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# Development of a brazing process for the production of water-cooled bipolar plates made of chromium-coated metal foils for PEM fuel cells

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**Abstract.** Beside lithium batteries, PEM fuel cells are the most promising strategy as a power source to achieve the targets for introducing and increasing the usage of electric vehicles. Due to limited space and weight problems, water cooled, metallic bipolar plates in a fuel cell metal stack are preferred in motor vehicles. These plates are stamped metal sheets with a complex structure, interconnected media-tight. To meet the multiple tasks and requirements in use, complex and expensive combinations of materials are currently in use (carbon fiber composites, graphite, gold-plated nickel, stainless and acid resistant steel). The production of such plates is expensive as it is connected with considerable effort or the usage of precious metals. As an alternative, metalloid nitrides (CrN, VN, W2N, etc.) show a high chemical resistance, hardness and a good conductivity. So this material category meets the basic requirements of a top layer. However, the standard methods for their production (PVD, CVD) are expensive and have a slow deposition rate and a lower layer thicknesses. Because of these limitations, a full functionality over the life cycle of a bipolar plate is not guaranteed. The contribution shows the development and quantification of an alternative production process for bipolar plates. The expectation is to get significant advantages from the combination of chromium electrodeposition and thermochemical treatment to form chromium nitrides. Both processes are well researched and suitable for series production. The thermochemical treatment of the chromium layer also enables a process-integrated brazing.

## 1. State of the Art

The solution to the energy and exhaust problems of our time, e.g. the exhaustion of greenhouse gases or the energy consumption from fossil sources, could be the fuel cell. It provides a development to a zero emission vehicle during the life time. Recent developments favor the *Polymer Electrolyte Fuel Cell (PEFC)*. The principle of this fuel cell is to produce a cell voltage by a redox-reaction between hydrogen and oxygen to water (see figure 1). Figure 2 demonstrates a full PEFC stack for the use in vehicles by Daimler AG. Advantages of the PEFC are: easiness to control, short circuit protection and quick response to changing loads. The electrolyte is less corrosive, and the cells are relatively easy to manufacture. Typical challenges of the PEFC technology are the moderate peak performance, limited service life of the membrane, electrode materials and the production costs of the full stack. To reduce production costs, a starting point are the bipolar plates (see figure 2-5). The bipolar plates are the main elements of a stack. They essentially determine cost, weight and function. These plates have high requirements to ensure a long life of the PEFC (see table 1). Therefor the manufacturing of the bipolar plates requires high effort and costs. With regard of the very high numbers of bipolar plates needed in case of a launch of fuel cell vehicles, there is a need for developing new materials and production techniques for mass production.

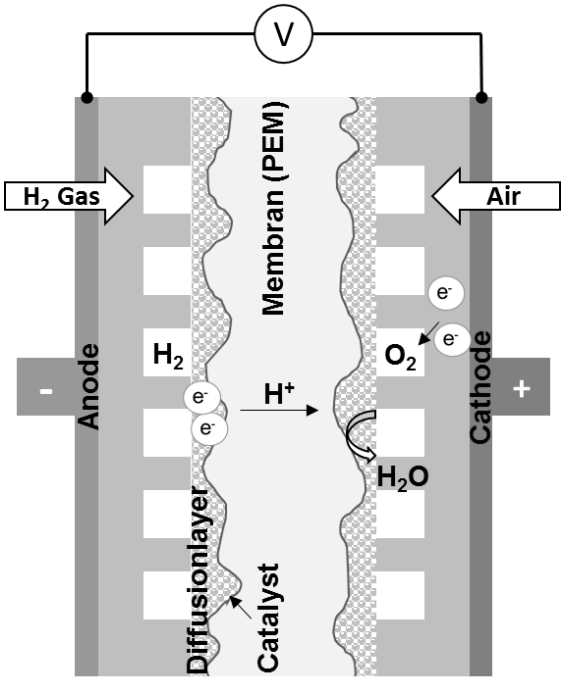


**Figure 1.** Basic design and schematic functionality of PEFC: feeding of pure hydrogen leads to anodic oxidation of hydrogen; diffusion through the polyelectrolyte membrane (PEM); feeding of air to cathode leads to reduction of oxygen; reaction between hydrogen and oxygen ions leads to water [own illustration]

