DEVELOPMENT AND PROCESSING OF CHROMIUM BASED ALLOYS FOR STRUCTURAL PARTS IN SOLID OXIDE FUEL CELLS

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ABSTRACT

The chromium base alloy Ducrolloy (Cr-5Fe-1Y2O3) has been developed for structural parts in solid oxide fuel cells, e.g. bipolar plates. The essential properties e.g. coefficient of thermal expansion, electrical and thermal conductivity, high temperature corrosion resistance, mechanical properties as well as the machinability are the reasons for the widespread use of this alloy as bipolar plate material in solid oxide fuel cells. The first part of the paper shows two powder metallurgical manufacturing routes that have been chosen to produce the desired metallic bipolar plates. In the second part the actual cost situation is discussed and an outlook for mass production of bipolar plates made of Ducrolloy is given.

INTRODUCTION

The many-sided requirements for bipolar plate materials in solid oxide fuel cells (SOFC) at operation temperature >800 °C (see table 1) were responsible
for the development of an entirely new metallic alloy group. Widespread tests turned out, that exclusively chromium base alloy can meet all listed requirements in table 1 [1, 2]. Up to now the best properties have been achieved by the oxide dispersion strengthened (ODS) alloy named Ducrolloy\(^1\) (Cr-5Fe-1Y\(_2\)O\(_3\)) [3]. The addition of 5 wt.% iron to chromium was chosen to have a thermal expansion coefficient slightly higher than the electrolyte (yttria doped zirconia). This leads, during cooling of a stack, to slight compressive strains in the ceramic, if it is sealed to the bipolar plate (e.g. Siemens design). By adding Y\(_2\)O\(_3\) to the alloy the high temperature corrosion resistance is improved, resulting in a markedly slower chromia scale growth compared to other conventional chromia forming alloys [2].

For SOFC operation a disadvantage of all pure chromia scale forming alloys is the evaporation of volatile Cr-oxide and -hydroxide species at the air side of the stack which causes cell degradation [1, 4, 5]. The implication of this evaporation can be limited for instance by using less sensitive cathodes, by protective layers or at least by reducing the operation temperature below 900 °C [1, 6, 7, 8, 9]. First results and an ongoing material development in these cases indicate that a solution of this problem can be expected.

**MANUFACTURING**

**PM Processing of Bipolar Plates**

The high melting point, the high evaporation rate of molten chromium, the necessity of costly melting techniques and the high reactivity of molten chromium with crucible materials were some of the reasons that predominantly powder metallurgical (PM) manufacturing routes were taken into consideration for the processing of Ducrolloy parts. A widespread screening of different PM-manufacturing routes (e.g. sintering, liquid phase sintering, hot pressing, hot

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\(^1\) Product-name of Plansee AG, Reutte/Tyrol, Austria
isostatic pressing, metal injection molding etc.) pointed out, that there are two routes for a commercially attractive production of Ducrolloy bipolar plates.

Figure 1 shows a schematic comparison of these two techniques. Both routes start with powder raw materials (chromium, iron and yttria) either mixed in an elementary mixer or mechanically alloyed in a high energy ball mill [10]. In the case of mechanically alloying, the yttria particles are better distributed and their size is much more smaller as in the case of elementary mixing [11, 12]. The alloyed powder is compacted by cold pressing and sintered under hydrogen. To achieve the desired prematerial (plates) for manufacturing the final shaped bipolar plate (e.g. figure 2), two different consolidation techniques can be used: The technique of hot rolling (route A) as well as the technique of hot isostatic pressing (route B). Conventional hot rolling is used for plate production in route A, whereas a high advanced sawing technique, called multi-wire sawing, is applied in route B after densification. Figure 3 shows a Cr-5Fe-1Y$_2$O$_3$ alloy block cut by this technique. This sawing technique can lead to excellent surface quality and therefore no additional surface machining like grinding or lapping is needed as in the case of route A.

At the present time hot rolling has been successfully applied to manufacture plates up to dimension of 400 mm in square and in a thickness between 1,5-10 mm. Route B has been successfully applied for diameters up to 250 mm and a minimum plate thickness of 0,5 mm. While the multi-wire saw is presently limited to diameters ≤300 mm further upscaling in the case of hot rolling is feasible.

