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The Laboratory Coal Ash Corrosion Test Results of Superheater Tube Materials in Oxyfuel Gas Conditions

Y. Matsunaga*, K. Nakagawa, T. Gotou,
T. Yamada, N. Fujiwara, T. Kiga
（IHI corporation)

K. Kurokawa
（Hokkaido University)

Purpose of this study

Effect of Oxyfuel combustion to the superheater tube corrosion:

Higher CO_2 : Carburization , Carbonate formation

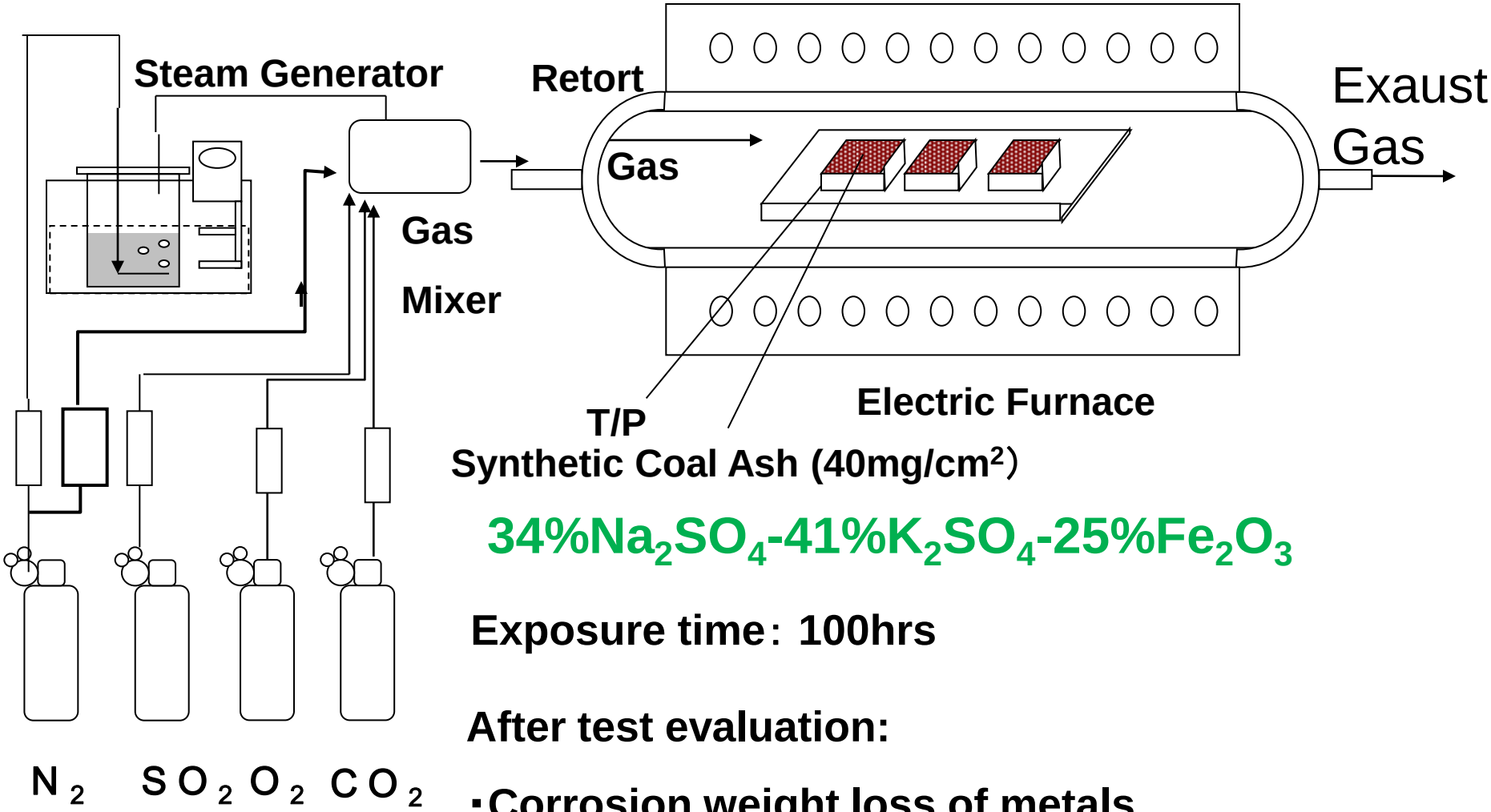
SO_x : Accelerate coal ash corrosion

by formation of molten alkali iron tri-sulfate

$$3(Na,K)_2SO_4+Fe_2O_3+3SO_2+1.5O_2= \underline{2(Na,K)_3Fe(SO_4)_3}$$

The effect of gas compositions on the corrosion rate of superheater tube materials (stainless steels , Ni-based alloys) were investigated

