Corrosion-erosion behavior of new Fe-based coating materials for chlorine-rich biomass combustion: Role of Ni, Si and B

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Biomass to energy conversion: Characteristics

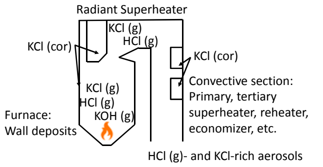


Fig. 1 Principal pathways of potassium and chlorine compounds in a biomass-fired boiler redrawn after [1]. (cor= corrosion, g= gas)

Corrosion ⇒ formation of porous, non-protective oxide scales

- Gaseous Cl and K compounds (via “active oxidation”)
- Molten alkali chlorides (as dominant species) depositing
  - Sulfation of alkali chlorides or reaction between chlorides and metal
  - Formation of eutectics with low melting temperatures ⇒ fluxing of protective oxide scales

Erosion ⇒ removal of corrosion-resistant oxide layers followed by accelerated corrosion of the unprotected substrate [2-5]

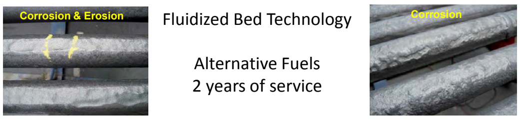


Fig. 2 Superheater tube damage due to corrosion and combined corrosion-erosion attack after corrosion layer removal (www.vivis.de under “Ersatzbrennstoff-Kraftwerke”)

Improvement of the corrosion-erosion resistance via material design

- Empirical results ⇒ Ni-base alloys with ca. 20-23 wt.% Cr and 8-10 wt.% Mo (i.e. IN 625) ⇒ excellent corrosion resistance & low resistance against erosion
- New results regarding the material performance in Cl-rich environments at high temperatures [3-10]:
  - **Carbides**: good against erosion & not corrosion resistant.
  - **Chromia** scales form chromates in wet environments ($2KCl_s + 1/2Cr_2O_{3s} + H_2O_g + 3/4O_{2g} \rightarrow K_2CrO_{4s} + 2HCl_g$)
  - **Refractory metals** and **silicon** improve the corrosion and erosion resistance
  - Comparable amounts of **silicon** and **boron** (self-fluxing alloys) lead to coatings with reduced porosity
  - **Iron** is not necessarily detrimental for the corrosion resistance

Approach: Model alloys ⇒ corrosion-erosion performance of the bulk materials

- Ingots obtained by centrifugal casting ⇒ coin-like samples via spark erosion
- **Main issue**: **the influence Fe, Ni, Mo, and Si on the corrosion-erosion performance**
  - Nb, W, and B were added in constant amounts
- **IN 625**(Ni-21Cr-10Mo-3.5Nb-0.1Si…wt%) as reference

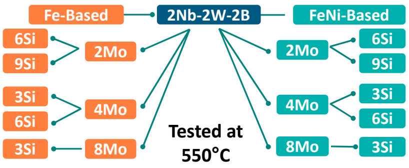
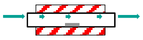


Fig. 3 Composition of the model alloys (wt.%)

Test 1: Corrosion Resistance (no Erosion)

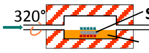


7%O_2-17% H_2O-2,5% HCl rest N_2

Simulated real biomass-firing atmosphere

- high Cl amount
- presence of water vapor

Test 2: Corrosion-erosion resistance



- Corrosion: Cl-, S- , K-, and Na-containing ash
- Erosion due to hard ash particles (SiO_2, Al_2O_3)

Results of test 1: Corrosion performance

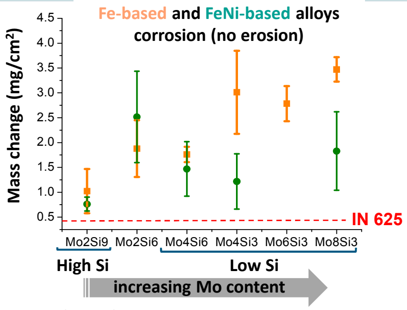


Fig. 5 (Test 1) Mass change after 1122 h at 550°C (common elements: Nb, W, and B; 30 wt% Ni)

