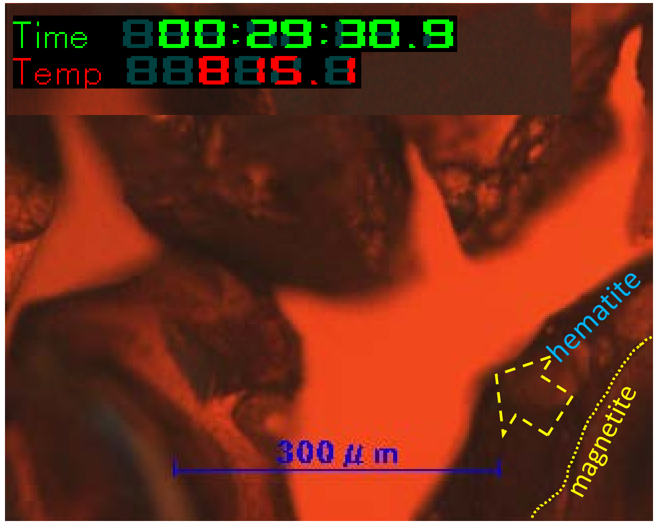
Kinetics of surface phase transition at 800°C

(Cycle 2: 10CO-90Ar)

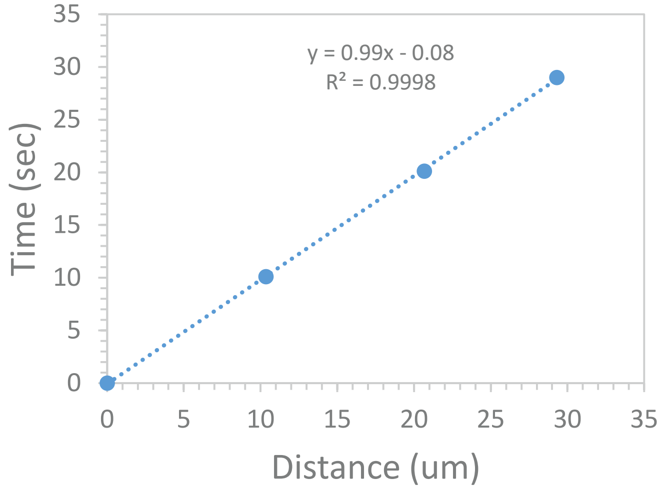




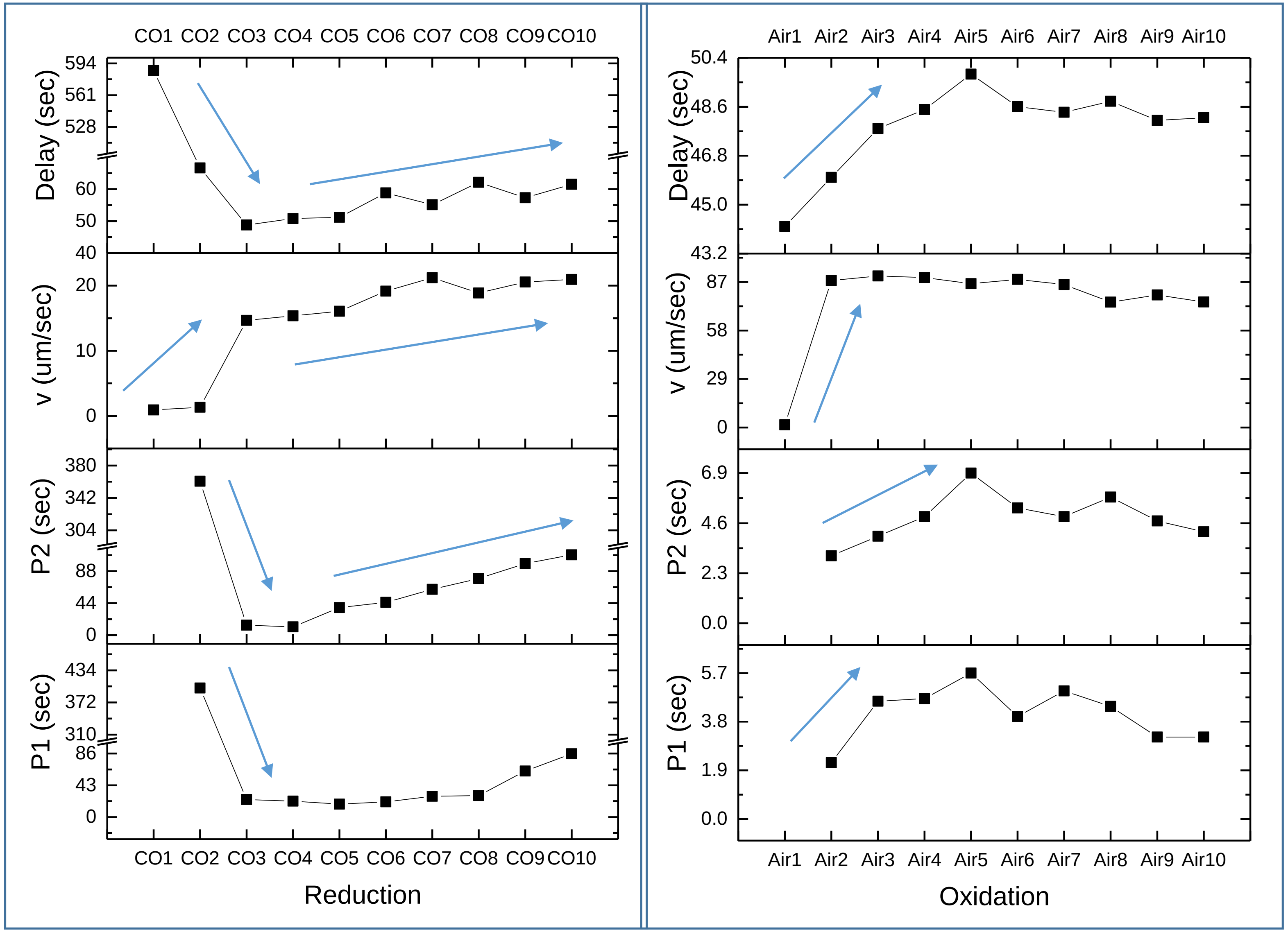




- Linear kinetics = interfacial
- Velocity = 0.99 um/sec



Kinetics at 800°C



- Delay = incubation time required for the onset of phase transition after gas switch
- v = velocity of surface phase transition
- P1 and P2 = time required for complete visual surface phase transition of the selected particles 1 and 2.

Natural hematite analysis (1200°C)