Coal ash corrosion test method



Synthetic Coal Ash (40mg/cm^2)

34%Na_2SO_4-41%K_2SO_4-25%Fe_2O_3

Exposure time：100hrs

After test evaluation:

- **Corrosion weight loss of metals**
- **Cross sections by Optical Microscope.**

Test conditions

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Gas Composition (vol.%)					Test Temperature (K)					
CO_2	SO_2	O_2	H_2O	N_2	773	873	923	973	1023	1073
15	-	4	13	Bal.	-	-	●	●	●	-
15	0.08	4	13	Bal.	-	-	●	●	●	-
15	0.25	4	20	Bal.	-	-	●	●	●	-
66	-	4	20	10	-	-	●	●	●	-
66	0.08	4	13	Bal.	-	-	●	●	●	-
66	0.25	4	20	Bal.	●	●	●	●	●	●

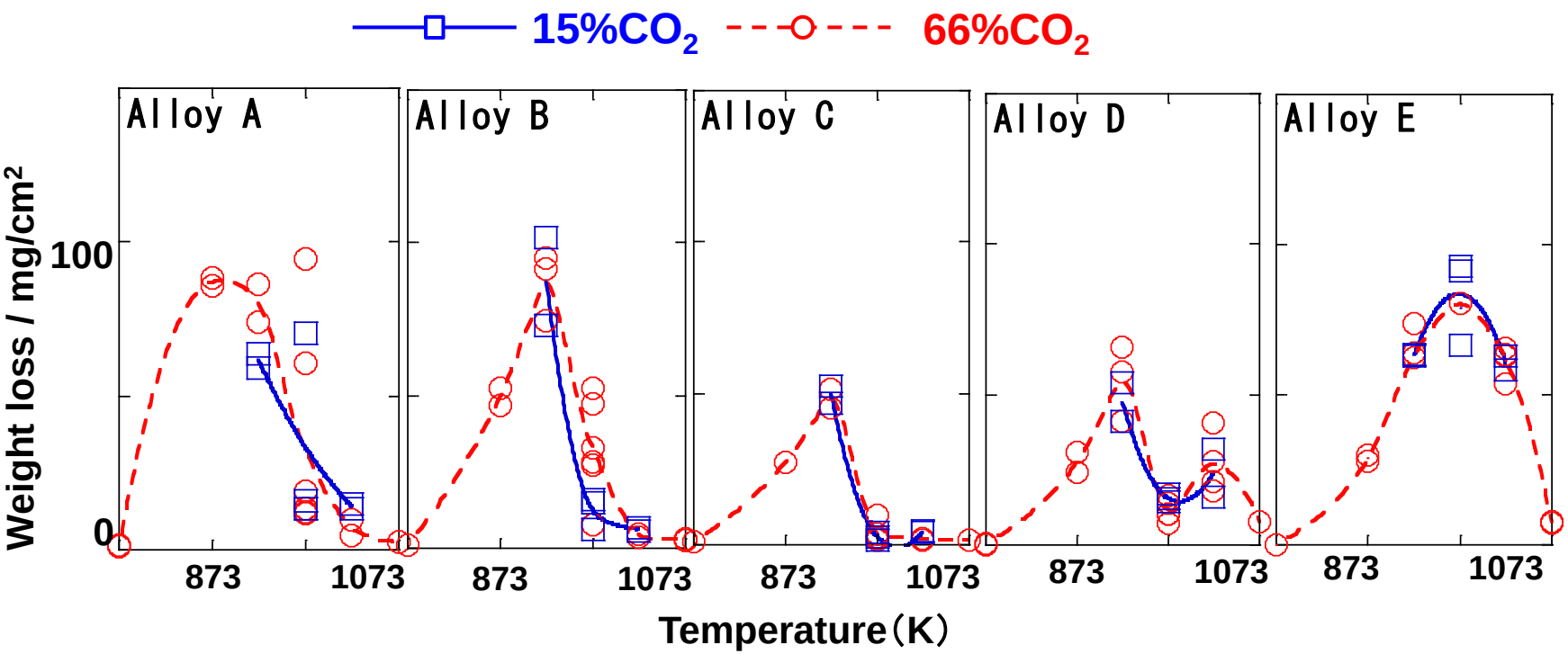
Gas Composition Change by Oxyfuel Combustion

Tested Materials

Stainless Steels : Alloy A（18Cr-9Ni-3Cu)
Alloy B(18Cr-12Ni-Nb)
Alloy C（25Cr-20Ni-Nb-N）

Ni base alloys : Alloy D(22Cr- 12Co- 9Mo-1Al- bal. Ni)
Alloy E(20Cr-20Co-6Mo-2.3Ti- bal. Ni)

