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Oxidation Behavior of Surface-modified Stainless Steel 316LN in Supercritical-CO_2 Environment

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Contents

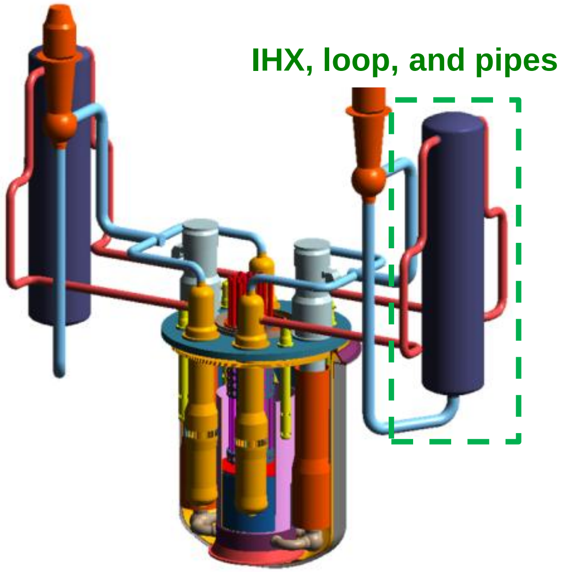
Introduction

❑ Supercritical-CO_2 (S-CO_2) Brayton cycle

- Cross-cutting power conversion technology
  - Sodium-cooled Fast Reactor (SFR)
    - Superheated steam Rankine → S-CO_2 Brayton cycle at 500-550°C (20MPa)

❑ Material issues

- Oxidation and carburization in S-CO_2 environment
  - Loss of load bearing area
  - Integrity of heat exchanger and turbomachinery
  - Mechanical property degradation



Prototype Gen IV Sodium-cooled Fast Reactor (PGSFR)

- Pool-type reactor (150MWe)
- Core in/out temperature → 390/545°C
- Liquid sodium coolant
- Superheated steam Rankine cycle

➔ S-CO_2 cycle considered as replacement

▲ **Schematic image and operating conditions of PGSFR**

Introduction

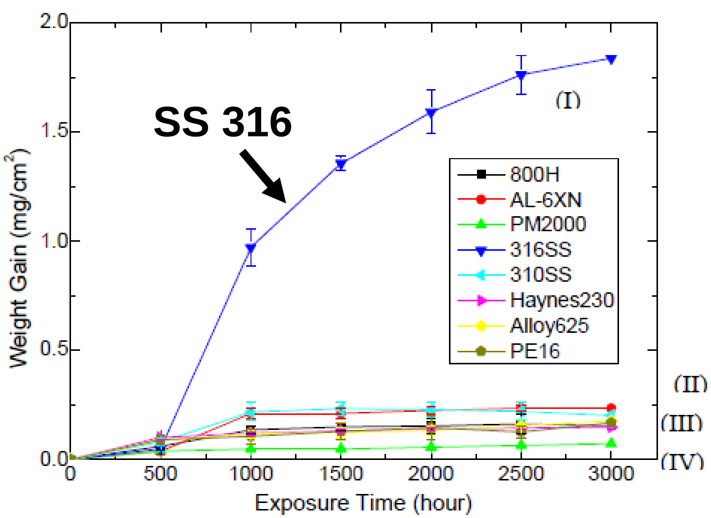
[1] M. Anderson, UWM Project Final Report (2012)
[2] G. Cao, Corrosion Science (2012)
[3] H.J. Lee, S-CO_2 Power Cycles Symposium (2014)

❑ Stainless steel 316LN

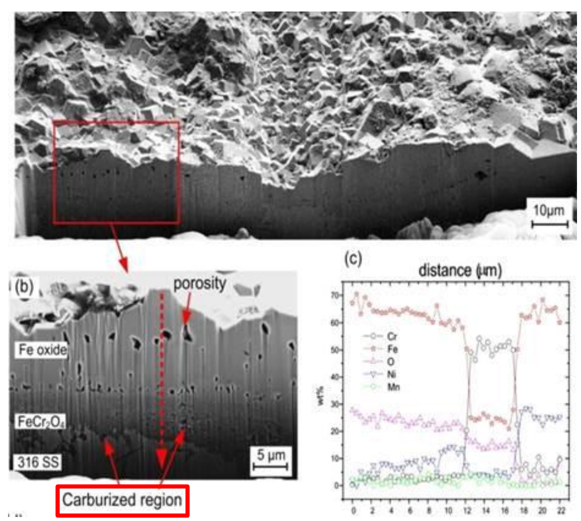
- Candidate material for key components and structures in SFR
- Comparatively poor oxidation behavior in S-CO_2 environment