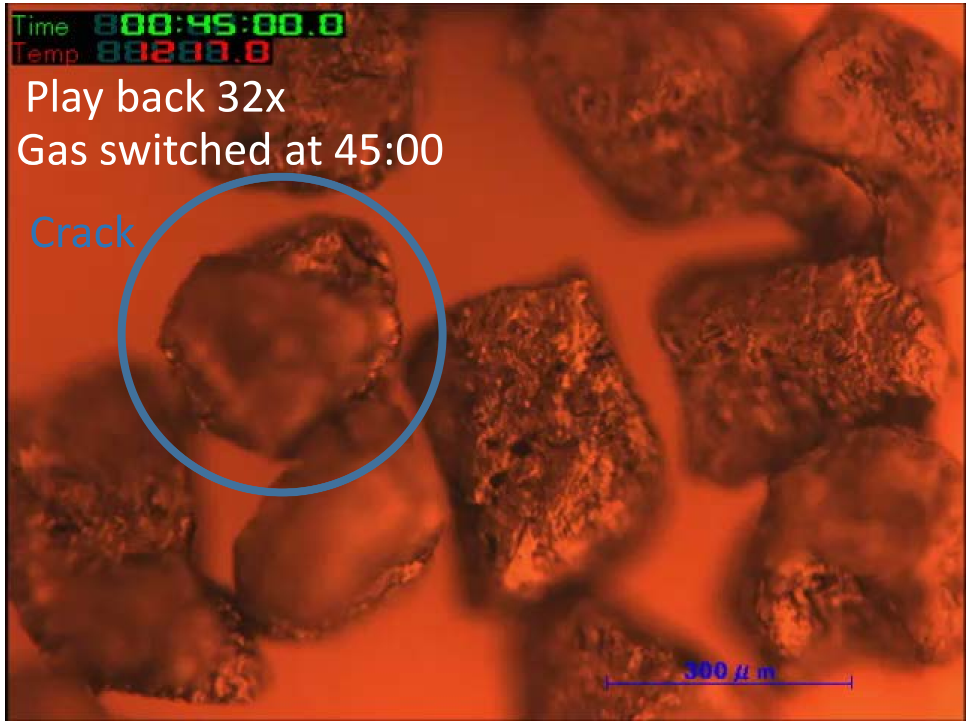
Natural hematite-1200ºC

Surface change
'front line'

Reduction. Cycle 1 (10CO-Ar)

Delay about 6 min before the front line was noted. Surface became rougher. Particles moved.

Reduction. Cycle 3 (10CO-Ar)



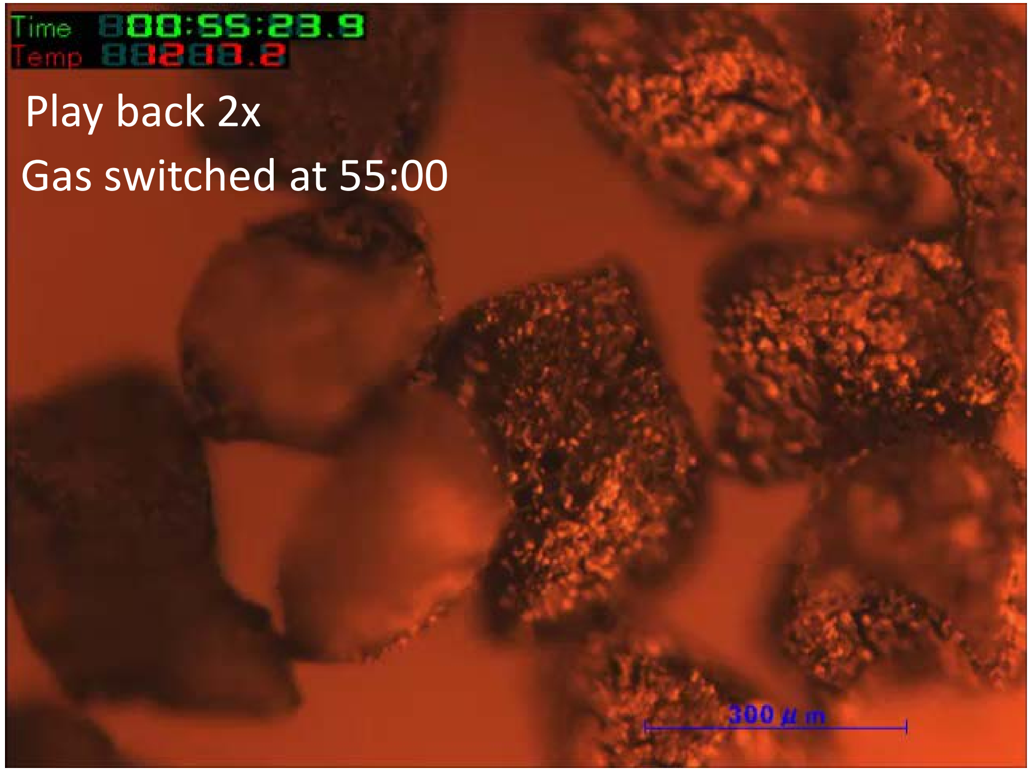
Delay about 45 sec before the surface change was noted. Surface became darker and rougher. Particles moved, expanded, cracked.