Temperature dependence of corrosion rate at 0.25%SO_2

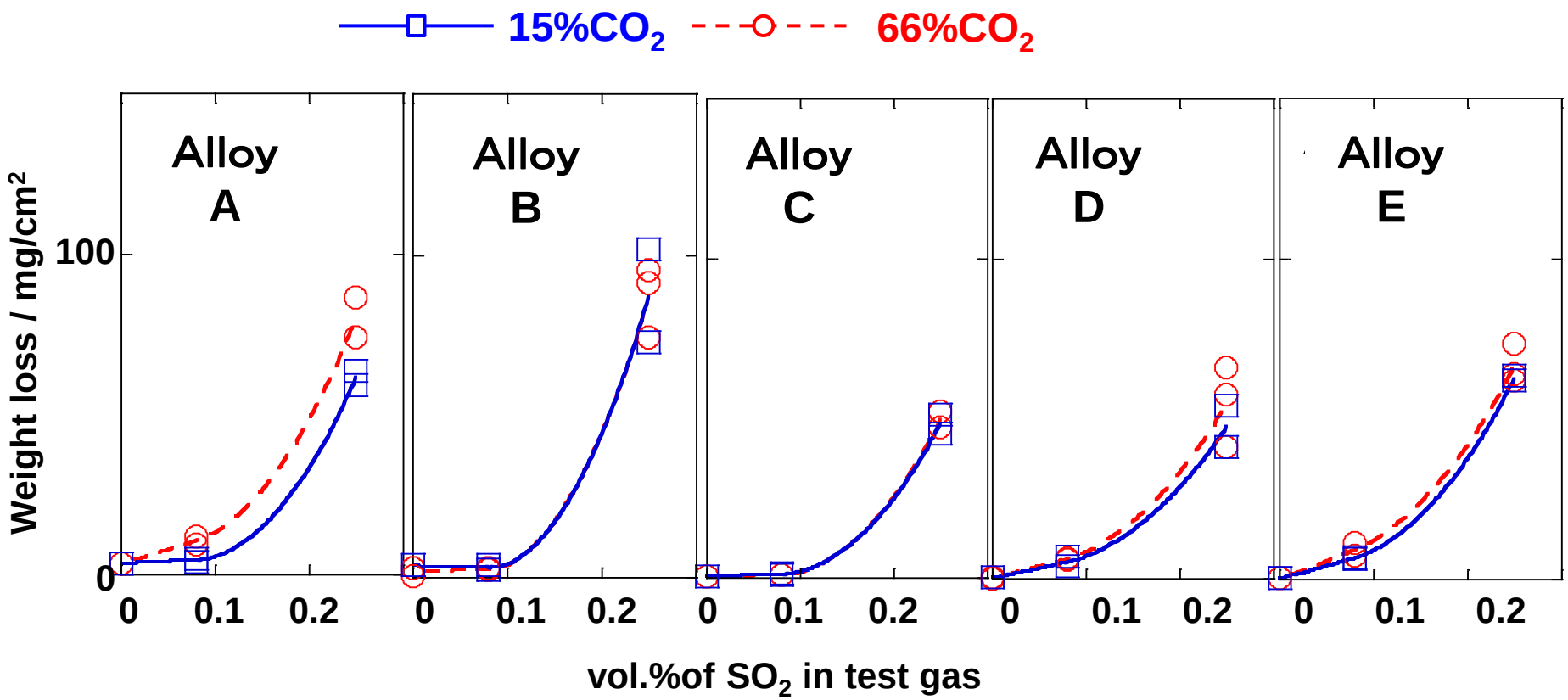


Maximum corrosion rate were observed at 923K.

At 1023K, Ni based alloy showed large corrosion rate than stainless steels.

CO_2 content increase (15% to 66%) did not affect on the ash corrosion rate.