  → Other various candidate materials considered
- Cr-rich oxide spallation followed by thick Fe-oxide formation

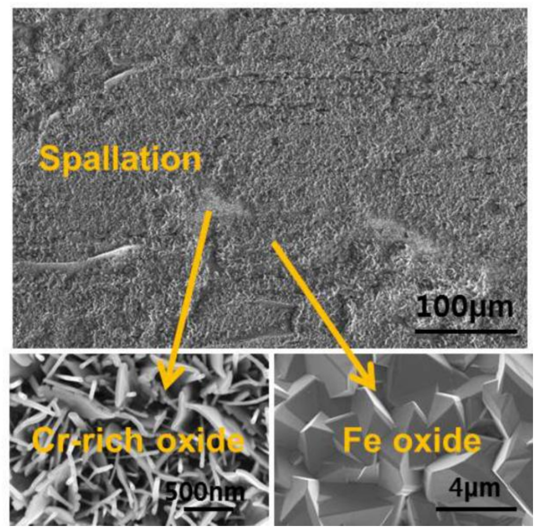
  → **Necessary to improve oxidation behavior of SS 316LN**



▲ **Weight gain of candidate materials after corrosion in S-CO_2 at 650°C (20MPa) up to 3000h [1]**



▲ **Corrosion behavior of 316SS in S-CO_2 at 650°C (20MPa) for 3000h [2]**



▲ **SEM micrograph of oxide surface of SS 316LN after exposure in S-CO_2 at 650°C (20MPa) for 1000h [3]**

Introduction

❑ Alumina (Al_2O_3)

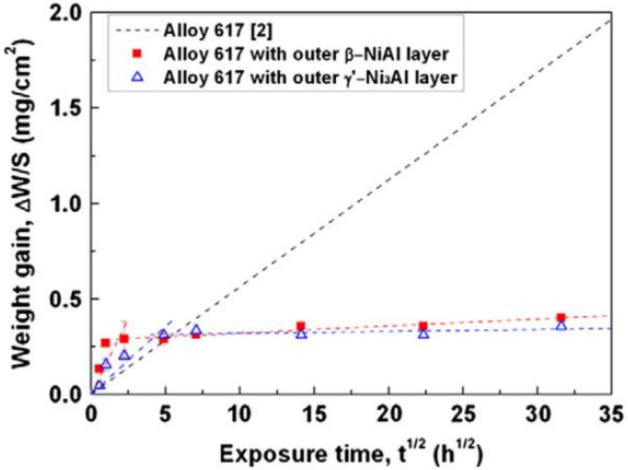
- Various transitional phases depending on temperature

$$\gamma\text{-AlO(OH)} \xrightarrow{500^{\circ}C} \gamma\text{-}Al_2O_3 \xrightarrow{750^{\circ}C} \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \xrightarrow{900\text{-}1000^{\circ}C} \alpha\text{-}Al_2O_3$$

- α-Al_2O_3: superior oxidation and carburization resistance
- Al content over 4-5 wt.% for continuous Al_2O_3 layer formation

❑ Surface-modification

- Diffusion coating of SS 316LN with Al
  - Surface enrichment → promote Al_2O_3 formation
- Past work on Ni-base superalloy
  - β-NiAl surface layer formation
  - Oxidation in air (900°C 1000h)
    - ◻ Transient oxidation behavior → $NiAl_2O_4$, α-Al_2O_3



▲ Weight gain curves of as-received and IDHTed Alloy 617 oxidized in air (900°C) up to 1000h [1]

Objective

❑ **Improvement of oxidation resistance of SS 316LN in S-CO_2 environment via surface-modification**

Al deposition via physical vapor deposition (PVD)

Inter-diffusion heat treatment (IDHT)