Natural hematite, CSLM (1200ºC)

Oxidation. Cycle 1 (Air)

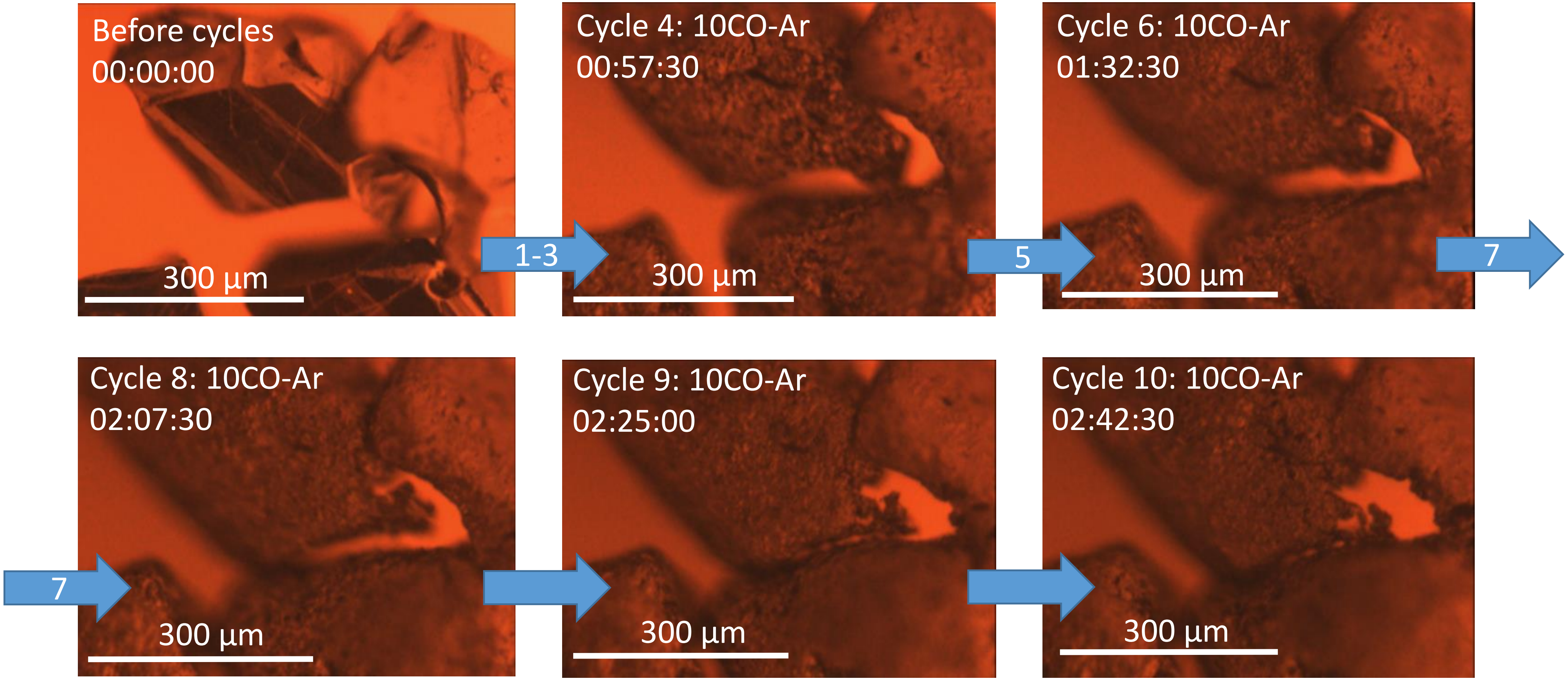
Delay about 45 sec. Surface brightened and became more rough.

Oxidation. Cycle 3 (Air)

