DEVELOPMENT AND PROCESSING OF METALLIC CR BASED MATERIALS FOR SOFC PARTS

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ABSTRACT

The newly developed chromium based alloys Ducrolloy represent a combination of excellent corrosion resistance against hot gases and exceptional physical and mechanical properties which offer a great potential for the use as constructive material e.g. bipolar plates of solid oxide fuel cells (SOFC). SOFC relevant material properties are discussed. Different powder metallurgical processing routes for the manufacture of semifinished plates as well as net shape processing techniques for bipolar plates are described. An outlook for further development is given.

1. INTRODUCTION

Planar SOFCs promise to capture the important advantages of SOFCs while easing such problems as the material limitations and fabrication difficulties of monolithic units and the high manufacturing costs that have slowed commercialization of tubular SOFCs (1). Furthermore, planar SOFC design concepts offer an attractive potential for achieving higher power densities compared to the competing design concepts (2, 3).

In the planar concept the SOFC, a reactor consists of several modules with single cells in parallel or serial connection (see fig. 1). Active cell elements are electrically connected by flat structural bipolar plates (interconnectors). In addition, the bipolar plate acts as a mechanical carrier for the electrolyte/electrode sandwich, distributes the anode and cathode gases in co-, cross- and/or counterflow and forms the constructional connection to the external inlets and outlets (2). For these reasons, bipolar plates are key elements for the function and long term reliability of the SOFC. The scientific, technical and commercial goal of the industrial realization of the planar SOFC will be significantly effected by the availability of suitable materials and low cost mass production of bipolar plates. In the present paper main emphasis is put on metallic materials for bipolar plates. Supplementary to this main application, the same metallic materials can be successfully used for other structural parts in SOFCs.
2. REQUIREMENTS FOR BIPOLAR PLATE (BIP) MATERIALS

The requirements for BIPs are determined by the stack design, the operating conditions and the cost target for electric power converted by SOFC. Table 1 shows widely used operating conditions for planar type SOFCs. The material properties requested for the BIP are described in detail in paper (4), also presented at this symposium. In general, the material has to be distinguished by outstanding high temperature corrosion resistance, long term chemical compatibility with the electrode materials, high mechanical strength as well as a thermal expansion coefficient adapted to that of the solid electrolyte. In addition, good electrical and thermal conductivity are decisive properties for this application. As some of the requirements are highly complex and to some extent contradictory, a large variety of materials like ceramics, cermets and metals have been taken into consideration. Out of the group of ceramic materials, at the present time, calcium-, magnesium- or strontium-doped lanthanum chromite appear to best meet these criteria (5, 6). Lanthanum chromite is mainly in competition to Ni or Fe based (containing 15 - 30 wt.-% Cr) chromia forming alloys and novel Cr based alloys (DUCROLLOY) developed at Plansee AG in collaboration with Siemens AG (KWU).

3. PROPERTIES OF CR BASED ALLOYS

As a result of wide spread screening tests of different metallic materials, it turned out that exclusively metallic Cr alloys will be able to meet the requirements (2, 4). The properties of these powder metallurgical (PM) produced alloys are the result of both the alloy design and the whole processing history and their interaction, respectively. Basic physical and mechanical properties of the Cr-alloys are presented in table 2. Regarding the functional properties, the Cr-based alloys have a superior electrical (low ohmic losses) and a remarkably good heat conductivity (uniform temperature distribution). The alloys are fully gastight and an ionic transport of oxygen through a BIP does not occur. Up to now, the best properties have been achieved by the oxide dispersion strengthened (ODS) alloys of the composition CrFe5Y2O3. By varying the Fe content, the thermal expansion behaviour can specifically be adjusted to that of the electrolyte/electrode sandwich (2). The mechanical strength (see fig. 2) is given by solid solution hardening with Fe and dispersion strengthening by uniformly distributed fine Y2O3 particles. The excellent hot strength in combination with the well adapted thermal expansion ensures the mechanical integrity of the stacks during cell operation. With other refractory metals such as Mo or W, the ODS Cr alloys share the limited ductility at low temperature having a ductile brittle transition (DBTT) temperature above ambient.
This is due to the body centered crystalline structure of Cr and its behaviour against interstitial elements. Nevertheless, the ductility is acceptable compared to ceramics even at room temperature. Above DBTT, the material is highly ductile with reliable stability against breakage during cell operation.