→ **Development of Al-rich surface layer (over 4-5 wt.% Al)**

Pre-oxidation

→ **Formation of α-Al_2O_3 layer**

Corrosion test in CO_2 (650°C 0.1MPa) for 100h

→ **Represents oxidation behavior in S-CO_2 environment**

Material and experimental

❑ Surface-modification

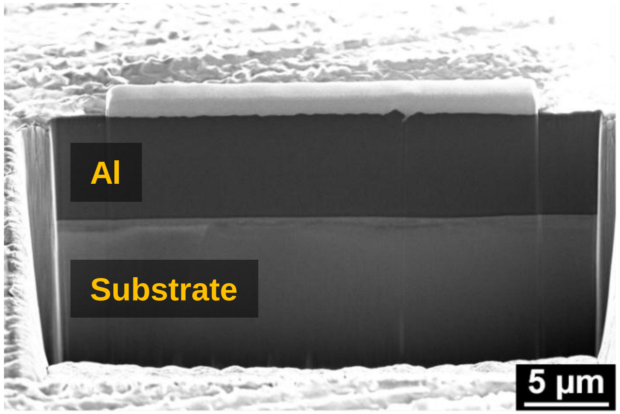
- Al coating via PVD

Target	Base pressure	Working pressure (Ar)	RF power	Duration	Coating Thickness
Al (99.999%)	≤ 2.0×10^{-6} torr	0.7×10^{-4} torr	200 W	4 h	~ 8 μm

- IDHT: 600°C 0.5h + 1000°C 0.5h (vacuum, ≤ 2.0×10^{-6} torr)
- Pre-oxidation: 900°C 1h (He, 99.999% purity)

❑ CO_2 corrosion test

- Once-through type quartz, three-zone heater
- CO_2: 99.999% purity with flow rate of 150 sccm
- Exposure to CO_2 at 650°C 0.1MPa for 100h



▲ Cross-sectional SEM micrograph of Al-coated SS 316LN

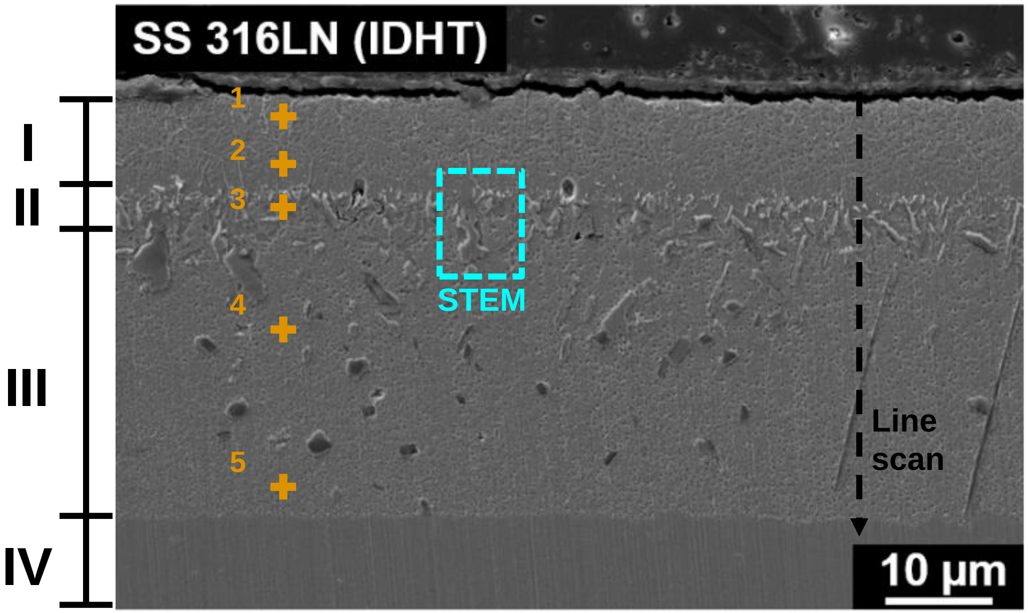
▼ Chemical composition of SS 316LN used in this study (in wt.%)