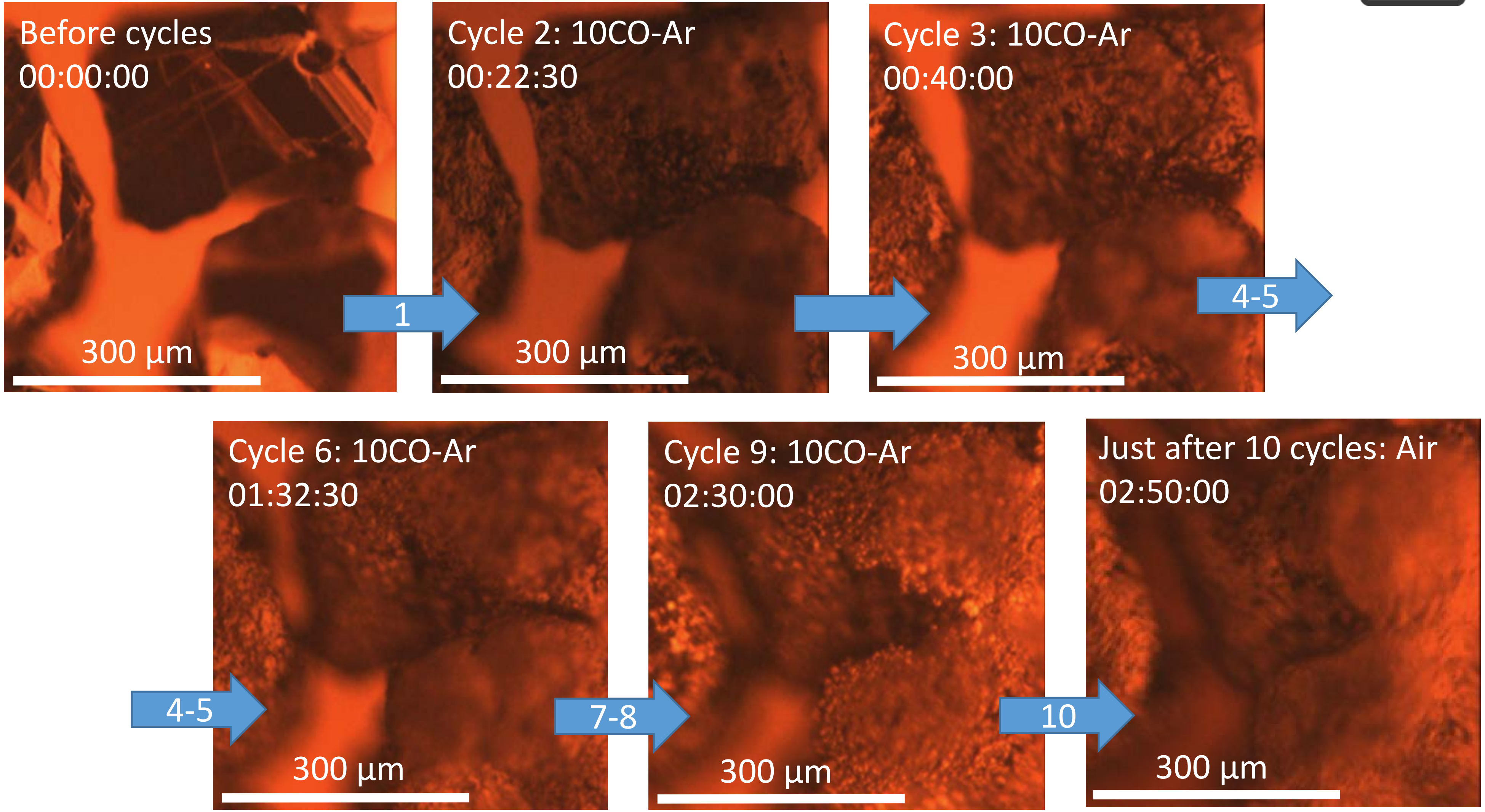


Delay about 45 sec. Surface darkened first and then brightened. Particles shrank.

