# *Oxidation Resistance of 9-12%Cr Steels: Effect of Rare Earth Surface Treatment*

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# 9-12 Cr Steels

- Various martensitic 9-12 Cr steels are utilized in advanced energy plants for their good elevated temperature properties:
  - ➢Creep strength
  - ➢Steam side oxidation resistance
  - ➢Fire side corrosion resistance
  - ➢Thermal fatigue resistance

# Applications

- **Boilers:**
  - Superheater tubing
  - Headers
  - Steam pipes
- **Steam Turbines:**
  - Rotors
  - Casings
  - Valves
  - Inlet pipes

# Motivation for Current Research

- Need for further improvements on the properties for higher temperature (>600$^{o}$C) use driven by the environmental concerns (i.e., improve efficiency to lower emissions and fossil fuel consumption)

# Motivation for Current Research

- Explore new subsitutional solute solution (Cu, Co) and precipitate (TiC) hardening mechanisms for improved strength of 9-12 Cr martensitic steels

# Objective

1. Evaluate the oxidation behavior of TiC strengthened Fe+(9-12) Cr steels.
   - ➢ Compare to conventional steel used in power gerneration applications: alloy P91.
2. Examine influence of RE additions on oxidation behavior of Fe+(9-12)Cr+TiC
   - ➢ Improve oxidation resistance

# Alloy Composition

| Alloy | Fe | Cr | Cu | Co | Ni | Mo | Ti | Other |
|---|---|---|---|---|---|---|---|---|
| **HR52** | Bal | 9.0 | 3.0 | 3.0 | 1.2 | 0.7 | 0.5 | |
| **HR53** | Bal | 10.5 | 3.0 | 3.0 | 1.2 | 0.7 | 0.5 | |
| **HR54** | Bal | 12.0 | 3.0 | 3.0 | 1.2 | 0.7 | 0.5 | |
| **P91** | Bal | 8.5 | 0.1 | --- | 0.3 | 1.0 | --- | 0.2V-0.08Nb-0.5Mn-0.3Si |

# Reactive Element Additions

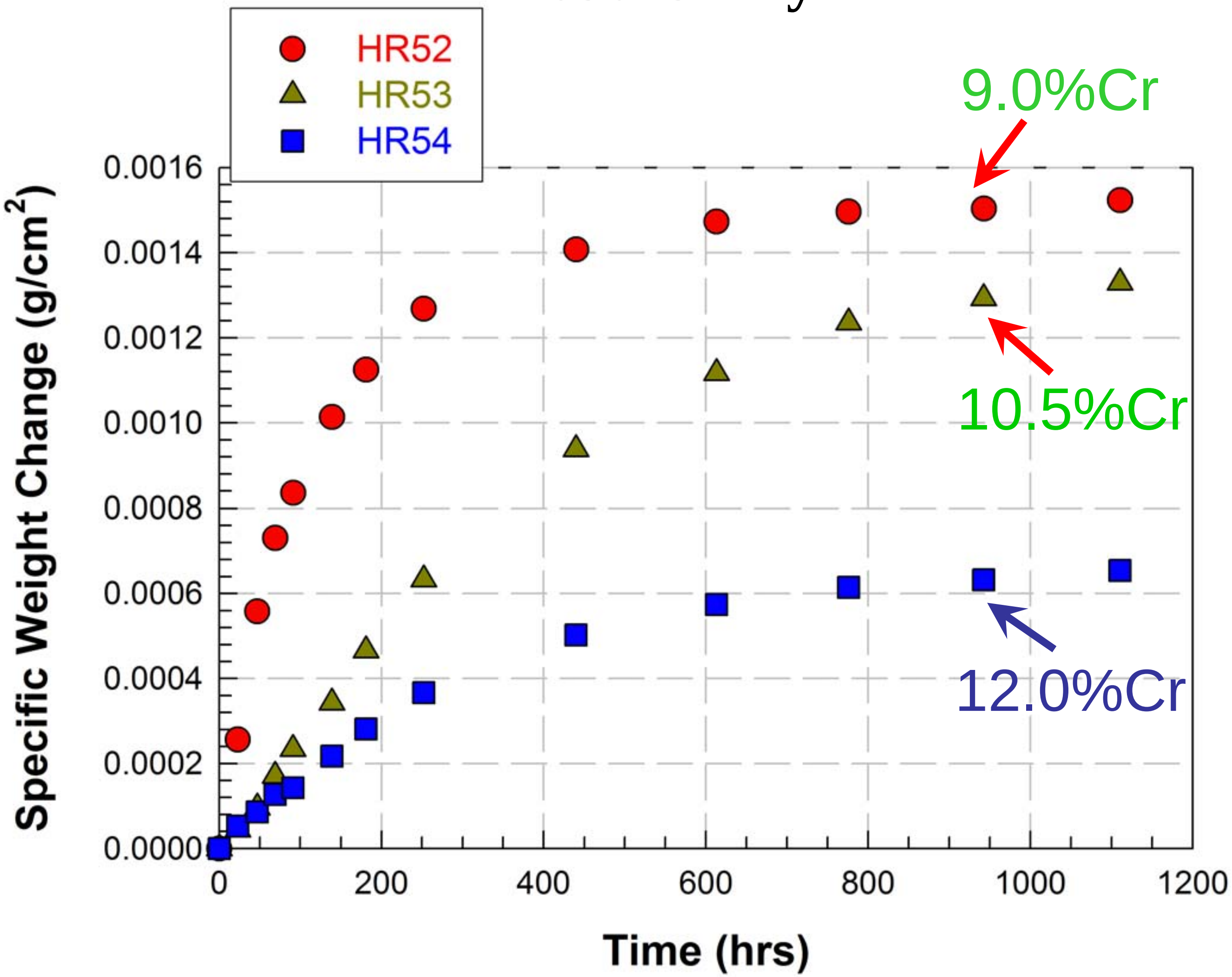
- Minor additions of rare earth (Ce, La, Y, etc.) improve oxidation resistance.
- Treatments to enhance rare earth element (RE) content at alloy surface effective in improving oxidation resistance.
  - ➢Developed method for incorporating RE into an metal/alloy surface.
  - ➢Patent application filed.
  - ➢Method utilized to incorporate Ce into the surface of HR52, HR53 and HR54.

# Experimental

- Sample Preparation
  - ➢ Machined from rolled plate.
    - Coupon dimensions ~ 19 x 19 x 5 mm.
  - ➢ Surfaces polished to 600 grit finish.
  - ➢ Dimensions and weight recorded
    - After cleaning surfaces with alcohol.
- Oxidation
  - ➢ 650$^{o}$C flowing dry air.
    - Samples placed in furnace on a quartz rack.
  - ➢ pseudo static/cyclical test.
    - Sample removed from furnace after a certain time
    - Weight recorded
    - Sample placed back into the furnace for the next cycle