Apart from the outstanding physical and mechanical properties, the ODS Cr alloy has improved corrosion resistance in oxidizing, nitriding as well as carburizing hot gases up to 1000°C. Exposure in hydrogen containing atmospheres does not cause embrittlement of the material.

The chemical properties of CrFe5Y2O31 related to SOFC application and the mechanism of improvement of the corrosion resistance by alloying Cr with Fe and fine oxide dispersions like Y2O3 are discussed in detail in 2, 4, 7, 8. Tests in SOFC stacks for more than 2000 hours have been demonstrating the high performance of the alloy. For SOFC operation, a disadvantage of all pure chromia forming metals has to be figured out (2, 9). At high operating temperatures the formation of volatile Cr-oxide and -hydroxide species at the air side in a stack could be a potential source for long term cell degradation, due to the reduction to Cr2O3 at the cathode interface and formation of new crystalline phases. For this reason several routes to solve or surpass this problem have been evaluated. Lowering the operation temperature to 850°C significantly reduces the evaporation of Cr-containing species, also protective coatings might be successful to prevent evaporation, as well as alternative cathode materials are considered which are less sensitive to degradation by Cr2O3 (2, 11, 12). Running tests have been indicating that the solution of this problem can be expected (see also fig. 3).

Results of the ongoing material development have shown that a further improvement of the chemical and the mechanical properties can be expected based on fine tuning of the alloy composition as well as on optimization of the microstructure.

4. PROCESSING OF BIPOLAR PLATES

Different manufacturing routes like sintering, hot pressing, hot isostatic pressing and vacuum melting are applied to consolidate Cr alloys. In the following the powder metallurgical (PM) methods based on Plansee processing technology for manufacturing of semifinished plates and the net shape processing of BIPs are described. Fig. 4. and fig. 5 exhibit differently shaped BIPs.

4.1. PM PROCESSING OF SEMIFINISHED PLATES

Raw materials: Degassed electrolytic Cr flakes are the starting material for the powder production (10). The alloying element Fe is used as a powder in elemental form or as a master alloy with Cr. Y2O3 is of commercial grade.

Prealloying: Different alloying techniques leading to a uniform distribution of the constituents are applied. Procedures such as high energy ball milling resulting in an uniform distribution of fine grained Y2O3 particles are prefered.
Pressing and Sintering: Prealloyed powders are compacted to blanks on conventional presses at room temperature. Further densification and to some extent purification of the pressed blanks is achieved by sintering under protective hydrogen atmosphere taking into account the high vapour pressure of Cr.

Canning and forming: The highly porous sintered blanks are prone to the uptake of oxygen and nitrogen during hot processing, which leads to a considerable embrittlement of the bulk material. Consequently the sintered blanks are protected by vacuum tight steel containers. After deformation by hot rolling, the plates are fully dense. High deformation rates in combination with a thermomechanical treatment during rolling allow the specific adjustment of optimized microstructures.

During hot working a diffusion layer is formed with the steel can at the Cr-Fe interface. The can and the diffusion layer have to be removed by pickling and/or machining prior to net shape finishing of bipolar plates.

Semifinished plates in the thickness range of 1.5 - 15 mm are currently manufactured at Plansee.

Apart from this processing route, other alternative PM production methods are considered. Starting with the same prealloyed powder the hot isostatic pressing technique (HIP) is under evaluation for consolidation of the Cr alloy. High advanced sawing techniques have to be adapted to obtain the desired thin metal plates from the HIPed ingots. This manufacturing process is comparatively easy to control and can lead to plates with reduced internal stresses. The reduced density of the plates achieved by HIPing (96-99% of theoretical density) has to be taken into account comparing the material quality.