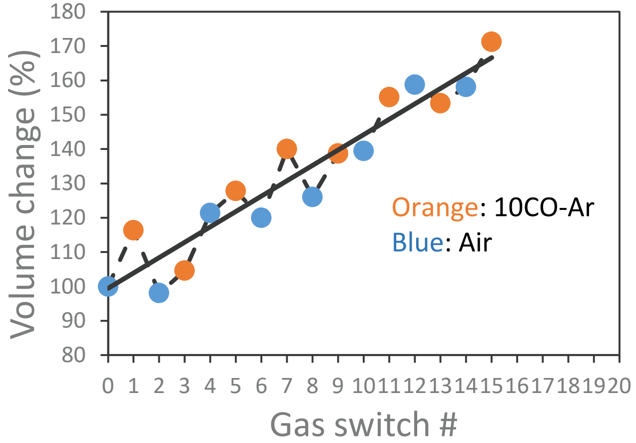
Particle breakdown at 1200ºC



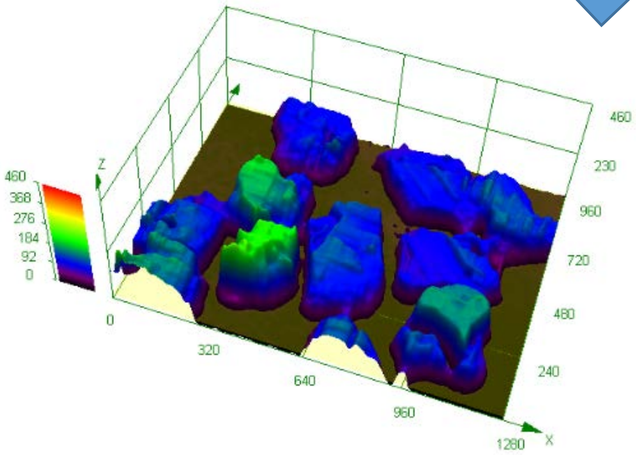
Agglomeration at 1200ºC



Volume change at 1200°C (color map)

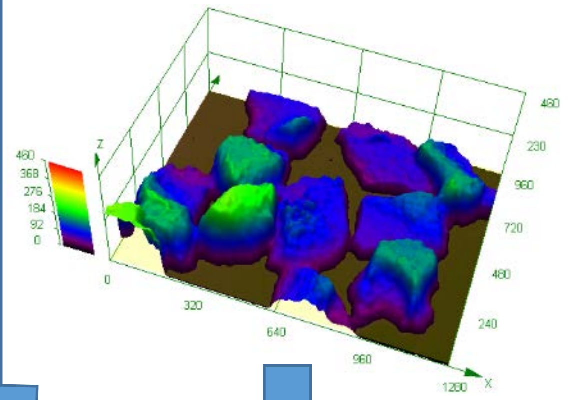


Before redox cycles

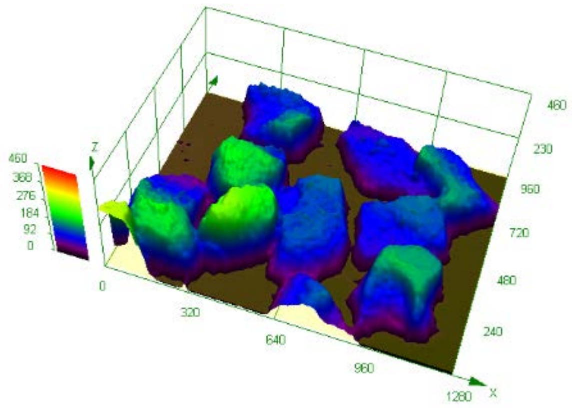


1-2

Gas switch # 3 (CO)

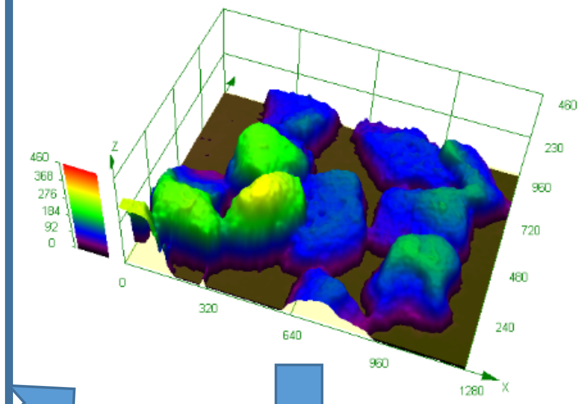


Gas switch # 4 (Air)

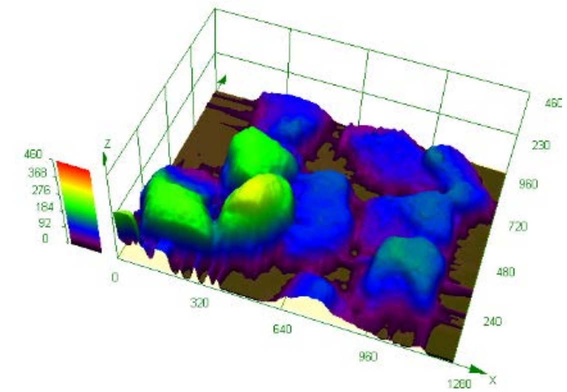


5-6

Gas switch # 7 (CO)