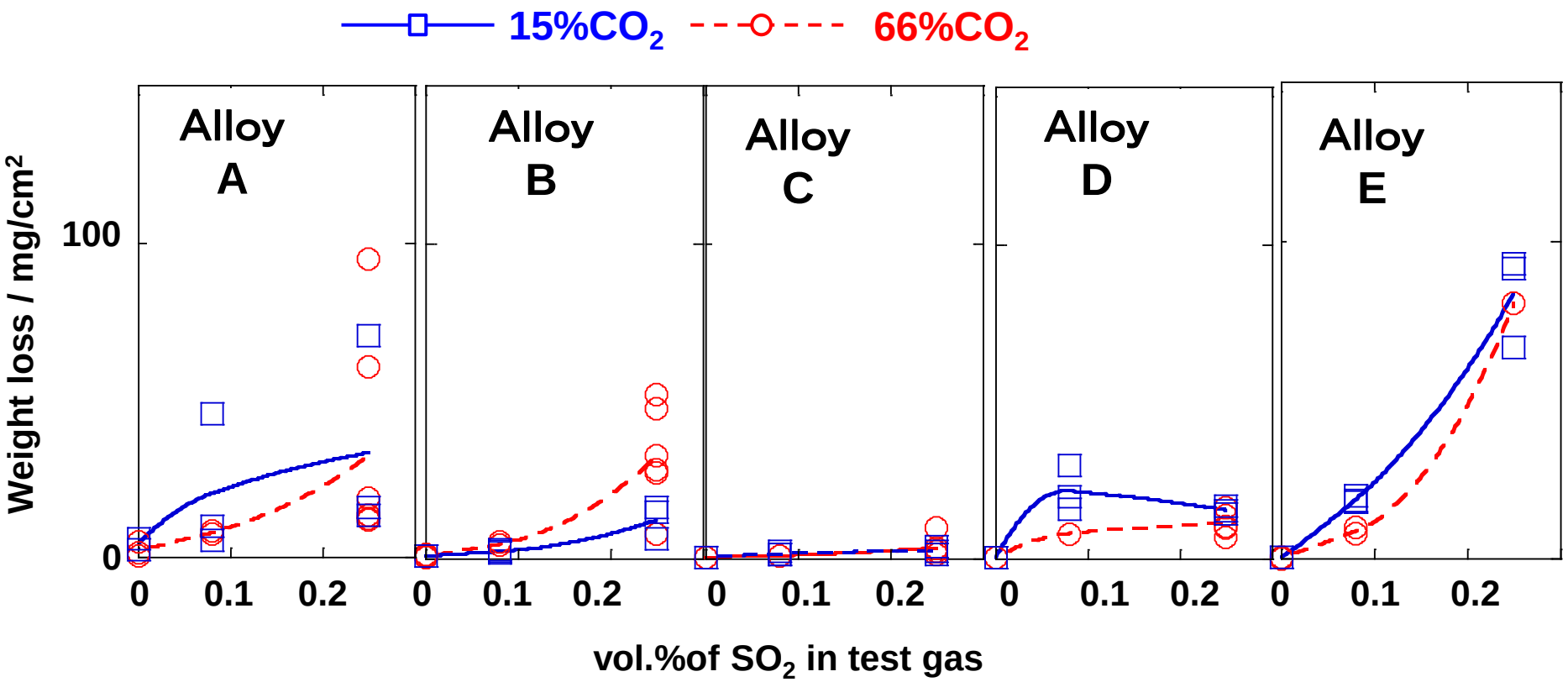
Effect of gas composition on the corrosion at 923K



SO_2 content increase accelerated the corrosion of alloys .

CO_2 content increase (15% to 66%) did not affect on the ash corrosion rates.