Material	Fe	Cr	Ni	C	Mo	Mn	Si	N
SS 316LN	Bal.	18.9	13.9	0.03	2.8	1.9	0.6	0.16

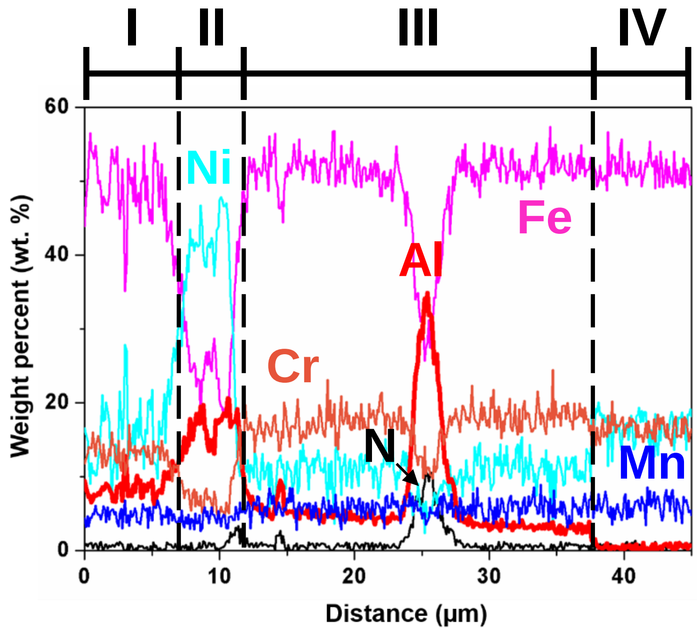
Results and discussion

❑ Microstructure of IDHTed SS 316LN

- Al-rich surface layer formed as result of inter-diffusion
  - Al content generally above 5 wt.% in aluminized region
- Distinct regions
  - I: Al-rich surface area (Al > 10 wt.%)
  - II: Ni-Al rich intermetallic
  - III: Al-rich area (Al > 4 wt.%) with AlN
  - IV: Substrate



▲ Cross-sectional SEM micrograph of IDHTed SS 316LN



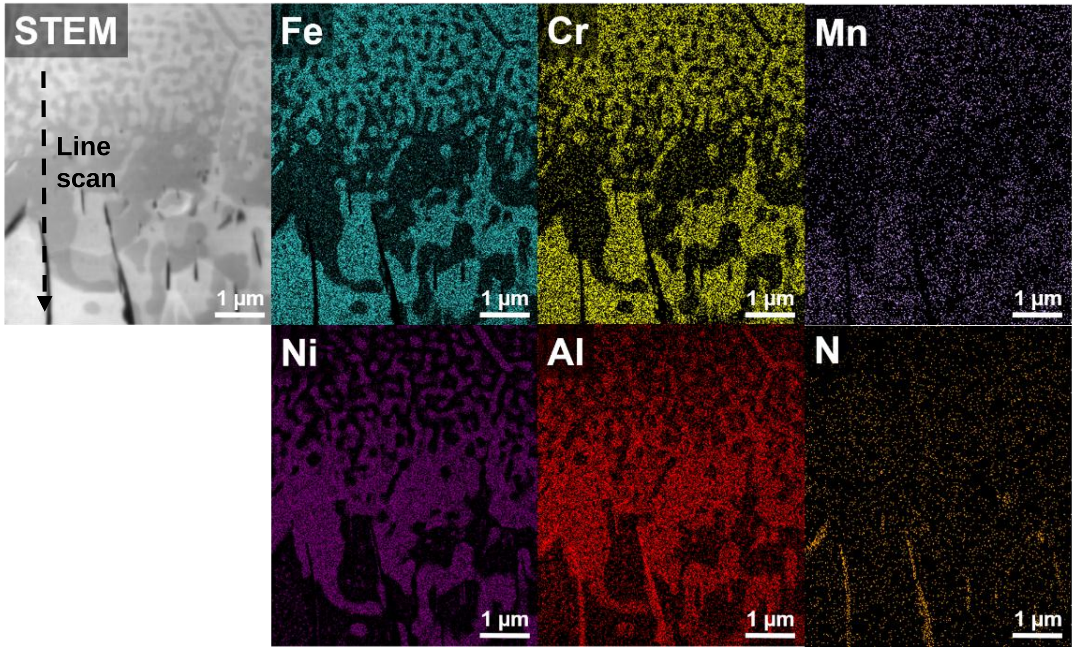
▲ EDS line scan analysis of IDHTed SS 316LN

wt. %	Fe	Cr	Ni	Al
Point 1	41.6	20.2	11.7	**12.0**
Point 2	34.9	17.8	19.0	**15.8**
Point 3	17.9	8.7	38.7	**24.3**
Point 4	44.3	28.7	6.3	**5.4**
Point 5	40.9	29.4	10.1	**4.4**