# Oxidation Behavior HR Alloys

## 650ºC-Dry Air

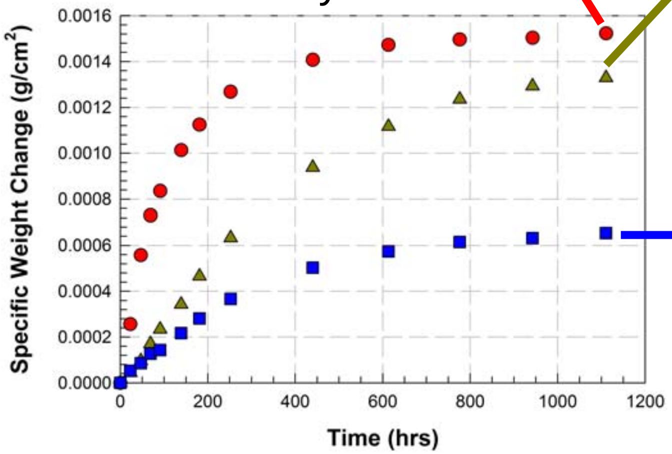


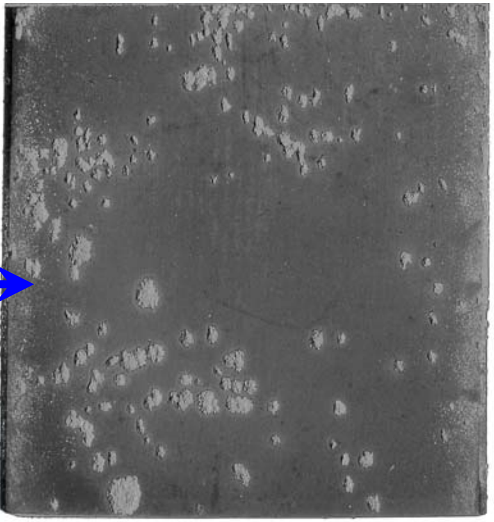
# Surfaces After Exposure

HR52
9.0%Cr

HR53
10.5%Cr

650$^{o}$C-Dry Air

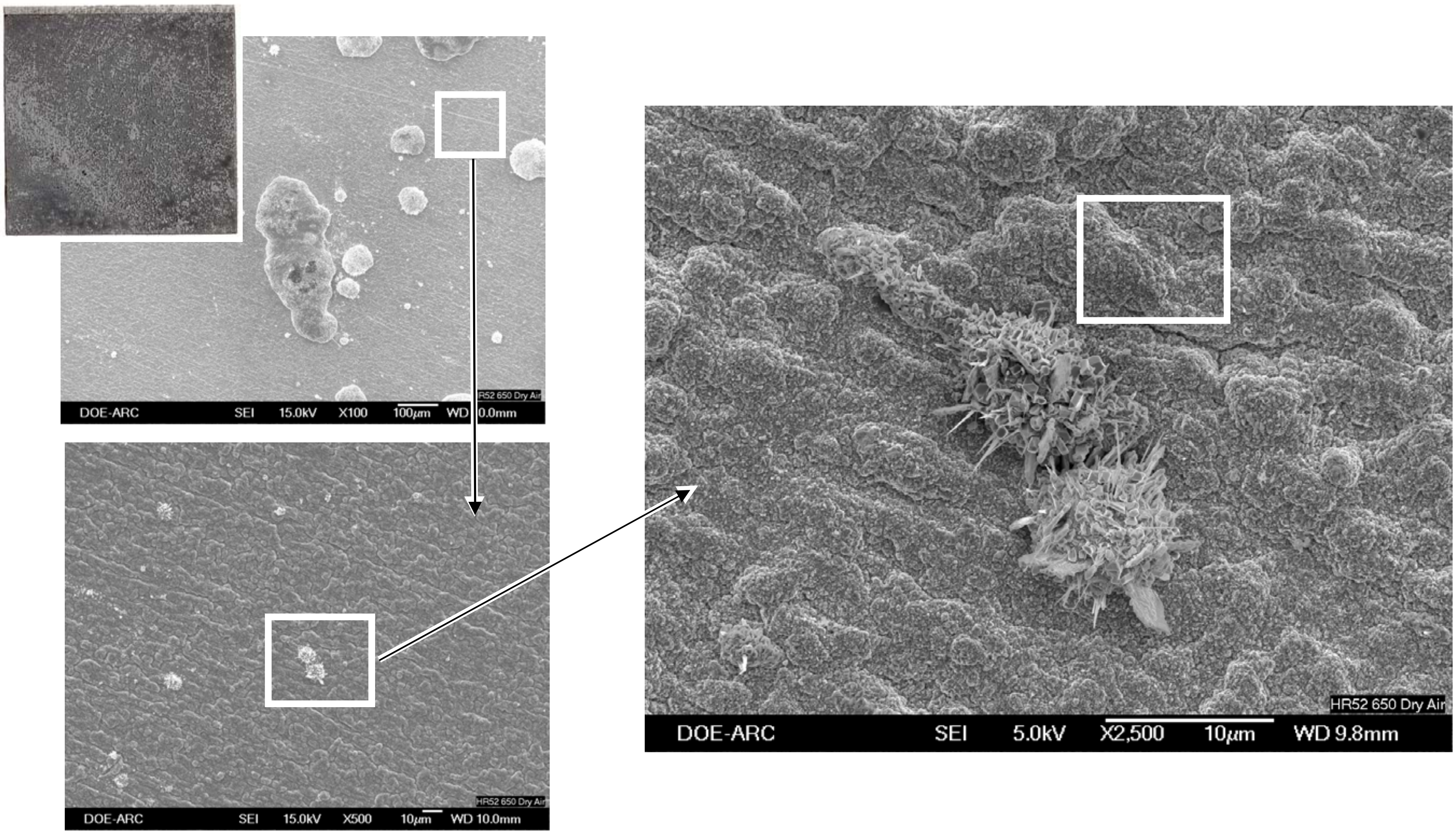


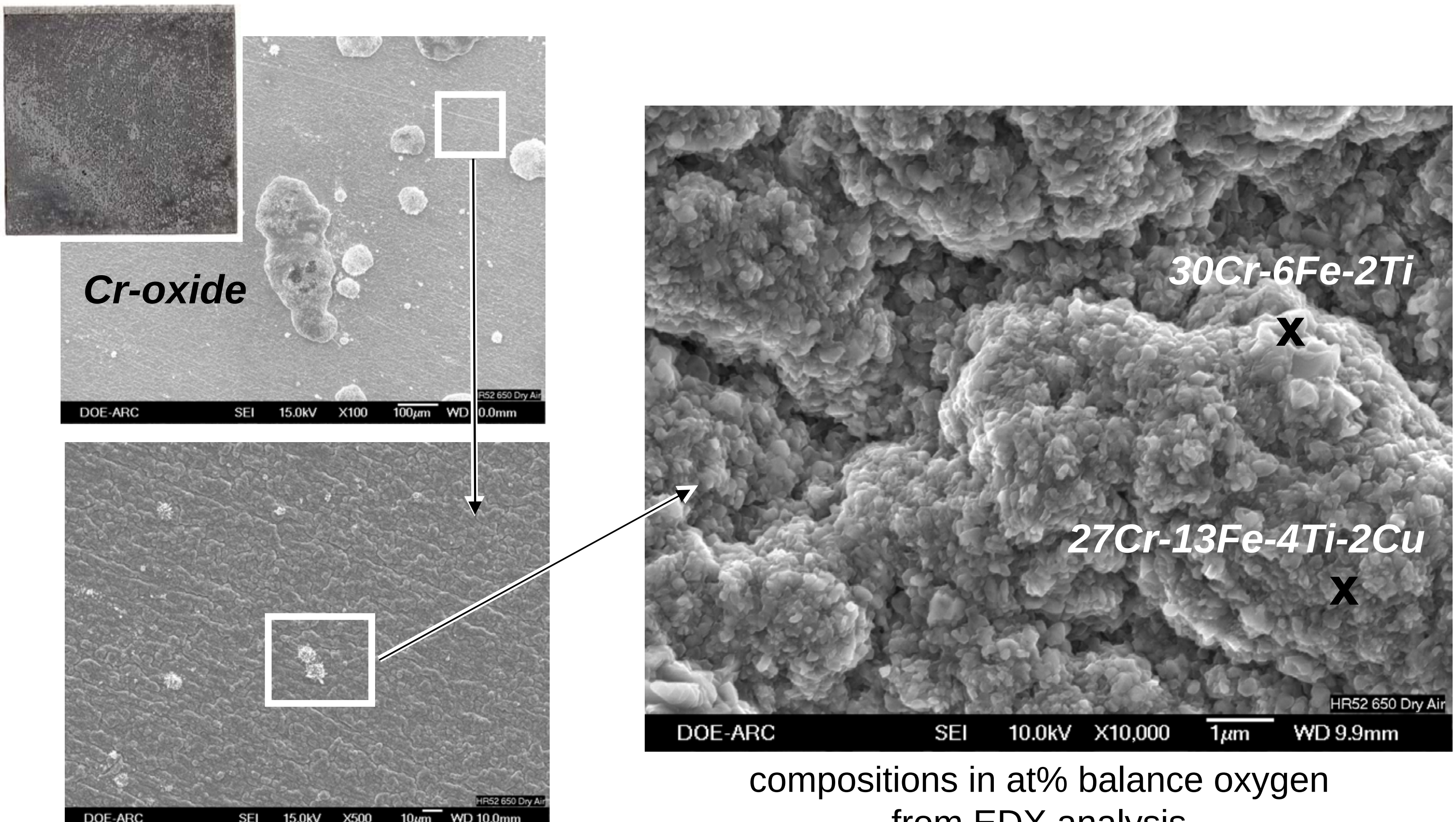
HR54
12.0%Cr

# HR52 Surface After Exposure

## (650$^o$C-Dry Air-1100hrs)

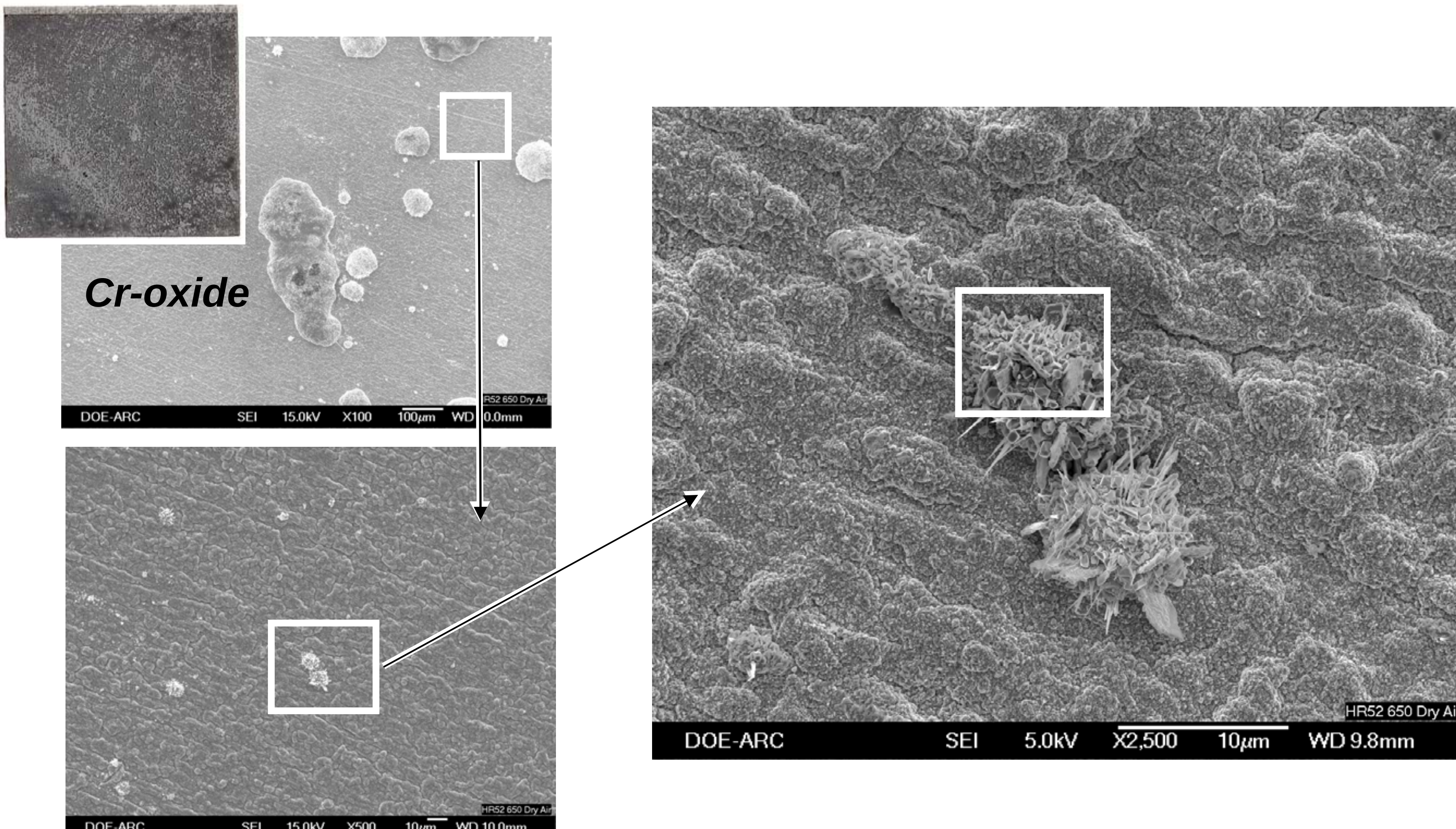