Effect of gas composition on the ash corrosion at 973K

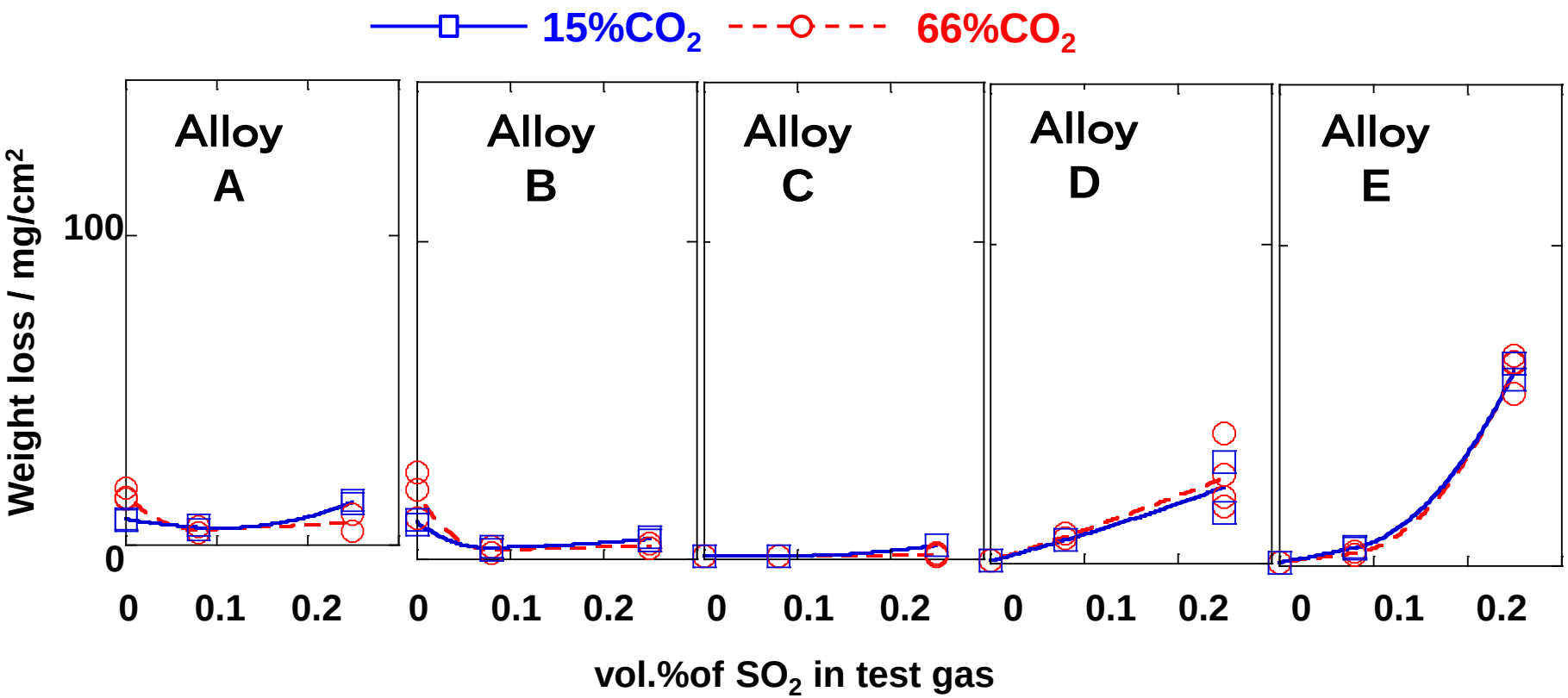


SO_2 content increase accelerated the corrosion of alloys .

CO_2 content increase (15% to 66%) did not affect on the ash corrosion rates.

Alloy C (25%Cr) showed lower corrosion rate than other alloys.

Effect of gas composition on the ash corrosion at 1023K



The corrosion rates of stainless steels are small.

Ni-based alloys showed large corrosion rate in high SO_2 atmosphere.

Cross Sections of Alloy A After Corrosion Test (66%CO_2)

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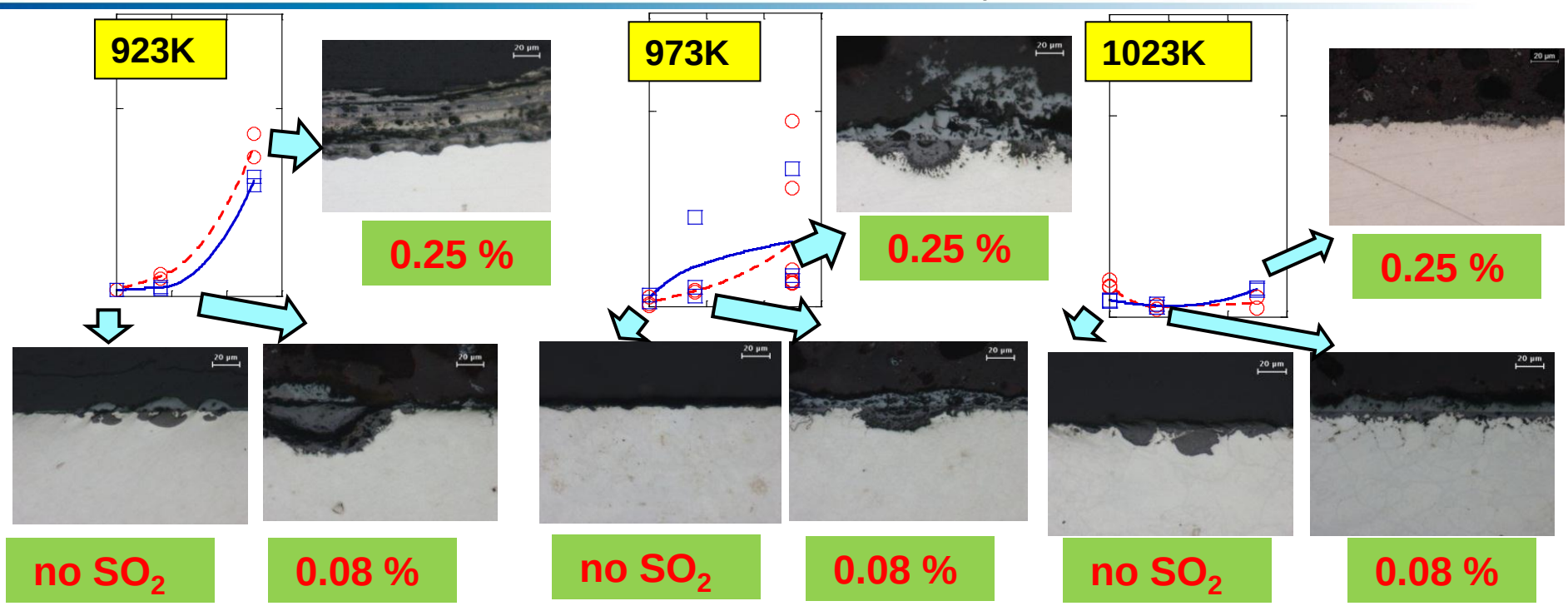