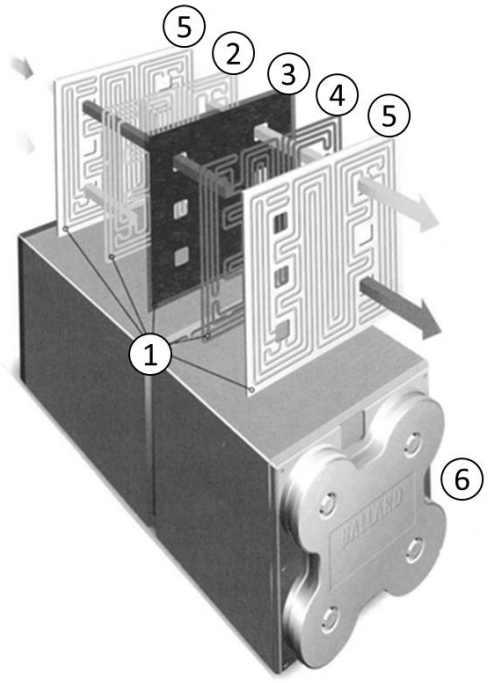


**Figure 2.** 1: PEFC stack; 2: H2 flow field; 3: membrane-electrode assembly; 4: air flow field; 5: bipolar plate; 6: endplate [1]

**Table 1.** Tasks and requirements of bipolar plates in a PEFC and the current materials in use [1]

| Tasks | Requirements | Materials |
|---|---|---|
| electrical contact | electric conductivity | graphite |
| gas supply | gas-tightness | carbon composite |
| water supply | corrosion resistance | titanium, zirconium |
| cooling | tensile and transverse strength | gold plated nickel |
| | | electrically conductive ceramic layer |

## 2. Approach

Materials selection: Most stack manufacturers use graphitic bipolar plates made of different materials and different production methods. However, the production technologies for mass production are not sufficiently developed. Therefor metallic bipolar plates, made of stainless steel, offer an advantage. The progress of deep drawing enables the production of 0.1 mm plates with fine channels. Though the passivation of stainless steel prevents a long-term use. The electric conductivity decreases noticeably.

Previous coatings (e.g. gold) are too expensive for mass production. Some patents introduce chromium nitride (CrN) as topcoat [e.g. 2–4]. It combines high corrosion resistance with electric conductivity. Resulting from this, CrN meets the high requirements for the use as topcoat for bipolar plate.

New production route: The production technology focuses on vapor deposition only. The process times are long and the layers are very thin. The new production route recommends chromium plated steel plates or foils as the starting point. They are a general alternative for stainless steel. The electrodeposition of chromium from chromic acid is a process suitable for mass production. The process times are low, thickness of layers are adjustable (from 5 µm to 1000 µm) and the production costs are also low, in comparison to PVD/CVD. To produce the CrN layer, a thermochemical treatment is carried out in a continuous furnance under $H_2/N_2$ atmosphere. The brazing of the plates takes place simultaneously. This ensures an economical process, suitable for mass production of bipolar plates. Furthermore, the choice of the basic material is variable according to the requirement profile.