# HR52 Surface After Exposure
## (650ºC-Dry Air-1100hrs)




compositions in at% balance oxygen
from EDX analysis

# HR52 Surface After Exposure
## (650$^o$C-Dry Air-1100hrs)



# HR52 Surface After Exposure
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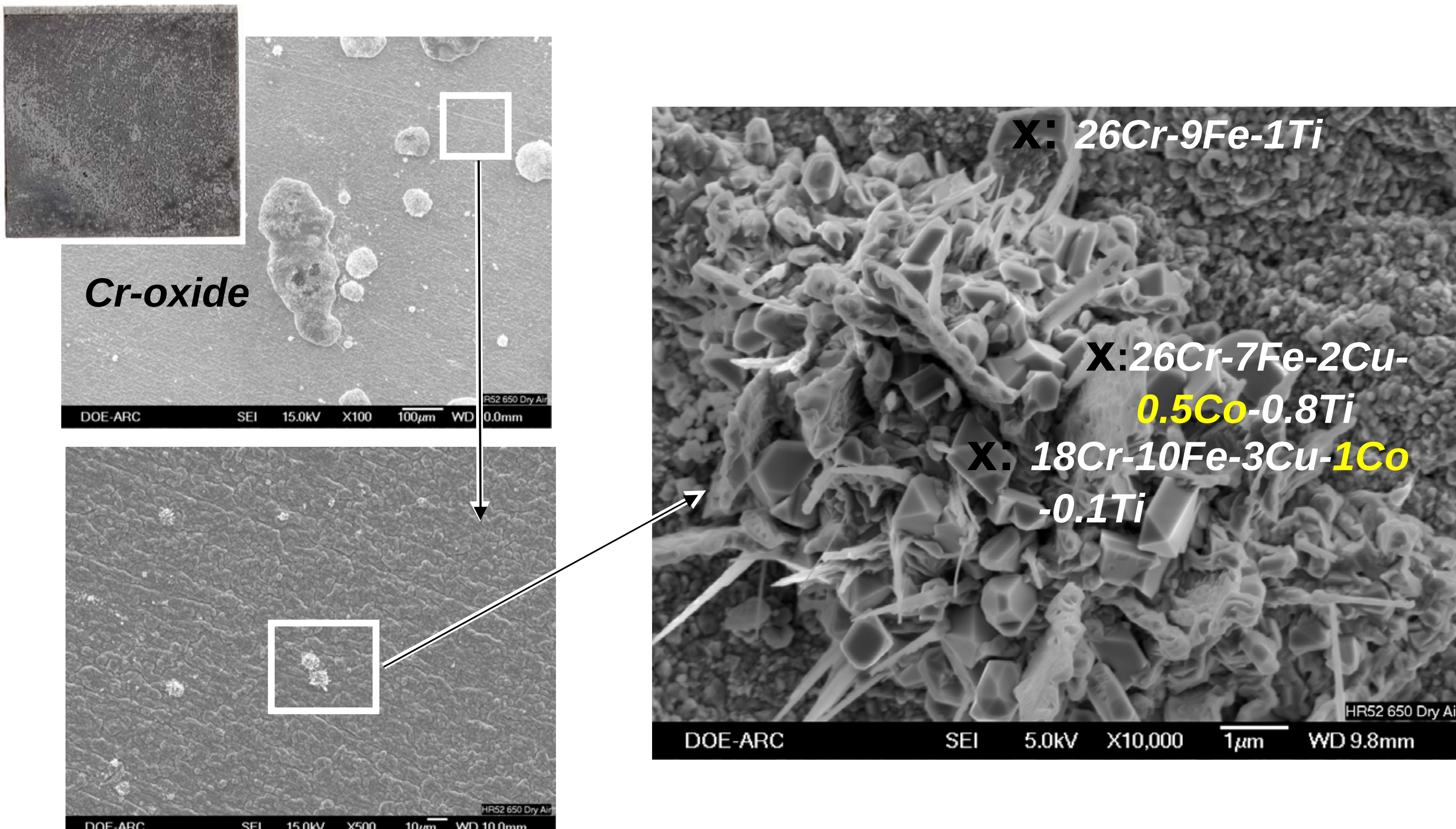

# HR52 Surface After Exposure
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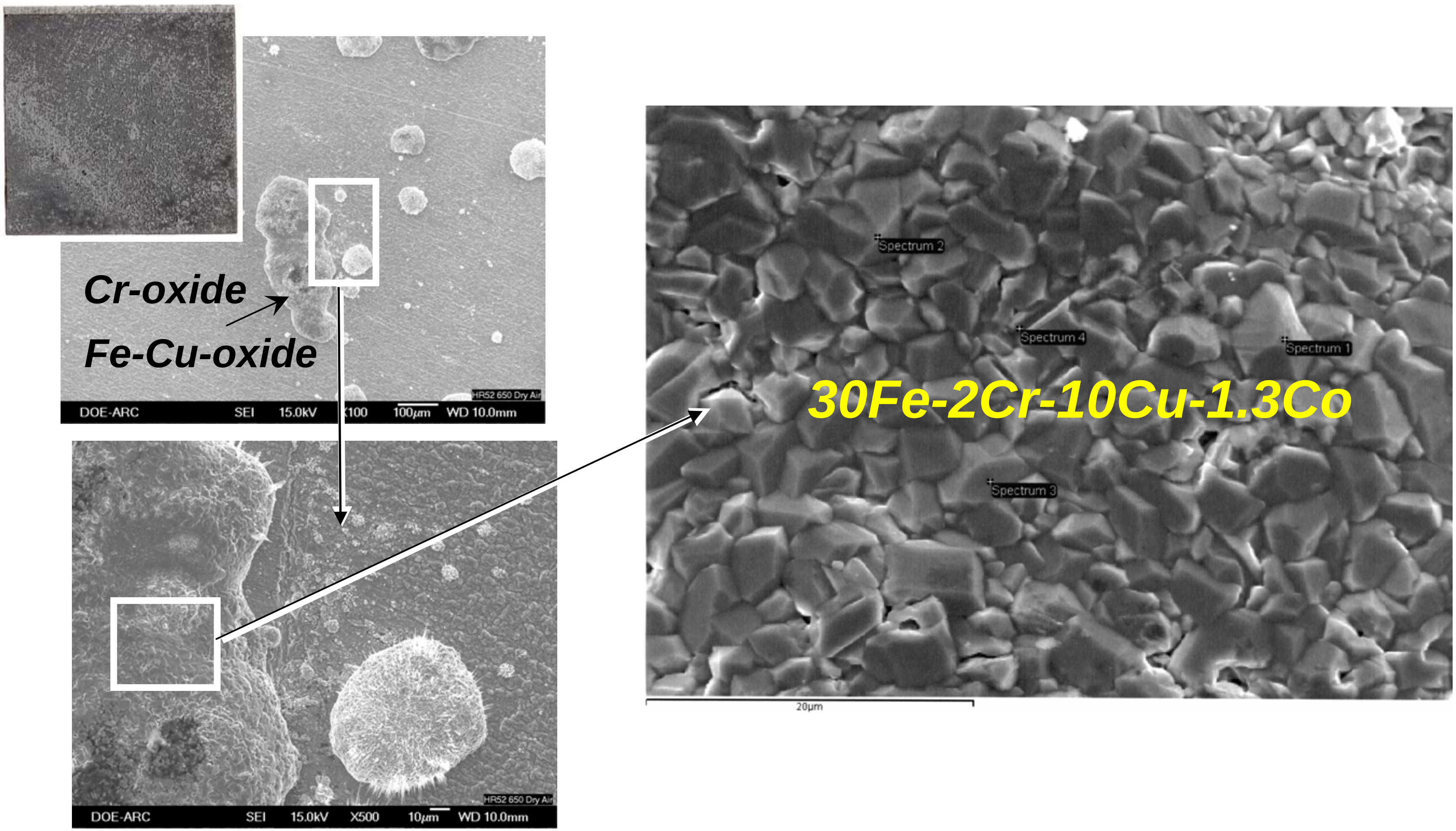