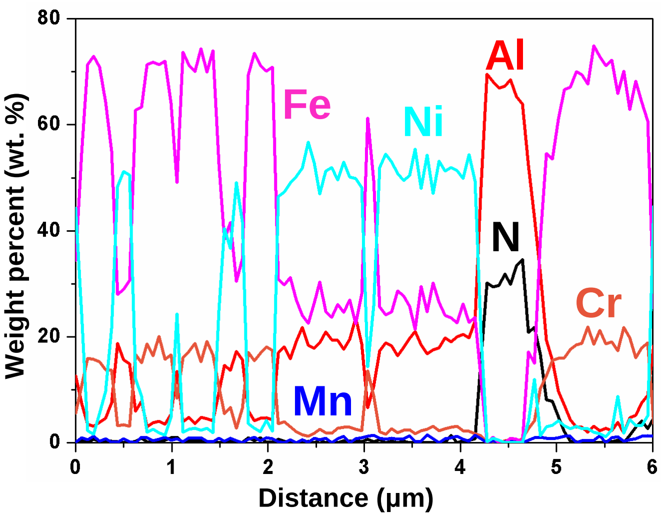
▲ Point EDS analysis of IDHTed SS 316LN

❑ Microstructure of IDHTed SS 316LN

- Al preferentially forming intermetallic with Ni → Nickel aluminide (β-NiAl)
- Comparative enrichment of Fe and Cr in Ni-depleted areas



▲ STEM and elemental mapping images of IDHTed SS 316LN

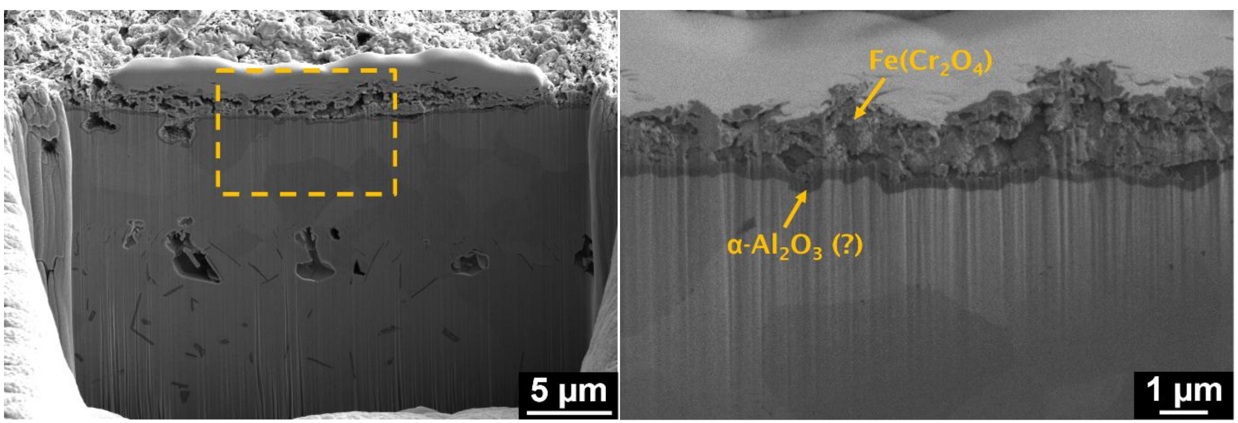


▲ EDS line scan analysis of IDHTed SS 316LN

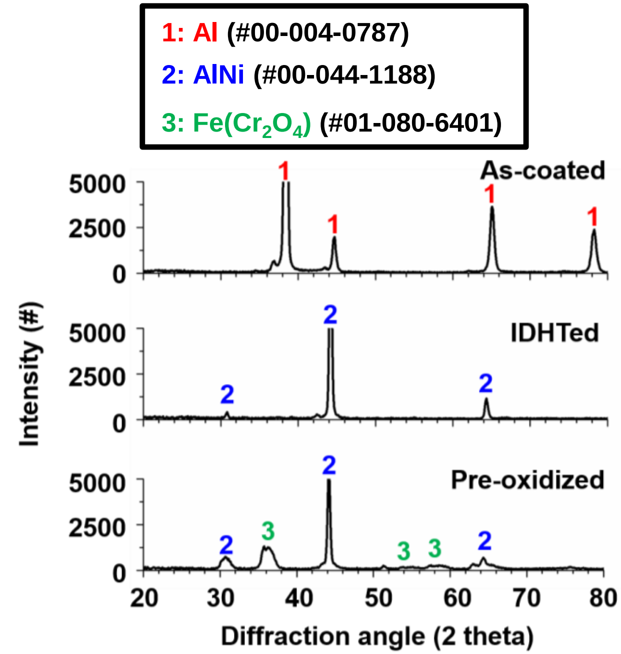
❑ Microstructure of pre-oxidized SS 316LN