Procedure for development:

a) Thermochemical treatment (Conveyor belt-protective gas-continuous furnace; Kohnle, Birkenfeld HT 1200-200/80-1500)
   - Parametric study with variation of temperature, annealing time, gas composition

b) Brazing (temperature monitoring with trailing thermocouples)
   - Braze filler selection
   - Wetting behavior
   - Brazing experiments at different temperatures

c) Characterization
   - XRD (x-ray diffraction) – phase analysis for detection of $Cr_xN_y$
   - SEM (scanning electron microscope) – optical evaluation of the coating and joining connection
   - Cross section and optical microscope – evaluation of the connection to the substrate

## 3. Thermochemical treatment

A parametric study takes place to identify the optimal parameters for the thermochemical treatment of chromium-plated samples. The parameters temperature, annealing time and the composition of the atmosphere in the furnace serve to secure the production of a chromium nitride layer. Preliminary tests carry out the restriction of the parameters (see Table 2). The full factorial design of experiments (32 experiments) ensures to find an optimal manufacturing route. The temperatures are based on typical brazing temperatures using standard braze filler material.

**Table 2.** Variables for the full factorial design of thermochemical experiments

| Temperature | Annealing time | Atmosphere |
|---|---|---|
| 900 °C | 15 min | 80 : 20 - $N_2$ : $H_2$ |
| 950 °C | 30 min | 50 : 50 - $N_2$ : $H_2$ |
| 1000 °C | | 20 : 80 - $N_2$ : $H_2$ |
| 1120 C | | $N_2$ + 15 ppm $SiH_4$ |

Steel (S235) acts as substrate, coated with a hard chromium layer (10 µm–20 µm) from a commercial chromic acid electrolyte. Figure 3 and 4 display two different thermo-chemical treatments. The conversion, from Cr to $Cr_xN_y$, is evident by the dark coloration of the coating. Chromium nitride layers

do not obtain in the atmospheres with lower nitrogen content. In comparison, the pure nitrogen atmosphere is the best, be-cause of a closed and partly continuous nitride layer at lower temperatures. The conversion of Cr to $Cr_xN_y$ closes residual cracks of the chromium coating due the increase of the volume.

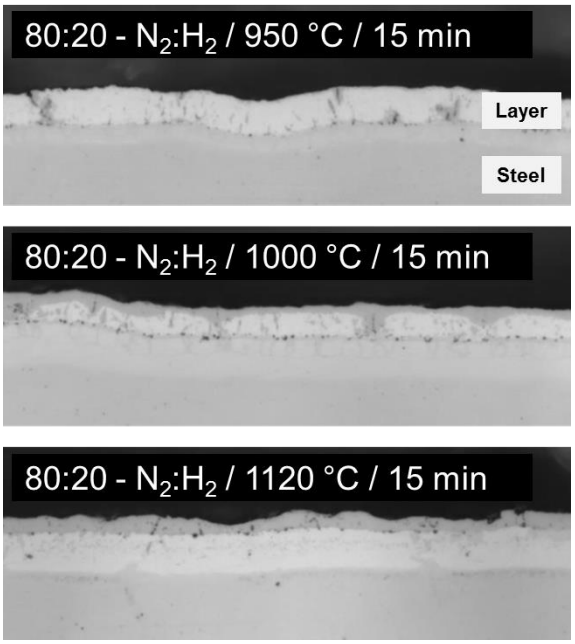


**Figure 3.** Cross section of chromium plated steel after thermochemical treatment at different temperatures in N2 / H2 atmosphere; nitride layer (dark) only few µm thick not continuously

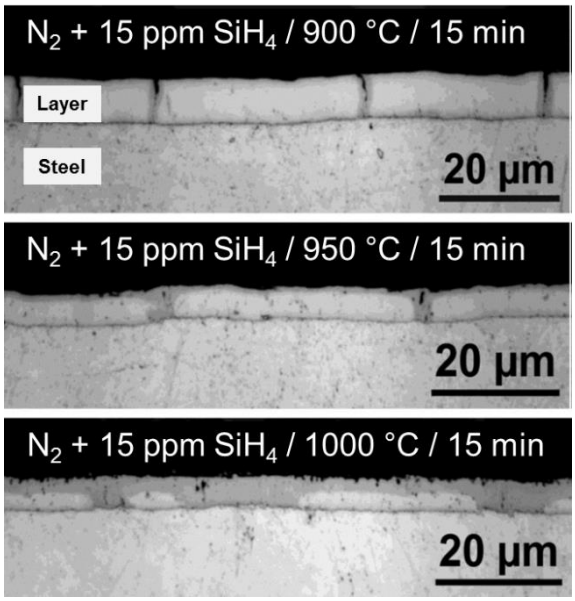


**Figure 4.** Cross section of chromium plated steel after thermochemical treatment at different temperatures in N2 atmosphere doped with SiH4; at 950 °C cracks of chromium coating closed; at 1000 °C about 5 µm thick nitride layer partly continuous