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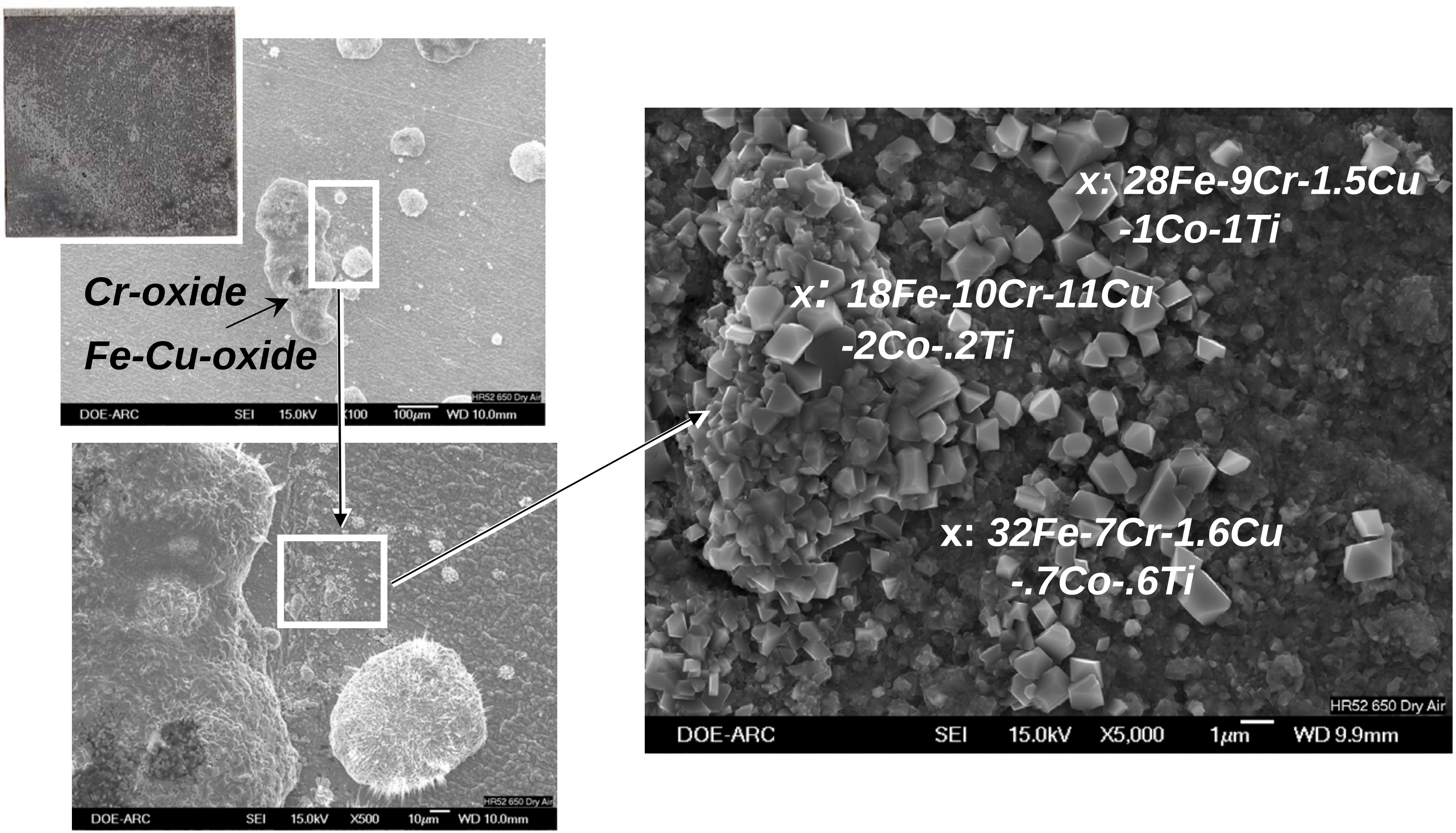
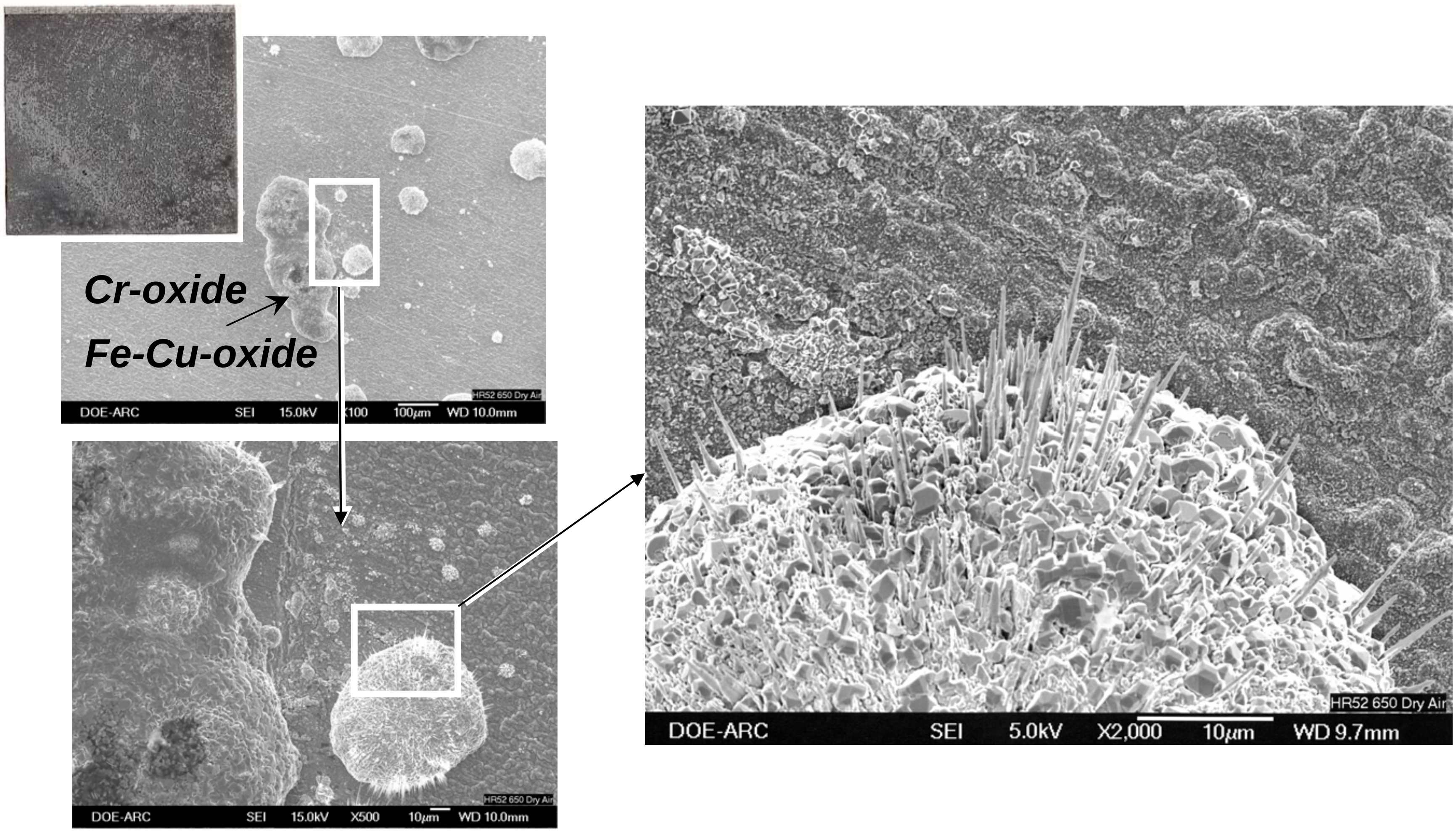
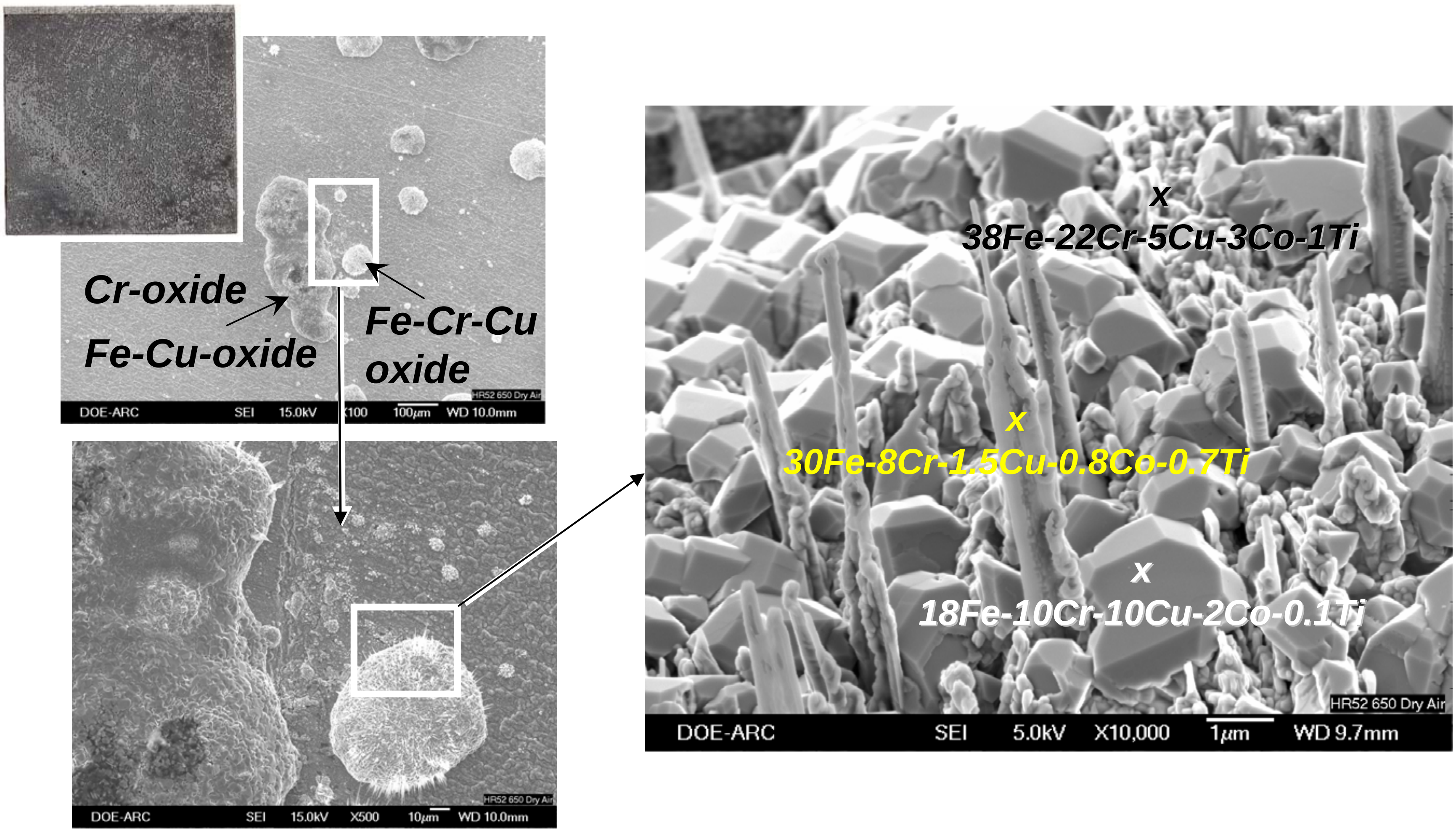


# HR52 Surface After Exposure
## (650$^{o}$C-Dry Air-1100hrs)

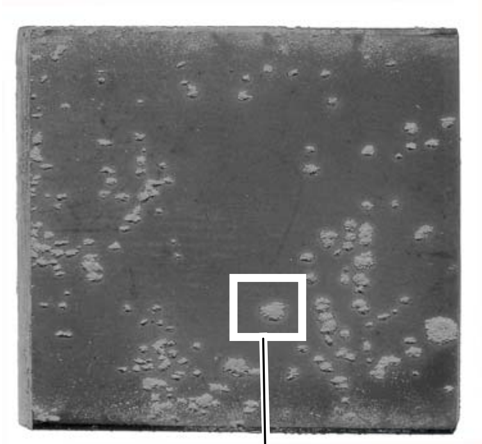


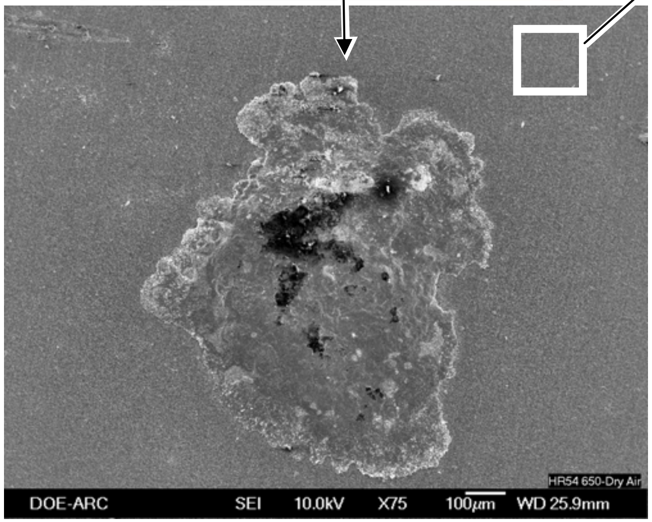
# HR52 Surface After Exposure
## (650$^{o}$C-Dry Air-1100hrs)