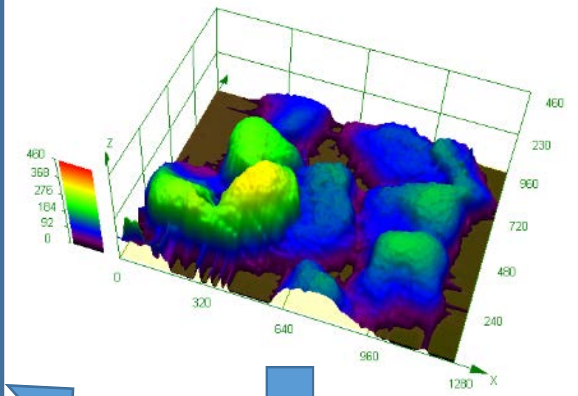


Gas switch # 8 (Air)

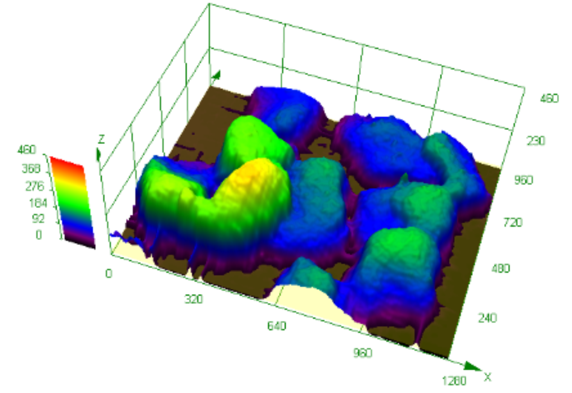


9-12

Gas switch # 13 (CO)



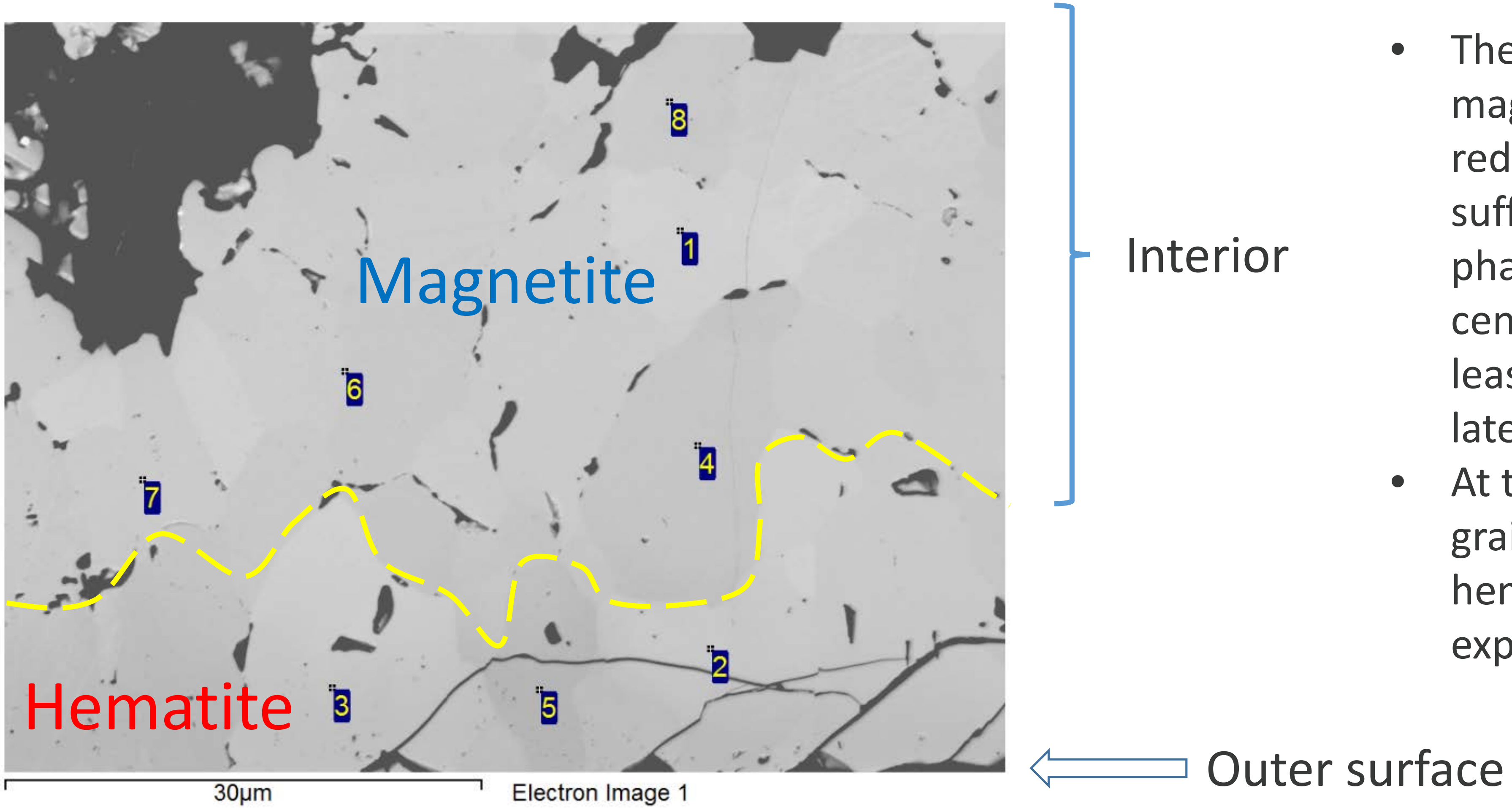
Gas switch # 14 (Air)



