Investigations for an improved corrosion resistance of micro reactor compounds towards aggressive chemical process media

T. Traut, W. Fürbeth
e-mail: traut@dechema.de
Funded by: BMWi via AiF
Period: 01.07.2014 - 30.09.2016
Gefördert durch: Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages

Motivation: Micro reactor compounds[1]

- higher heat transfer due to large surface
- continuous syntheses possible
- fast & improved manageable reactions at higher temperatures and pressures
- no solvents needed (eco-friendly, easy to purify products)

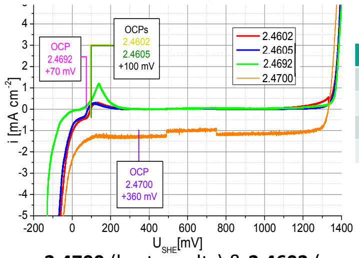
Problems

- thin walls between micro channels & aggressive chemical process media (H_2SO_4)
- fast corrosion → minor lifetime of reactor
- diffusion welding: possible with uncoated raw material, low cooling rate leads to grain growth & grain boundary precipitations →intergranular corrosion

Approach 1: Use of new corrosion resistant material

- **electrochemical current density potential measurements of corrosion properties (close to reality in micro reactors: 70%b H_2SO_4, T= 85°C):**
  - 4 different raw materials:

2.4602 & 2.4606: Ni-based alloy, currently used
2.4656: Ni/Fe-based alloy, improved alloy 31
2.4700: Ni-based alloy, new material with rare earth metals



corrosion rates:

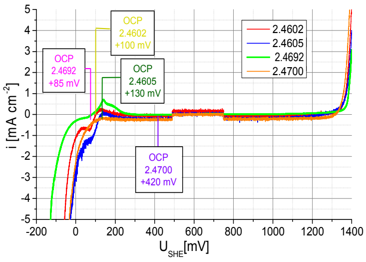
	i_{korr} [µA/cm²]	U_{korr} [mV]	W [µm/a]
2.4602	25	93	181
2.4606	20	95	231
2.4692	74	62	677
2.4700	-	-	0

- comparable results using glass beaker corrosion tests were achieved at KIT[2]

→ **2.4700** (best results) & **2.4602** (as comparison) for further measurements

Approach 2: Alternate joining process: laser welding

A) electrochemical current density potential measurements on sensitized material (1100°C, 4h, vacuum) ≙ diffusion welding process

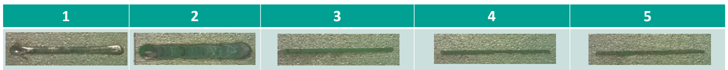


corrosion rates:

	i_{korr} [µA/cm²]	U_{korr} [mV]	W [µm/a]
2.4602	55	101	507
2.4606	59	129	545
2.4692	91	88	834
2.4700	-	-	0

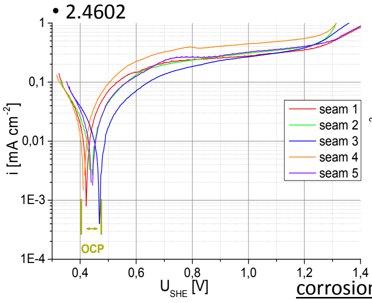
- higher corrosion rates than for raw materials due to sensitizing

B) electrochemical local current density potential measurement of corrosion properties on 5 different types of laser welded seams

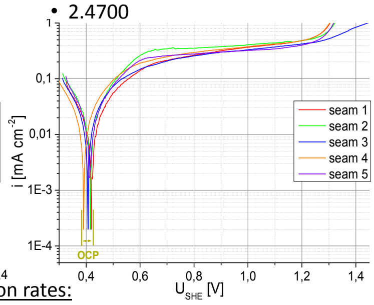


1	2	3	4	5
continuous wave mode, P = 2.5 kW		pulse mode, P_{tip} = 1.0 kW		
		P = 750 W, t = 0.75 ms	P = 300 W, t = 0.75 ms	P = 120 W, t = 0.40 ms
v = 8.0 m/min	v = 1.0 m/min	v = 6.0 m/min	v = 2.4 m/min	v = 0.2 m/min
focus: -1 mm	focus: +5 mm	focus: +1 mm		
		f = 1000 Hz	f = 400 Hz	f = 3000 Hz