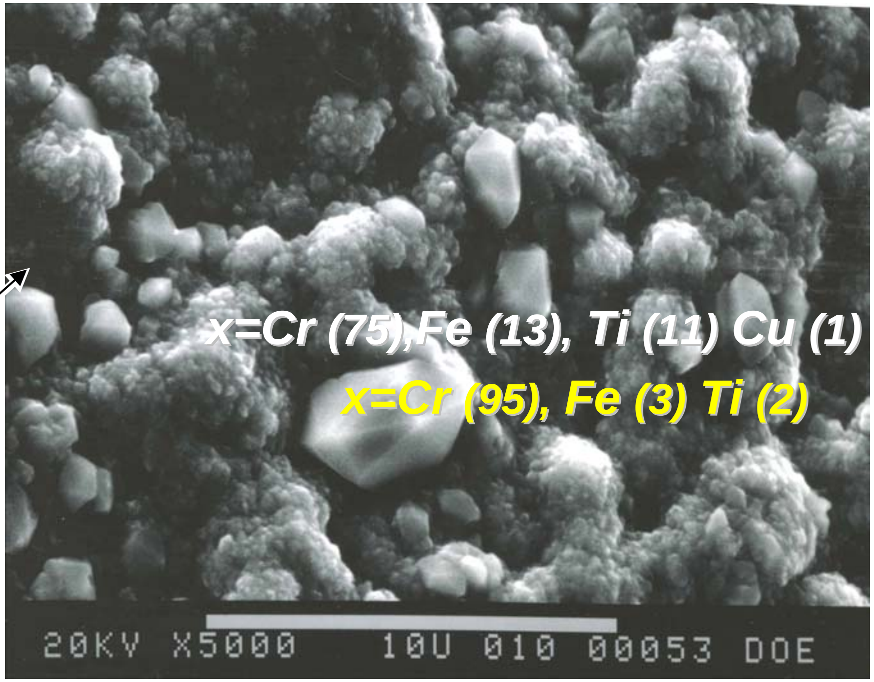


# HR54 Surface After Exposure

## (650ºC-Dry Air-1100hrs)

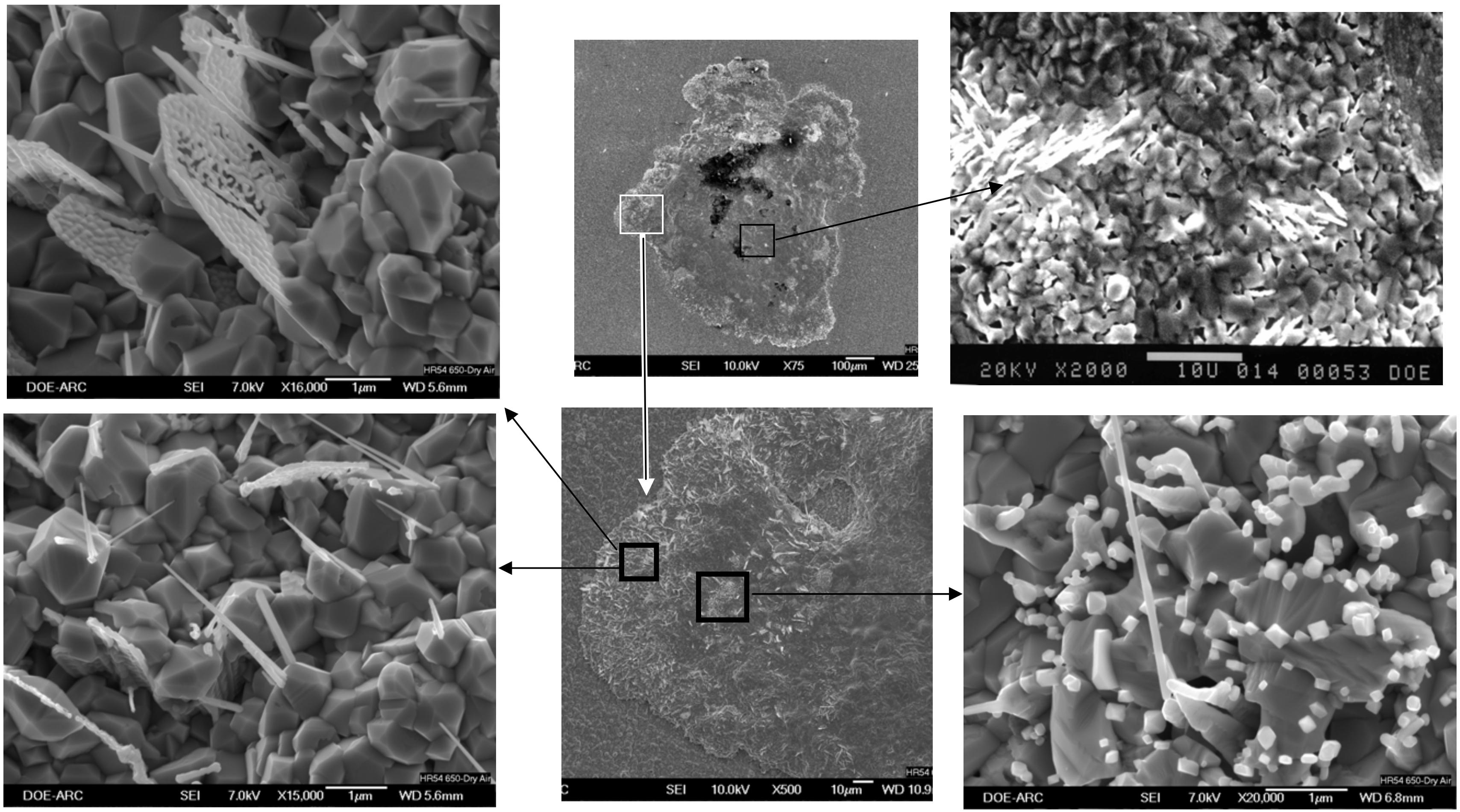




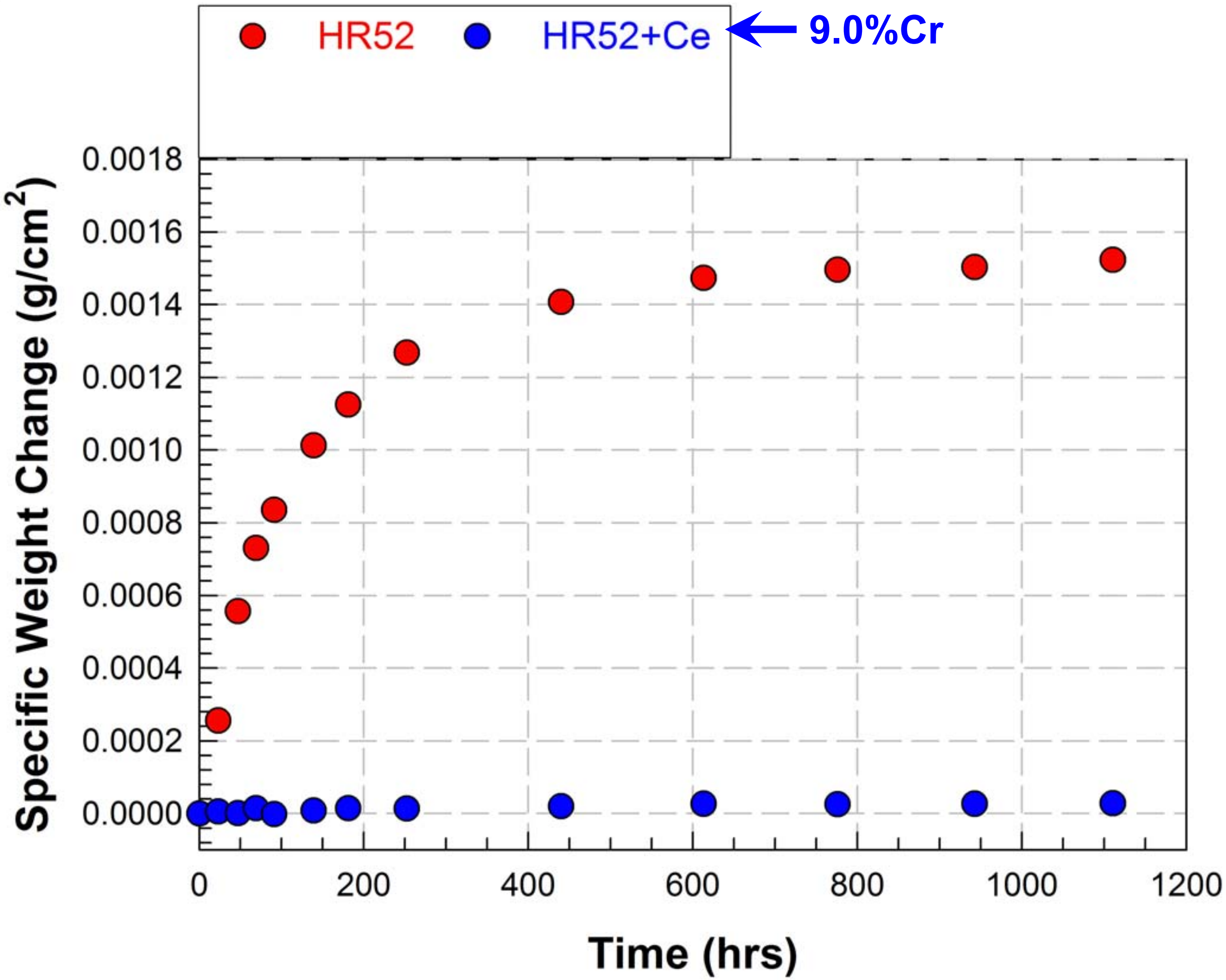
# HR54 Surface After Exposure

## (650ºC-Dry Air-1100hrs)



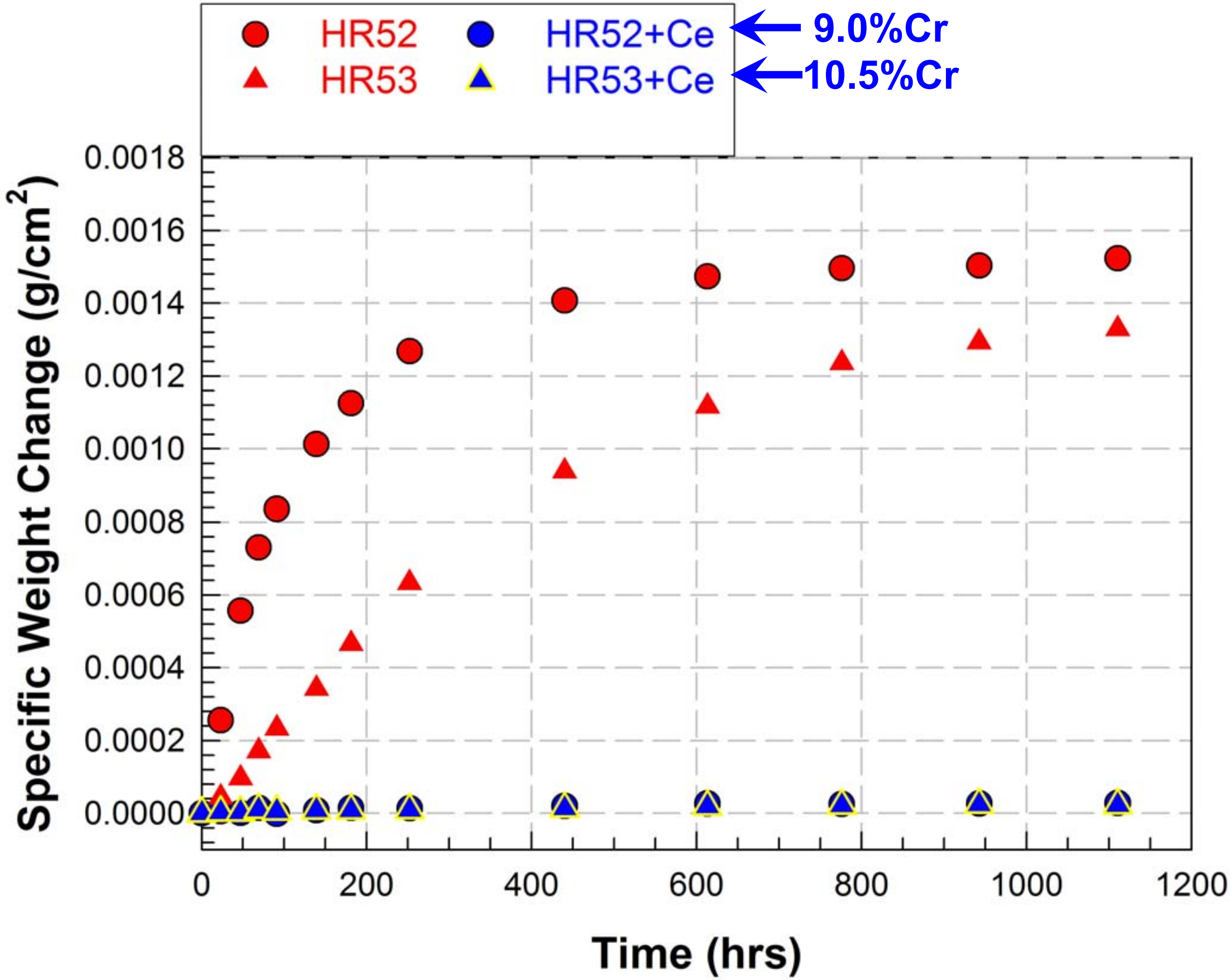