Corrosion morphologies of Alloy A (stainless steel) :

In no SO_2 atmosphere: Corrosion were very slight

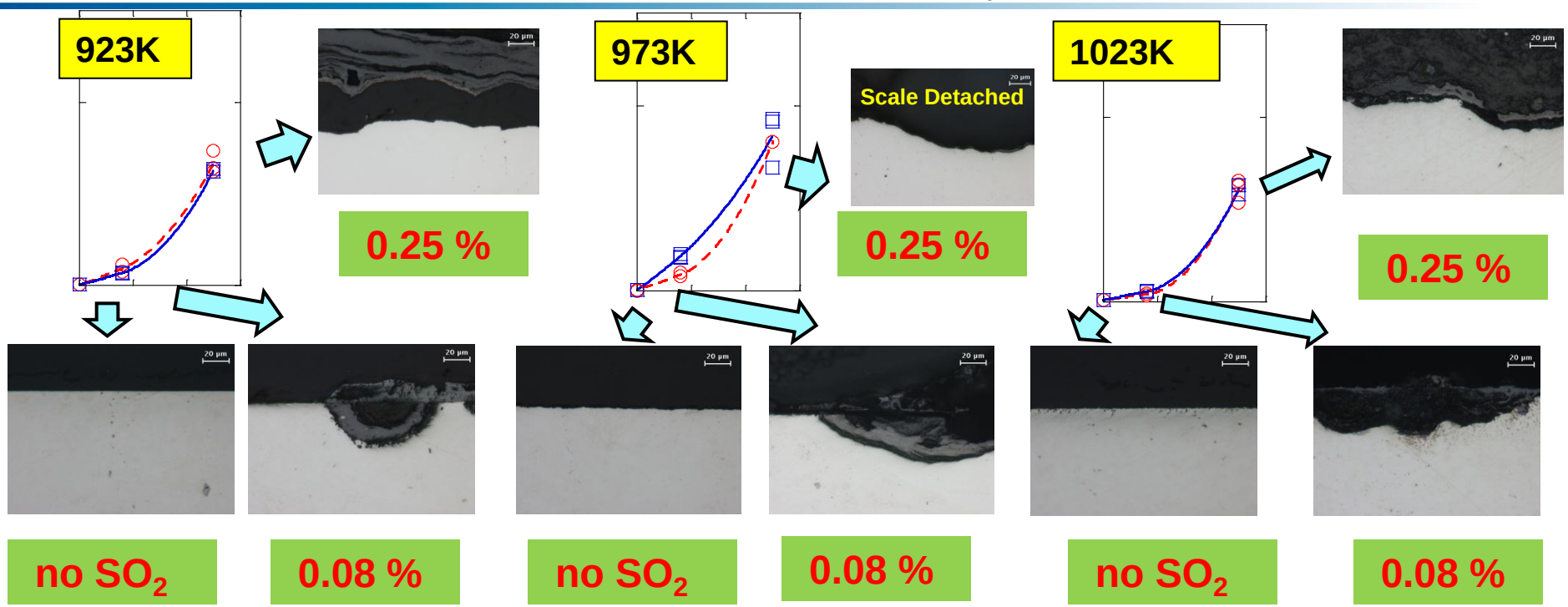
At 923K-973K in 0.25% SO_2 : Severe general corrosion

At 923 - 973K in 0.08% SO_2 : Localized corrosion

(localized formation of molten salt by reaction of salt and corrosion product)

At 1023K : General corrosion with small corrosion rate

Cross Sections of Alloy E After Corrosion Test (66%CO_2)



Corrosion morphologies of Alloy E (Ni-based alloy)

In no SO_2 atmosphere: Corrosion were very slight

In 0.08% SO_2 : Localized corrosion

In 0.25% SO_2 : Severe general corrosion

Alloy E showed severe corrosion at 1023K.

Synthetic Ash after 100hrs exposures（66%CO_2）

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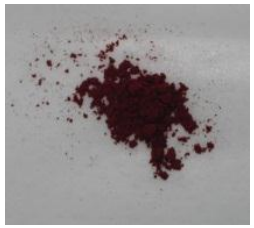
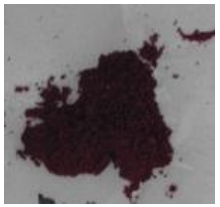
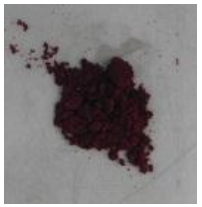
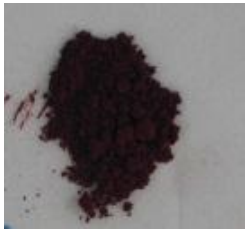
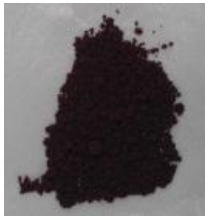
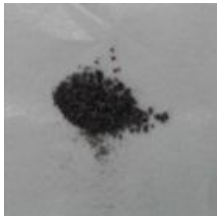
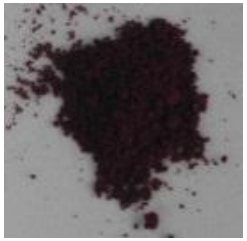
34% Na_2SO_4-41% K_2SO_4-25% Fe2O3 ash mixture before exposure