- 2.4602



- 2.4700



corrosion rates:

seam	U_{korr} [mV]	i_{korr} [µA/cm²]	W [µm/a]
1	424	12,1	112
2	434	36,2	335
3	460	12,7	118
4	419	21,5	199
5	442	18,2	169

seam	U_{korr} [mV]	i_{korr} [µA/cm²]	W [µm/a]
1	425	13,3	121
2	413	32,6	296
3	411	16,7	152
4	400	16,3	148
5	425	14,5	132

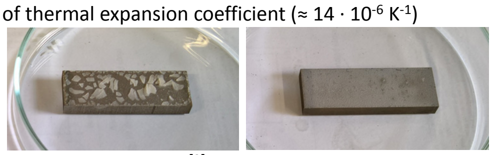
- *#2:* high corrosion rate; parameter: slow welding in cw-laser mode with high focus → broad seam → unqualified for welding micro reactor compounds
- *#1, 3-5:* no significant difference → wide set of parameters for laser welding
- corrosion rates lower than sensitized material → **laser welding good alternative**

Approach 3: Subsequent application of coating

A) Nano particle based enamel coating (sol-gel based):

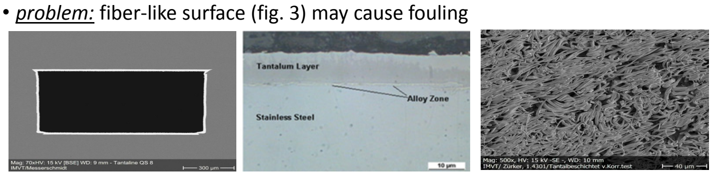
- requirements: low viscosity, fast evaporating solvent (ethanolic alkoxides), pretreatment of surface: only degreasing, similar thermal expansion coefficient
- *components:* **Si** (TEOS, MTESO), **B**$(OEt)_3$ (flux), **Al**-Sol (network strengthener), **Li**OEt & **Ba**$(NO_3)_2$ (th. exp. coef.), **Zr**$(Oprop)_4$ (cross-linking to metal surface), **Ti**$(i\text{-}prop)_4$ (acid resistance), **Co**$(NO_3)_2$ (slow gelification), **Ca**$(NO_3)_2$ (durability)
- *process:* mixing of ethanolic alkoxides → stirring for hours → add nitrate salts → stirring → sample pretreatment → apply coating with brush → drying over night → sintering
- *sintering process:* 5 K/min ↗ 350°C, 2 h, synthetic air ↘ cooling in furnace
- *first results:* different sol-gel compositions on 2.4602 & 2.4700 → find best adhesion & adjustment of thermal expansion coefficient (≈ 14 · 10^{-6} K^{-1})

adhesion of sol-gel enamel on 2.4700
left: bad or even no adhesion
right: good adhesion



B) CVD tantalum coating (Fa. Tantalum) at KIT[2]:

- complete coverage of surface in micro reactor channels (fig. 1)
- good adhesion to stainless steel surface via alloy zone (fig. 2)
- flow rate corrosion tests 70%b H_2SO_4, T= 100°C : no corrosion after 6 weeks
- *problem:* fiber-like surface (fig. 3) may cause fouling



Outlook (future project)

- investigations on corrosion resistance of enamel coatings
- application of enamel coatings to micro reactor channels → flow rate test (KIT[2])
- corrosion & fouling test of tantalum coating (KIT[2])
- application of enamel coating on tantalum coating → for smoothing surface & further corrosion protection

[1] Hessel, V., Gürsel, I.V., Wang, Q., Noel, T., Lang, J.; „Potenzialanalyse von Milli- und Mikroprozesstechniken für die Verkürzung von Prozessentwicklungszeiten – Chemie und Prozessdesign als Intensivierungsfelder“. Chemie Ingenieur Technik 2012, 84, No. 5, 660–684
[2] Institut für Mikroverfahrenstechnik (IMVT), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

Project partners

Th. Gietzelt, R. Dittmeyer: Institut für Mikroverfahrenstechnik (IMVT), Karlsruher Institut für Technologie (KIT), Eggenstein-Leopoldshafen