# Oxidation Behavior HR Alloys+Ce

## 650°C-Dry Air



# Oxidation Behavior HR Alloys+Ce

## 650°C-Dry Air



# Oxidation Behavior HR Alloys+Ce

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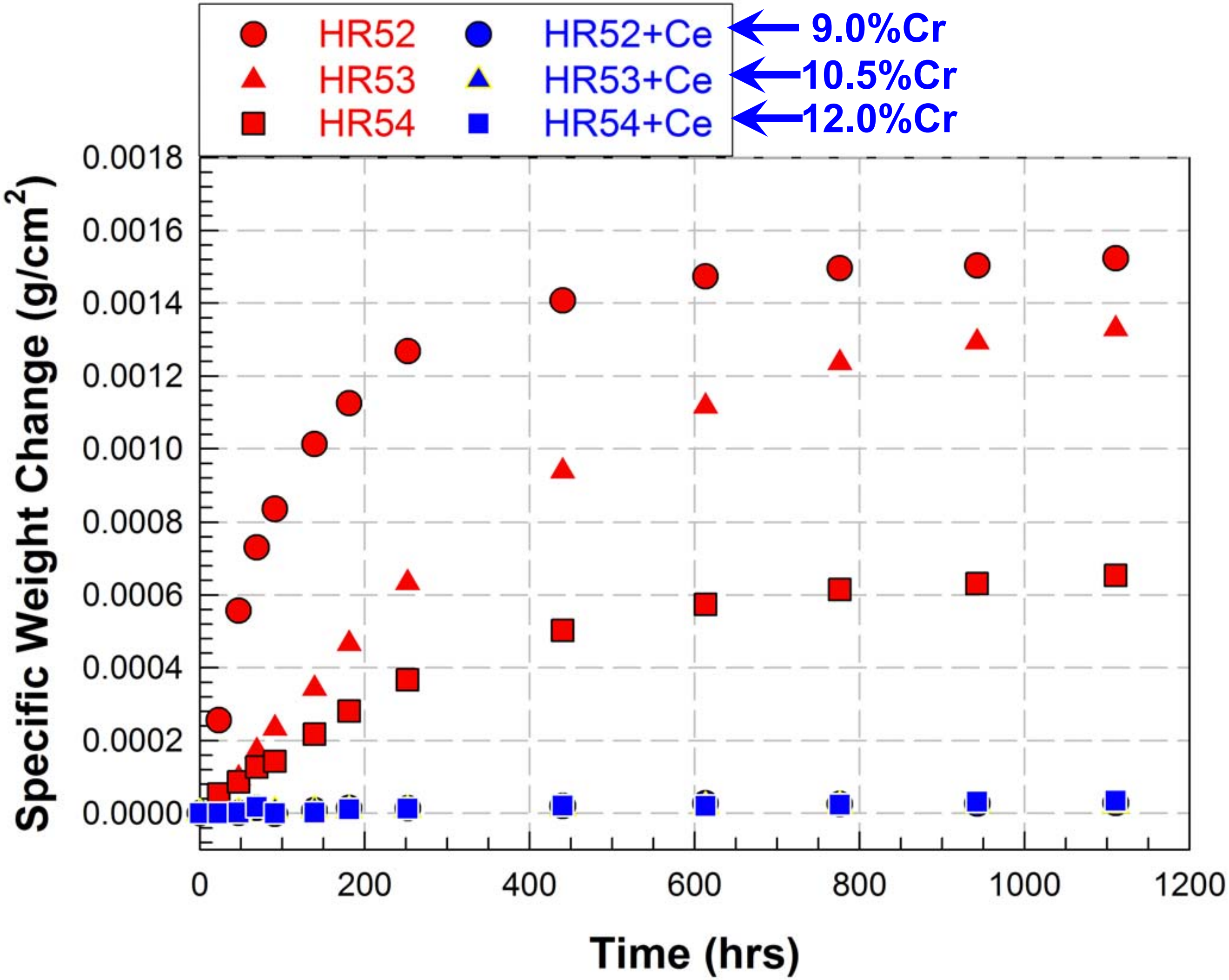
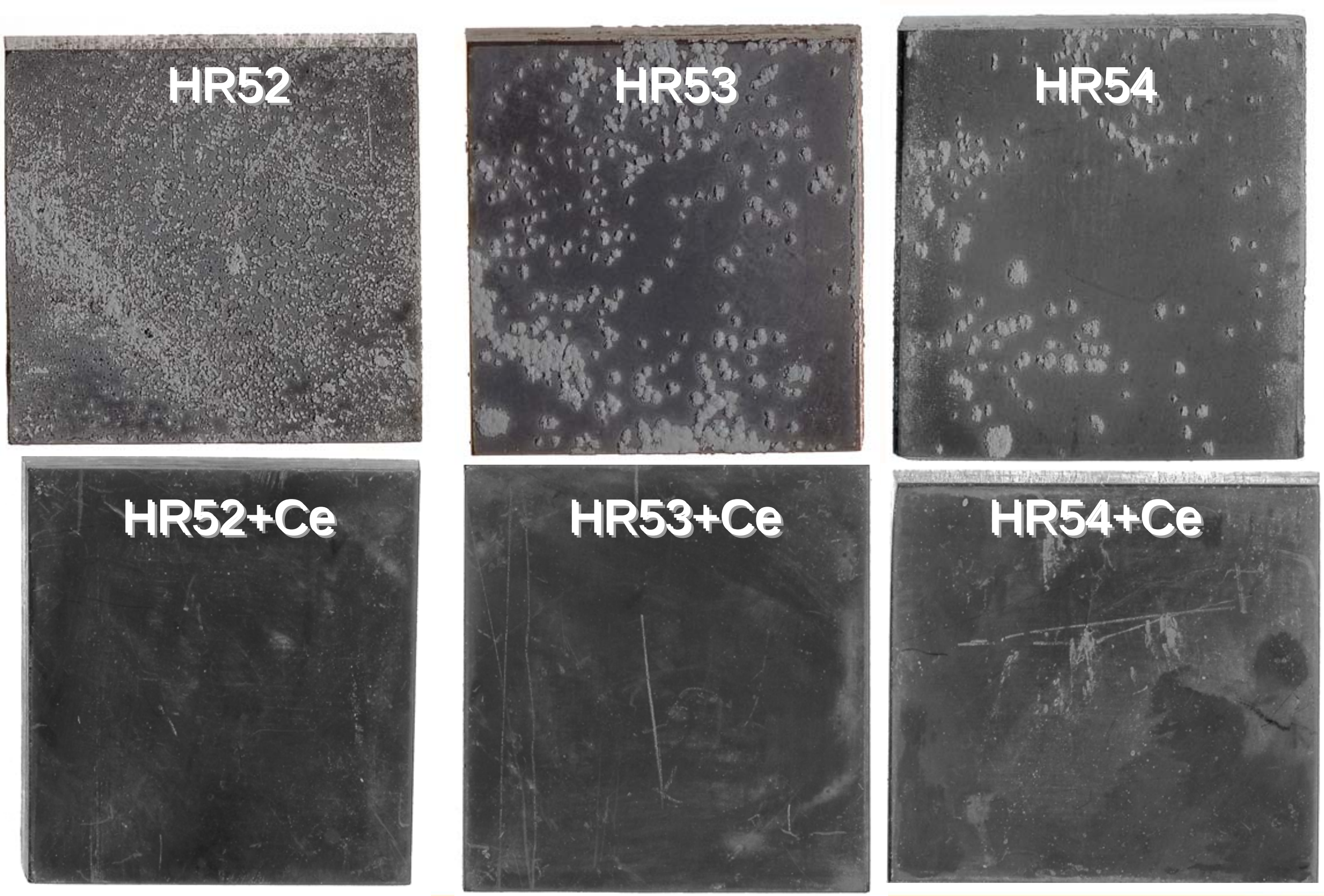