	SO_2 in gas / vol.%		
Temperature / K	No	0.08	0.25
1023	× 	× 	× 
973	× 	× 	△ 
923	× 	× 	○ 

○:melt △:partially melt ×:not melt

Since alkari- iron- tri- sulfate（Na,K)$_3$Fe(SO$_4$)$_3$ is unstable at high temperature, the ash melts under low (923-973K) temperature and high SO_2 atmospher.

Relation of ash melting and the corrosion morphologies

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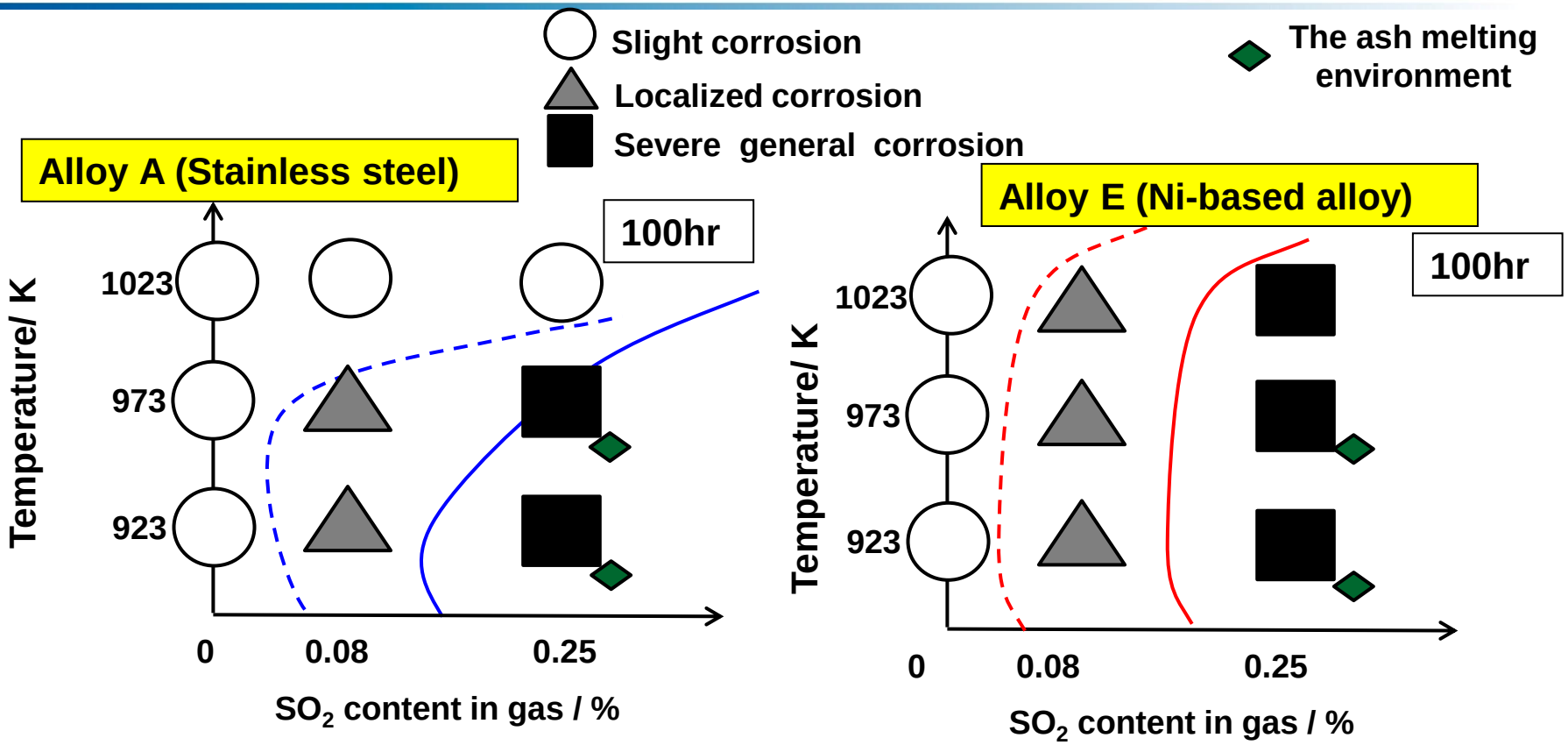


In the environment in which the synthetic ash melt, severe general corrosion were observed after 100hrs corrosion test.