Note: Quartz window fogged after gas switch 15

After the redox gas cycles at 1200°C

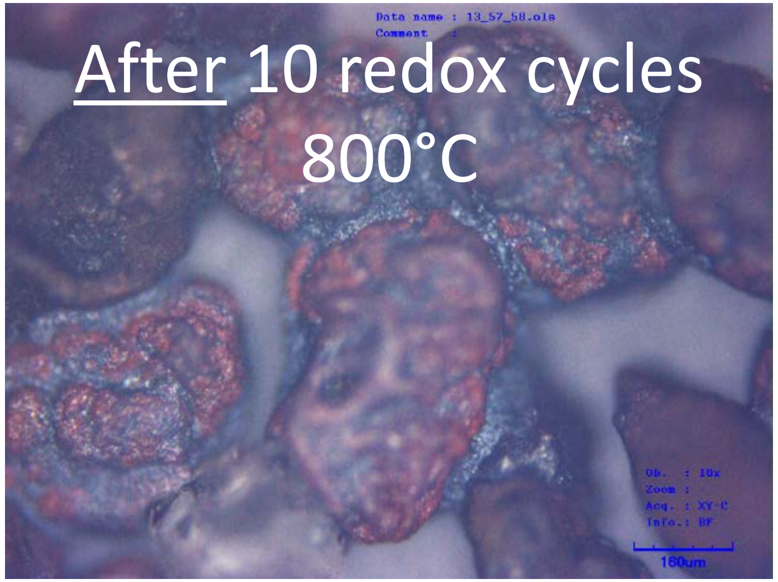
SEM-WDS analysis: cross-section



- The presence of interior magnetite implies 10 min reduction exposure was sufficiently long to induce phase transition at the center of the particle, at least at some point if not at later stages.
- At the last cycle, only surface grains transformed to hematite during 7.5 min air exposure.

Hematite surface change after redox exposures

(General groups of hematite particles)



Hematite surface turned reddish on cooling

Heavily sintered

White light images

Conclusions

- Materials behaviors of natural hematite (Fe_2O_3) particles at 800°C and 1200°C were investigated under redox gas cycles (synthetic air and 10CO-90Ar) using HT-CSLM

- During isothermal gas cycling, the hematite particles showed phase transitions across the surfaces corresponding to a hematite transforming to magnetite in 10CO-90Ar and magnetite to hematite when switching back to air (phases confirmed by SEM-WDS)

- In general, particle volumes, area, and roughness increased in transitioning to magnetite and decreased in transitioning to hematite, while, overall, all increased with cycles

- Layering around the particles was noted but full transition to magnetite throughout the particle indicates hematite would be suitable for CL application if appropriately processed

Acknowledgement

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