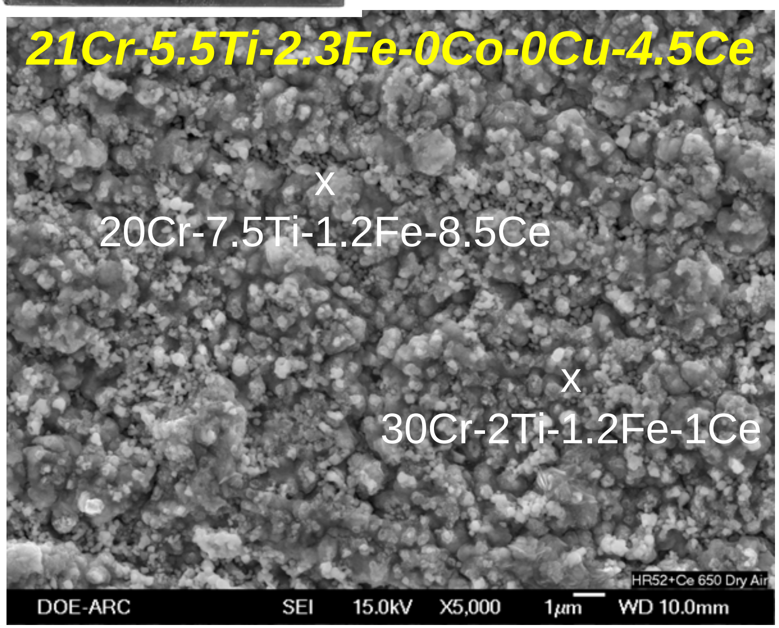
# Surfaces After Exposure
## (650°C-Dry Air-1100hrs)

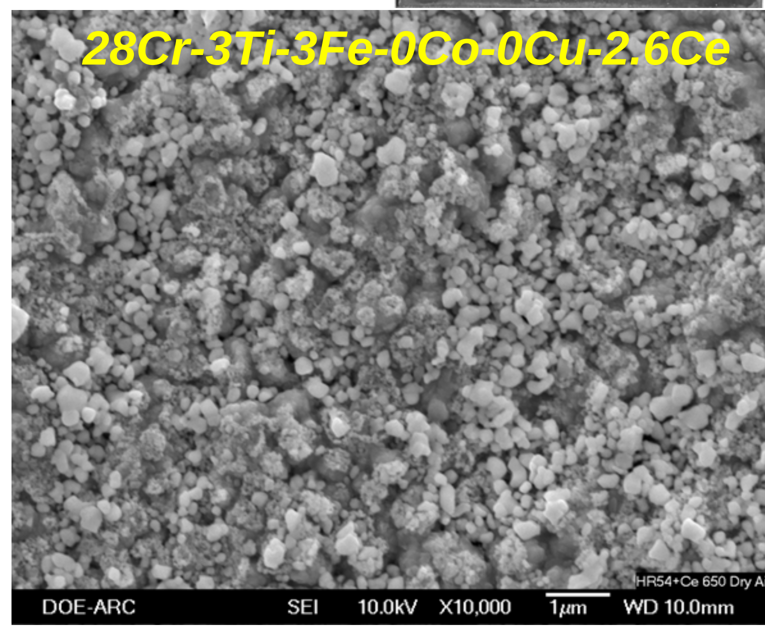


# Surfaces After Exposure

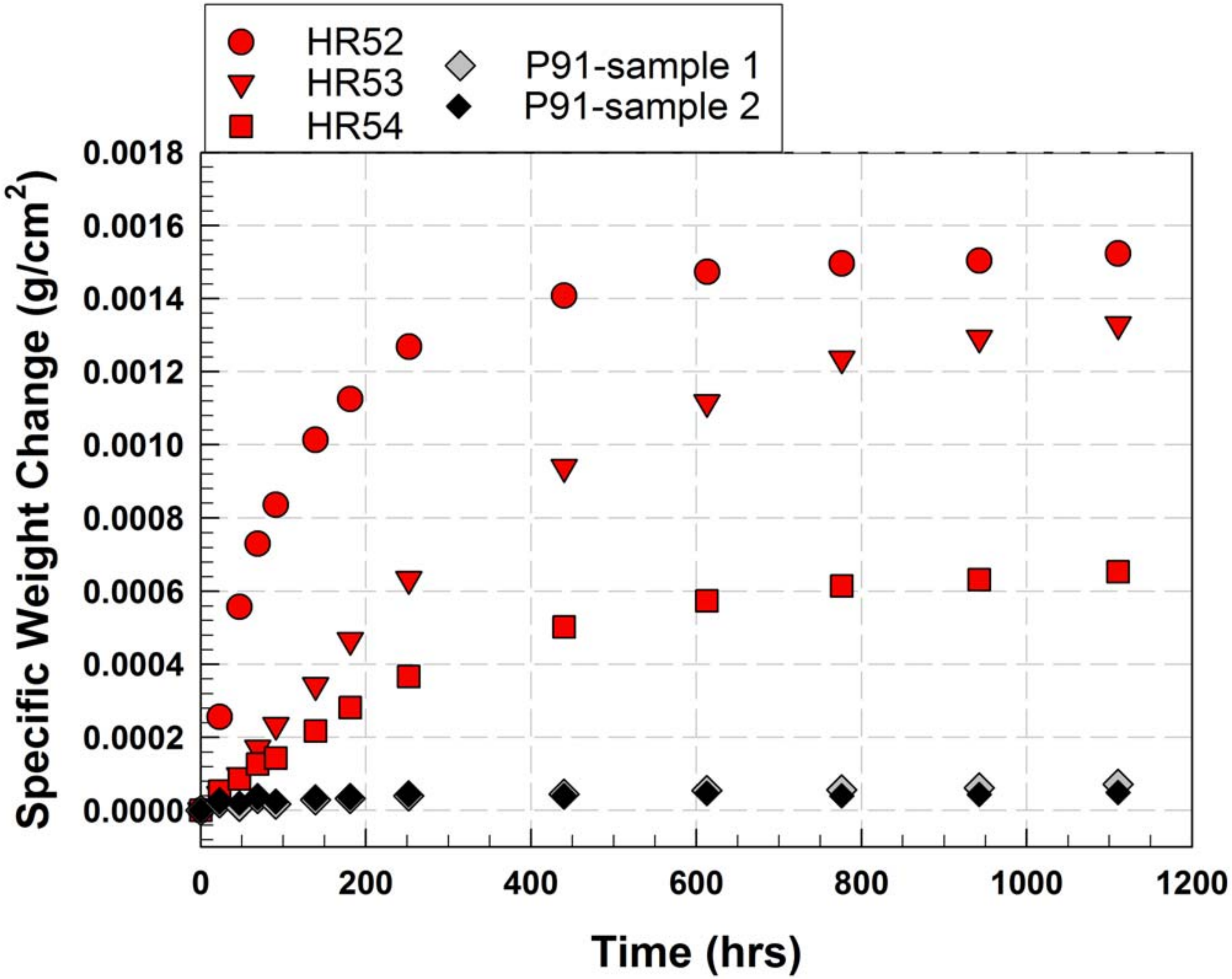
## (650$^{o}$C-Dry Air-1100hrs)