In 0.08% SO_2 atmosphere, reaction of metal corrosion products and ash cause molten salt corrosion : Localized corrosion were observed after 100hrs.

Severe corrosion of alloy E at 1023K will be caused by other mechanism.

Effect of Mo in alloy on corrosion at 1023K

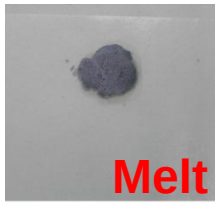
Alloy D: 22Cr-12Co-9Mo-1Al-bal.Ni
Alloy E: 20Cr-20Co-6Mo-2.3Ti-bal.Ni

MoO_3 will form as corrosion product

10% of MoO_3 was added to the synthetic ash

and exposed at 1023K in 0.25%SO_2 atmosphere

With MoO_3



Without MoO_3

The formation of MoO_3 causes the formation of molten salt at 1023K, without formation of molten alkali iron tri- sulfate..

Effect of MoO_3 in ash on corrosion rates at 1023K

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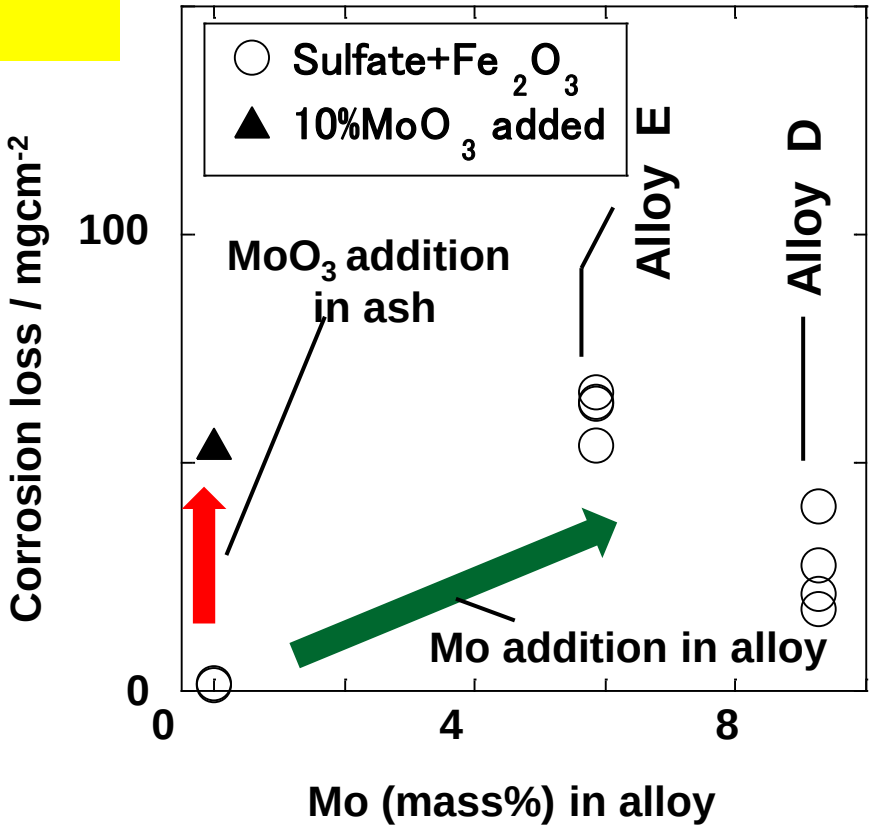
Alloy D: 22Cr-12Co-9Mo-1Al-bal.Ni
Alloy E: 20Cr-20Co-6Mo-2.3Ti-bal.Ni
Alloy F: 22Cr-1.5Al-10Fe-bal.Ni

Corrosion test of Alloy F (without Mo) was carried out with the synthetic ash (With and without MoO_3 addition) at 1023K in 66%CO_2-0.25%SO_2 gas

MoO_3 addition in the synthetic ash accelerates the corrosion of alloy F.



MoO_3 or Mo sulfate in the corrosion product reacts with the synthetic ash and accelerate the formation of molten salt.

Conclusions

- **The difference of CO_2 content (66% vs 15%) in gas did not affect the ash corrosion rates of alloys.**
- **The SO_2 content increase accelerated the corrosion at 923K and at 973K.**
- **At 1023K, alkali iron tri-sulfate became unstable, therefore the corrosion rates of stainless steels became small. In the case of Mo containing Nickel based alloys, formation of MoO_3 cause the molten salt formation at 1023K and accelerate corrosion.**

- The longer term (- 1000hrs.) laboratory corrosion test

- Tube material exposure in Callide Oxyfuel boiler

are planned now

Acknowledgement

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