The detection of the composition of the $Cr_xN_y$ is carried out with XRD at low diffraction angles (2° / 6°). This method permits the detection of the phase composition at the surface of the samples. The penetration depth is maximum 10 µm. Figure 5A illustrates SEM pictures of the surface of electrodeposited chromium as reference and samples after thermochemical treatment at different temperatures. The atmosphere ($N_2$ with doped $SiH_4$) and the annealing time are constant. These are examples of the different parameters of table 2. XRD phase analysis results in the detection of polycrystalline $Cr_2N$ as the main phase. CrN phase does not appear under these conditions and production route. This means an advantage for the use as topcoat for bipolar plates. The transition resistance of $Cr_2N$ is up to 30 % lower compared to CrN, which means a much better electric conductivity. The use of nitrogen gas as atmosphere prevents also the oxidation of the chromium layer. Starting from a minimum temperature of 950 °C, appears a closed $Cr_2N$ layer with a minimum thickness of 4 µm.

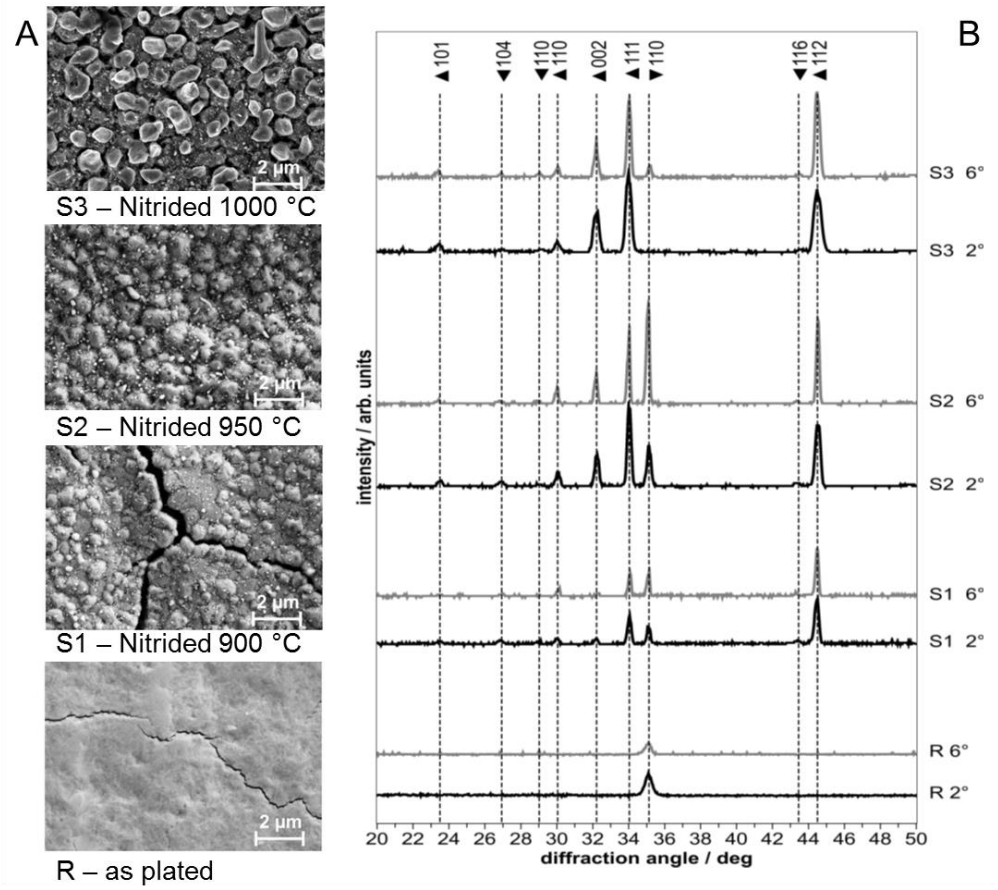


**Figure 5.** A – SEM surface pictures of different thermochemical treated samples in $N_2$ atmosphere doped with 15 ppm $SiH_4$ / annealing time 15 min | B – X-ray diffraction patterns of the samples of Fig. 5A under different diffraction angles (2° / 6°); marked crystal orientations Cr (►), $Cr_2N$(◄) $Cr_2O_3$ (▼); no CrN detected and very low intensity of $Cr_2O_3$ under these conditions; instead $Cr_2N$ and metallic Cr as main phases

## 4. Brazing Tests

The annealing temperature range between 900 °C and 1120 °C and holding time for the