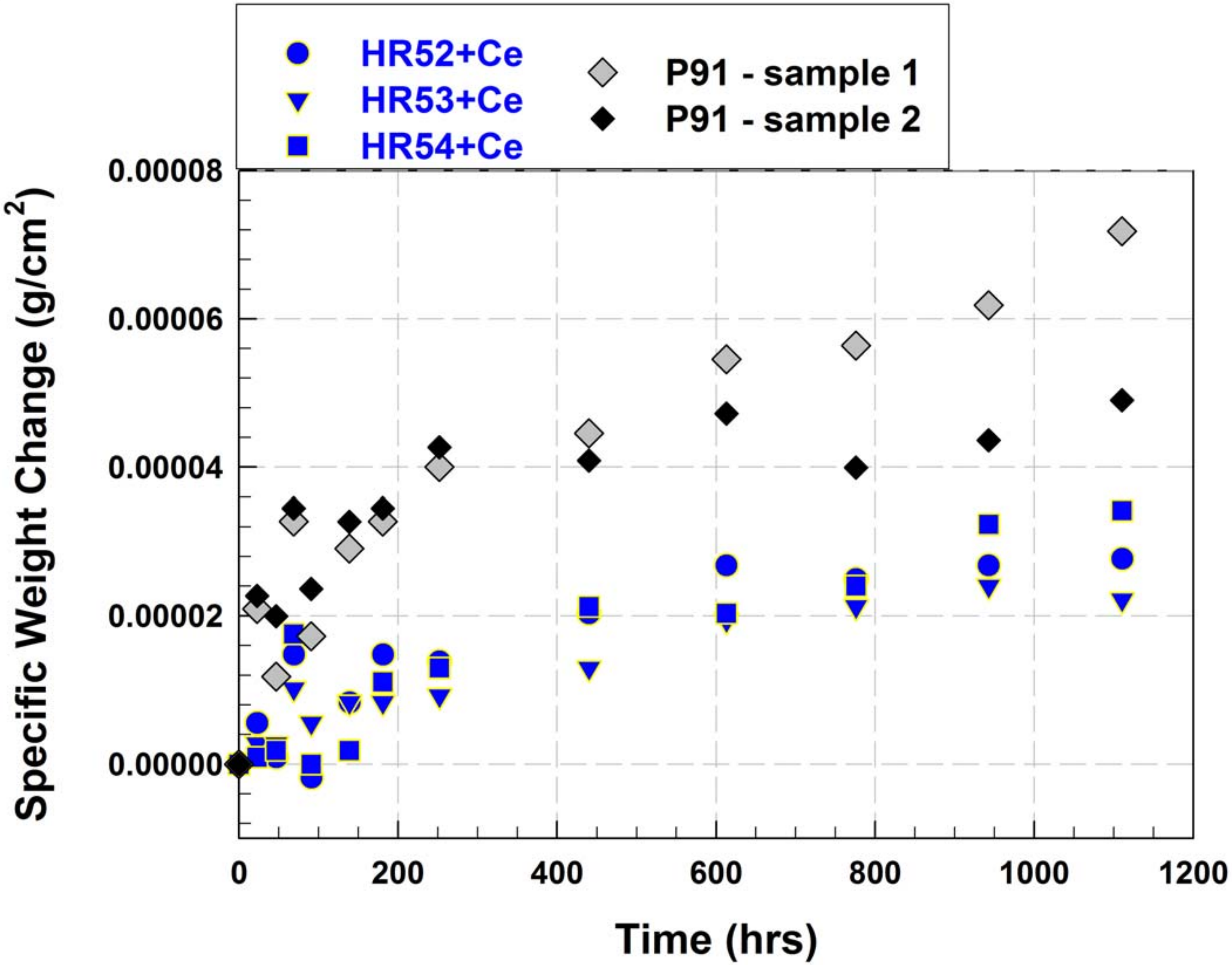


# Oxidation: 650ºC-Dry Air

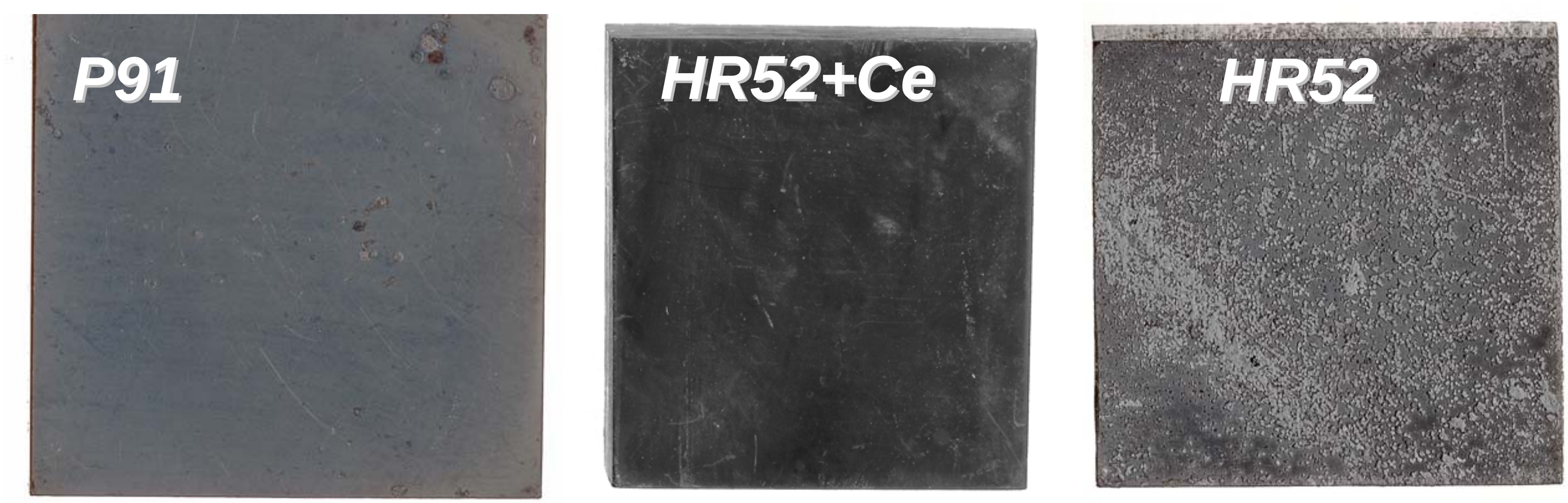


# Oxidation: 650ºC-Dry Air



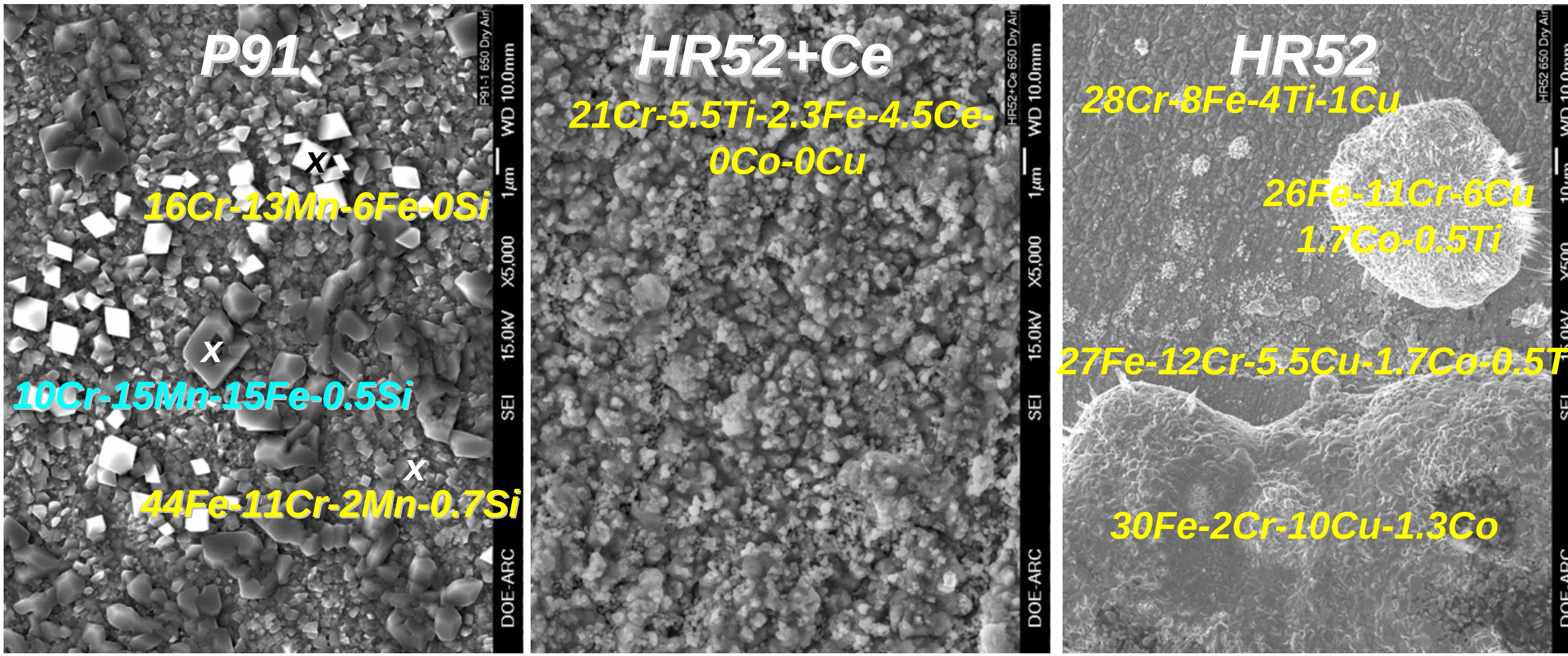
# Surfaces After Exposure

## (650$^{o}$C-Dry Air-1100hrs)



# Surfaces After Exposure

## (650$^{o}$C-Dry Air-1100hrs)



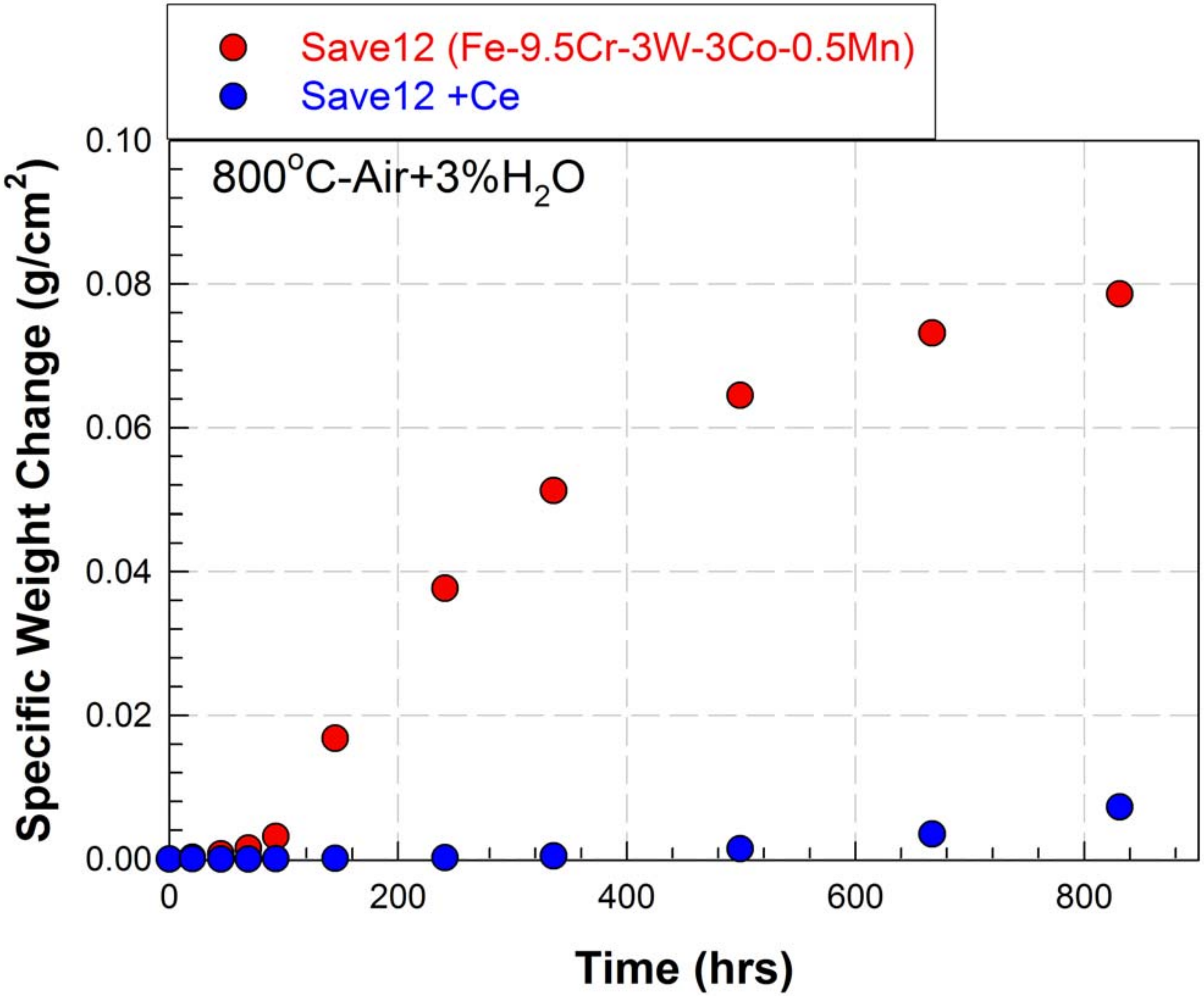
# Summary

- Oxidation behavior of experimental Fe+(9-12)Cr+TiC based steels (HR Alloys) was examined at 650°C in dry air.
- Higher Cr content → lower weight gain = more resistant.
  - Cr-oxide surface
  - Fe-oxide blisters
  - Increasing Cr → decreased amount of blisters.
- P91  a conventional steel was more oxidation resistant than the HR alloys.
  - Cr-**Mn**-Fe spinel as protective oxide.
  - **Si**  in alloy (potentially $SiO_2$).
- Incorporation of Ce into surface of HR alloys ***significantly*** improved oxidation resistance.
  - Comparable (or better) than P91
  - Ce completely suppressed the formation of Fe-oxide blisters.

# Work in Progress

- Continue to evaluate oxidation behavior of HR52, HR 53 and HR54
  - ➢ More complete scale analysis → X-ray diffraction, ESCA, cross sections, etc.
- Modify HR alloy composition to improve oxidation
  - ➢ Mn and Si additions (similar to P91)
  - ➢ Add RE in melt (similar to treated versions).

# Oxidation: 800°C-Air+3%$H_2O$



# Oxidation: 800ºC-Air+3%$H_2O$