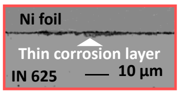


Fig. 6 Micrograph of the corrosion layer in the reference material (IN 625): Best performance for Cl corrosion in terms of mass gain

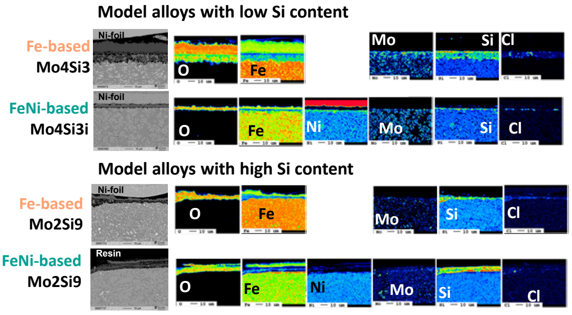


Fig. 7 (Test 1) EPMA element maps of the main elements after 1122 h at 550°C showing the influence of Si on the element distribution of Fe-based and FeNi-based alloys with low Mo content (Mo distribution is valid for Nb, W, and B as well and displays refractory metal borides)

Model alloys: Ni and Si have a significant influence on the thickness and morphology of the corrosion layers

Results Test 2: Corrosion-erosion performance

- No agglomeration of ash observed
- Spalled scale gets lost in the surrounding ash ⇒ therefore, qualitative mass change diagrams

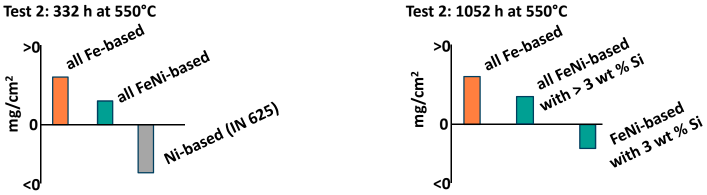


Fig. 8 (Test 2) Qualitative mass change diagrams of the model alloys. The mass change of IN 625 remains negative, therefore not shown in the left diagram.

- IN 625 develops a thin oxide layer ⇒ oxide removal followed by oxide growth phases ⇒ “oxidation-affected erosion“ [3] ⇒ negative mass change
- Fe and FeNi alloys develop thicker oxide layers ⇒ partial damage, cracks, and local removal due to erosion ⇒ more diffusion paths, increased corrosion rate ⇒ “erosion-accelerated oxidation“ [3] ⇒ positive mass change

Corrosion vs. corrosion-erosion performance

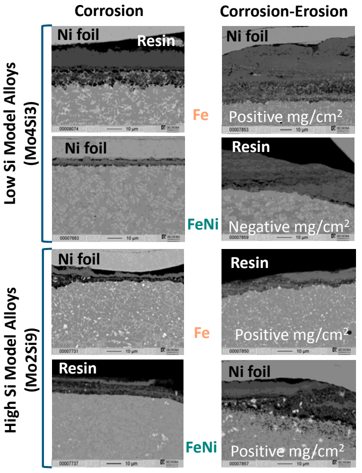


Fig. 9 Test 1 vs. Test 2: comparison between the corrosion scale morphologies

- Common elements: Nb, W, and B
- Refractory metal borides (i.e. white phases in grey scale micrographs) are resistant against Cl corrosion
- Duration of experiments > 1000 h
- Low Si model alloys:
  - Ni reduces the corrosion rate
  - Erosion enhances the corrosion rate of Ni-containing alloys
  - Fe-based (Ni-free) alloys ⇒ more resistant against corrosion-erosion
- High Si model alloys ⇒ comparable performance independent from the Ni content
- Decreasing the corrosion rate ⇒ no significant effect of Mo; Si is more effective
- Reference material IN 625:
  - Best performance for Cl corrosion
  - Worst performance for combined corrosion-erosion attack

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