thermochemical treatment allows a simultaneous brazing. The process integrated joining reduces the process cost and saves a production step regarding to the PEFC stack. The typical joining of metallic bipolar plates is made by laser welding. The selected braze filler materials have a melting range similar to the temperatures of thermochemical treatment (see table 3).

**Table 3.** Selection of the used braze filler as a paste

| Label | Alloy composition [wt.%] | Melting range | Minimum brazing temperature |
|---|---|---|---|
| Ni 710 | Ni-14Cr-10P | 890 °C | 900 °C |
| B-Ni60CrPSi-980/1020 | Ni-30Cr-6P-4Si | 980 °C – 1020 °C | 1120 °C |

Chromium plated steel with different braze filler undergoes a wetting test at the same conditions as the thermochemical treatment (see figure 6). The experiments show the braze filler Ni 710 needs a minimum temperature of 1000 °C to have a good adhesion to the chromium plated substrate. At this temperature, a wetting angle is barely visible. The second braze filler needs 1120 °C as a minimum temperature. Under these conditions, the connection to the substrate is good; the diffusion zone is homogenously developed. The wetting angle is nearly 0°. Both braze filler are suitable for a simultaneous thermochemical treatment and brazing. The definition of the parameters for thermochemical treatment and brazing leads to the production of test panels. Therefore, the simulation under production conditions starts with easy structured steel sheets (see figure 7).

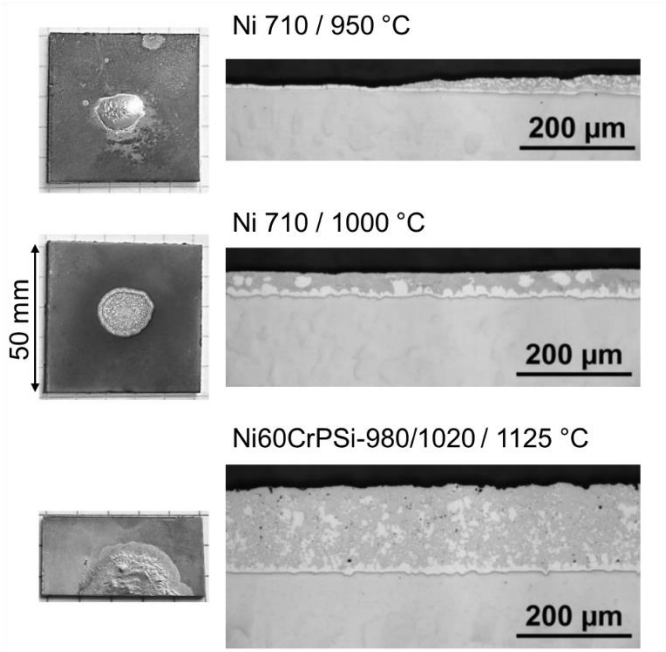


**Figure 6.** Wetting test with chromium plated steel and braze filler of Table 3 after annealing for 15 min and different temperatures