- Pre-oxidation performed to form α-Al_2O_3
  - Operational temperature (~ 550°C) not high enough for formation of α-Al_2O_3
- XRD analysis: mainly $Fe(Cr_2O_4)$ → Fe, Cr enriched areas at surface
  - α-Al_2O_3 peaks undetected → comparatively too thin to be detected
- Cross-sectional BSE micrograph reveal oxide inner layer of different composition than outer layer

  → possibly α-Al_2O_3 layer



▲ Cross-sectional SE/BSE micrographs of pre-oxidized SS 316LN

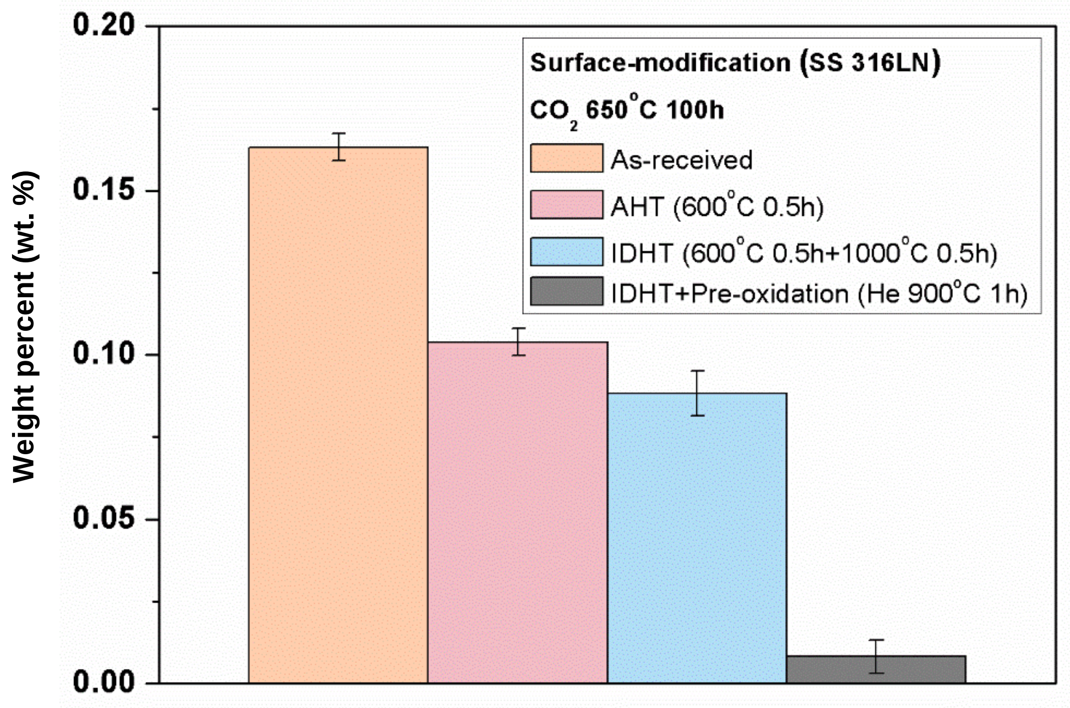


▲ XRD analysis of surface-modified SS 316LN

Results and discussion

❑ Oxidation behavior in CO_2 environment

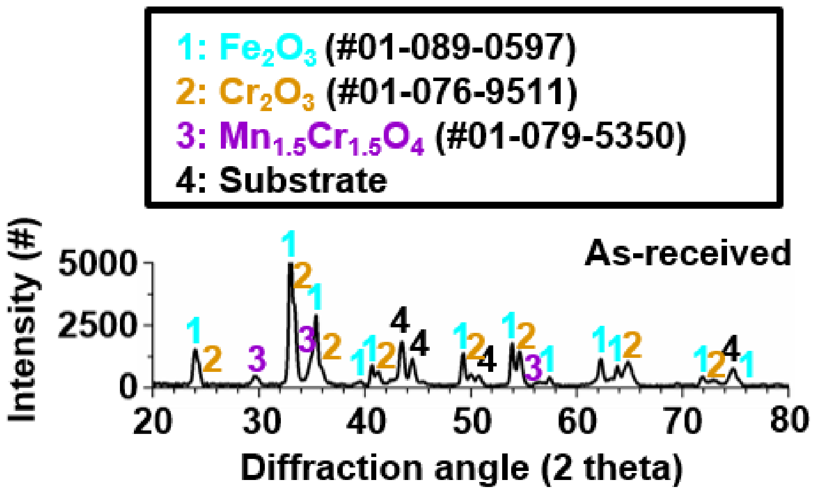
- Weight change
  - As-received > IDHTed > Pre-oxidized
  - Necessary to evaluate **extent of pre-oxidation** → weight gain & oxide thickness