4.2. NET SHAPE PROCESSING OF BIPOLAR PLATES

Net shape processing is necessary to achieve the final BIPs for stack assembling. Mechanical machining procedures like cutting, grinding and milling have been applied for structuring the plates. Waterjet cutting has proven to be a more reliable technique compared to mechanical or laser based methods for cutting Cr alloy plates.

A very interesting technique for the production of the channel structure is electrochemical machining (ECM). ECM means the controlled partial anodic electrolytical dissolution of material, using a complementary shaped cathode. Depending on the channel design ECM can be a more cost effective manufacturing route, compared to conventional machining techniques. Very smooth surfaces have been obtained by this careful treatment of the plates avoiding mechanical loads.

Manufacturing of BIPs via wet powder pouring or metal injection moulding is also under evaluation. Subsequent densification by sintering and/or HIPing and/or forging seems necessary for net shaping.
5. SUMMARY AND OUTLOOK

The use of metallic BIPs instead of ceramic ones in SOFCs offers advantages for reliable SOFC operation as well as for economical manufacturing of large plates. Practical tests in different planar type SOFCs (kW-size) have demonstrated the high performance of the ODS Cr alloy.

The ongoing material development of ODS Cr alloys will concentrate on further fine tuning of the alloy composition and optimization of the microstructure to improve the SOFC relevant properties.

Main attention will be put on the development and installment of advanced manufacturing methods including coating and joining techniques to reach the cost target for BIPs used in SOFC plants up to MW-size. Related to the current situation a reduction of manufacturing costs in the order of a magnitude for BIPs is requested for successful commercialization of SOFCs on large scale at the beginning of the next century.

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Table 1: SOFC power plant operation conditions

| Parameter                          | Value                           |
|------------------------------------|---------------------------------|
| Temperature                        | 850-1000°C                      |
| Predicted life time                | ≥ 40,000 hours                  |
| Anode gas                          | H₂/CO/CH₄/CO₂/H₂O               |
| Cathode gas                        | Air                             |
| Operating pressure                 | 1 - 20 bar                      |
| Current density                    | ~ 0.3 A/cm²                     |
| Cell voltage                       | 0.7 V - 0.8 V                   |

Table 2: Physical and mechanical properties of Cr alloys

|                        | DUCROPUR CR(Cr) | DUCROLLOY CRL(Cr₁₇O₃) | DUCROLLOY CRF(CrFeY.₇O₅) |
|------------------------|-----------------|-----------------------|--------------------------|
| Melting point          | 1900            | ~ 1800                | ~ 1700                   |
| Density (RT)*          | 7190            | 7190                  | 7200                     |
| Electrical conductivity (RT) | 7.7x10⁶       | 7.6x10⁶                | 3.4x10⁶                  |
| Thermal conductivity (RT) | 92              | 85                    | 35                       |
| Coefficient of thermal expansion (RT-1273 K) | 9,6x10⁻⁶ | 9,6x10⁻⁶                | 11,3x10⁻⁶                |
| Young's modulus (RT)   | 250             | 250                   | 260-300                  |
| Hardness (RT) HV 10    | 120-140         | 140-220                | 280-350                  |
| Ductile brittle transition temperature | 100-300 | 100-300                | 100-400                  |

* RT......room temperature
Fig. 1: Example of planar cell design

Fig. 2: Tensile properties of CrFe5Y2O31 at different temperatures — sheet material (as rolled, 94% deformation)
Parameter List:

Housing/BIP: CrFe5Y2O31
Functional layer cath.: LaCoO3
Functional layer anode: Ni-mesh
Two serial PEN
PEN: ECN/ENI
Fuel gas: H2 dry
Oxidant: O2 dry
PEN size: 100 x 100 mm2

Fig. 3: Long term SOFC-test/Siemens KWU
Fig. 4: Siemens design of a CrFe5Y2O31 bipolar plate

Fig. 5: Sulzer HEXIS design of CrFe5Y2O31 interconnectors