## 5. Conclusions and Outlook

The state of the art shows the need of a mass production process for bipolar plates. The combination of electroplating, thermochemical treatment and brazing could solve this problem, not only for the plates but also for the production of the stack. The thermochemical treatment and brazing of chromium coated steel produces closed $Cr_2N$ coatings joined together adherent. To perform these processes simultaneously, the material selection and the use of equal conditions is critical. The article clarifies both points. The next tasks are the corrosion tests, in the medium of the fuel cell, and the bond strength testing. Both test should clarify if the material selection is suitable for the application in PEFC. Because of the REACH regulation, the use of chromic acid, as an electrolyte for chromium electrodeposition, is restricted at 2017. As an alternative plating technology, chromium coatings obtain from Chromium-(III)-salt electrolytes. At this time, no commercial thick coatings are available on the market. The base of the process is a chromium coated substrate. Switching to a new chromium layer requires further experiments.

The whole development ends with the thermochemical treatment and koining of a real produced bipolar plate. A performance test will show, if the proposed production route and material selection suits the requirements of a life cycle of bipolar plates.

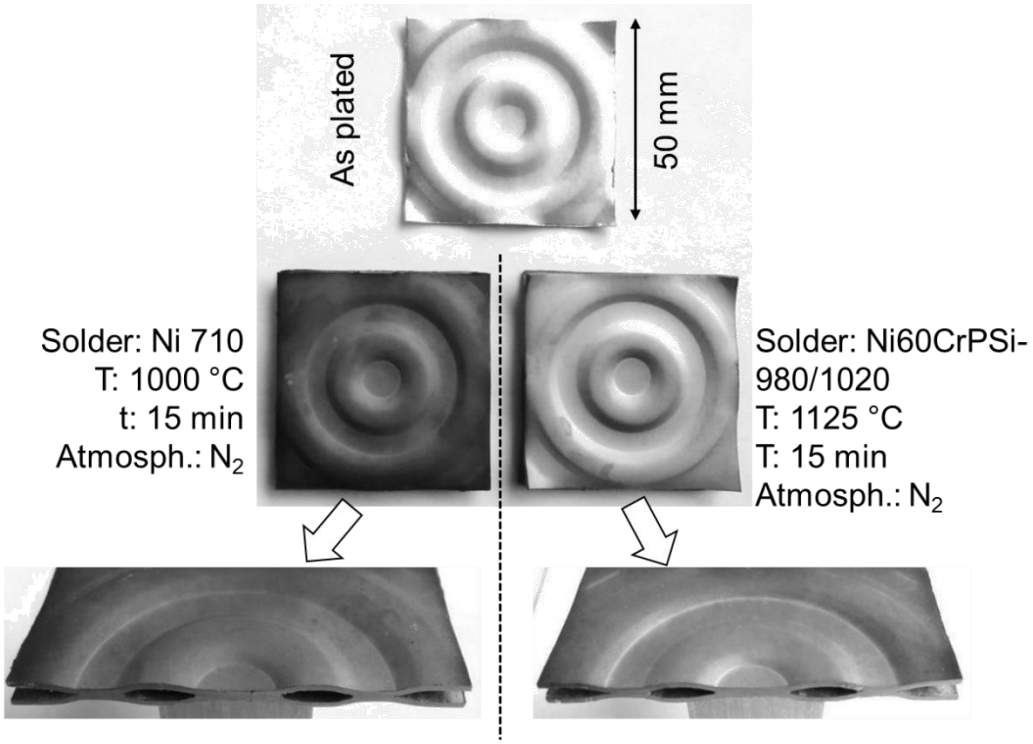


**Figure 7.** Production route of a stamped steel sheet coated with chromium; simultaneous thermochemical treatment and brazing with two different solders and process temperatures in a continuous furnance; annealing time 15 min; atmosphere $N_2$ doped with $SiH_4$

**Acknowledgement**

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