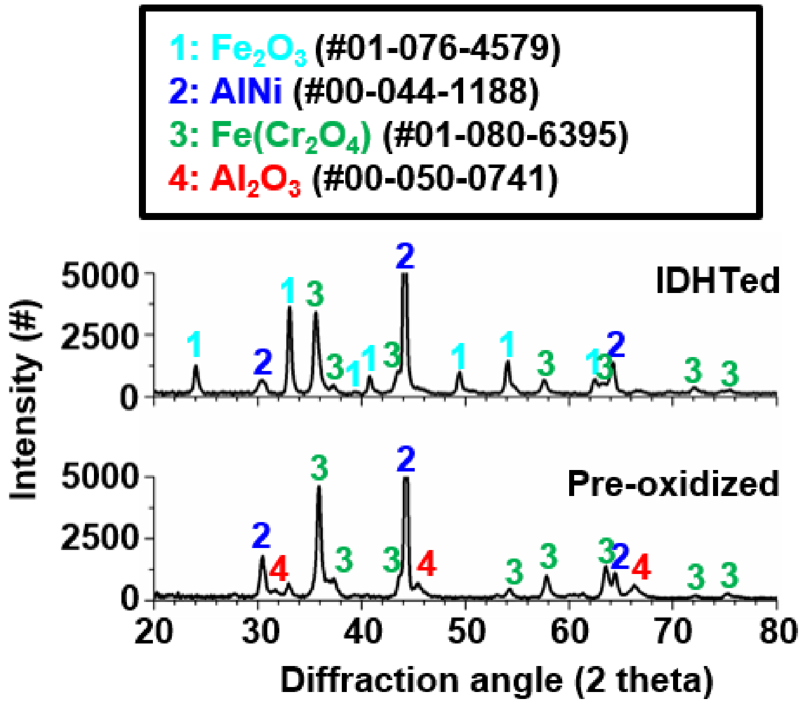
▲ Weight change after exposure to CO_2 (650°C 0.1MPa 100h)

❑ Oxidation behavior in CO_2 environment

- XRD analysis
  - As-received, IDHTed → Fe_2O_3 formation
    - Weight gain difference → detailed oxide analysis necessary
  - Pre-oxidized → No Fe_2O_3, Al_2O_3 formation ➔ low weight gain



▲ XRD analysis of as-received SS 316LN after exposure to CO_2 (650ºC 0.1MPa 100h)



▲ XRD analysis of surface-modified SS 316LN after exposure to CO_2 (650ºC 0.1MPa 100h)

Summary and further research

❑ Summary

- SS 316LN was coated with Al and heat-treated (IDHT)
  - Development of Al-rich surface layer (above 4-5 wt.% Al)
  - Nickel aluminide (NiAl), AlN formation
- IDHTed SS 316LN was pre-oxidized
  - Formation of α-Al_2O_3 prior to CO_2 exposure
- After CO_2 exposure at 650^{o}C for 100h
  - Weight gain: As-received > IDHTed > Pre-oxidized

    → May be attributed to pre-formation of Al_2O_3
  - CO_2 of 650^{o}C not high enough temperature for formation of protective α-Al_2O_3

    ➔ Pre-oxidation procedure necessary for significantly improved oxidation behavior

Summary and further research

❑ Concerns

- Diffusional loss of Al in longer durations
  - Insufficient Al content to maintain stable Al_2O_3 layer
  - Formation of brittle aluminides in affected bulk
- Carburization resistance

❑ Further research

- Detailed analysis of CO_2 (650^{o}C 100h) exposed specimens
- Longer exposure times
- Evaluation of co-deposited Ni, Al coating performance
  - Diffusion barrier for Al at surface
- Corrosion tests in S-CO_2 (20MPa) environment
  - Comparison with CO_2 (0.1MPa) results
- Assessment of carburization resistance
- Mechanical property evaluation

Energy for Earth !!

Thank you!