In order to produce the desired channel structure for gas supply of the electrodes, the electrochemical machining (ECM) method has been established in the case of manufacturing large quantities (see figure 2). Depending on the channel geometry, ECM can be a cost effective method compared to other techniques such as grinding or milling. The reasons are a very high precision, low specific tool costs and a short processing time especially for mass production.
Next to the technical performance the most important point for commercialization of SOFCs is the realization of an acceptable cost level. The costs of a SOFC system can be divided into material, capital, labour, maintenance and utility costs. Considering the material costs for the stack unit, in many cases the bipolar plate, irrespective of using a metallic or a ceramic solution, is the most expensive part.

A cost evaluation was done for Ducrolloy bipolar plates manufactured by route A, considering a dimension of 365-365-2 mm³, a SiC free surface, a maximum thickness variation ±0.01 mm/plate, a flatness ≤0.1 mm/plate and an electrochemically machined channel structure as can be seen for instance in figure 2.

Table 2 shows the actual (R&D-scale) and the expected future (industrial scale) cost share of the manufacturing steps. As can be seen for the present R&D-scale, 50% of the final bipolar plate costs are caused by the powder fabrication (20%) and the densification/forming step (30%). 50% are consumed by end shape processing resulting in final costs of around 3000 DM for a Ducrolloy bipolar plate. These high costs in the R&D scale result primarily from the low manufacturing quantity and not finally optimised techniques including labour and manufacturing expenses.

Figure 4 gives an outlook of the expected development of the cost level for an optimized mass production (one-product line) up to a commercial scale (>1000 t/a). This cost level is strongly dependent on the quantity of bipolar plates. The high potential of cost reduction, at least one order of magnitude, between the R&D scale and the industrial scale results from the fact, that common techniques for mass production like hot rolling and ECM are applied. These techniques are for instance successfully used in the steel and superalloy industry and will result in much lower labour and manufacturing expenses leading to a reduction of the actual costs for at least one order of magnitude.
SUMMARY AND OUTLOOK

For the present time there are two promising powder metallurgical routes for manufacturing bipolar plates made of Ducrolloy (Cr-5Fe-1Y_2O_3). The conventional route uses hot rolling and the alternative route uses hot isostatic pressing in combination with a multi-wire saw to achieve the plates desired. Followed by ECM for end shape processing both techniques have been proven for manufacturing metallic bipolar plates of Ducrolloy.

The actual costs for bipolar plates are primarily influenced by the low quantity and the high dimensional precision demands and not yet established optimised mass production techniques in scales known from the steel and superalloy industry. The application of these techniques for the production of bipolar plates at large quantities would lead to a reduction of the actual costs for at least one order of magnitude.

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Table 1: Requirements for bipolar plates [2] and power plant operation conditions in SOFCs [3].

| Requirements for bipolar plates                                                                 |
|-----------------------------------------------------------------------------------------------|
| • High mechanical strength and sufficient ductility at operating temperature to ensure the mechanical integrity of the stack |
| • Good thermal and electrical conductivity to minimise thermal stresses and optimise power output |
| • Compatibility of thermal expansion behaviour with the thin ceramic foils to avoid tensile stresses in the ceramics during thermal cycling |
| • Long term stability under exposure to the relevant gases (see below) and high temperature corrosion resistance to guarantee a high reliability of the stack |
| • Low transition resistance of the formed oxide layers during operation                        |

| Operation conditions                               |                                             |
|----------------------------------------------------|---------------------------------------------|
| • Temperature                                      | 800-1000 °C                                 |
| • Predicted life time                              | ≥40,000 h                                   |
| • Anode gas                                        | H₂/CO/CH₄/CO₂/H₂O                           |
| • Cathode gas                                      | O₂/air                                      |
| • Operating pressure                               | 1-20 bar                                    |
| • Cell voltage                                     | 0.7-0.8 V                                   |

Table 2: Recent and expected distribution of the costs for Ducrolloy.

| Manufacturing step      | R&D scale | Industrial scale |
|-------------------------|-----------|------------------|
| Powder fabrication      | 20 %      | 40 %             |
| Densification and Deformation | 30 %      | 30 %             |
| End shape processing    | 50 %      | 30 %             |
Figure 1: Powder metallurgical manufacturing routes for Ducrolloy.

PM manufacturing of CRF bipolar plates

Route A
- Raw material
- Prealloying
- Pressing and sintering
- Canning and forming
- And shape processing
- Machining e.g. ECM
- Bipolar plate (interconnector)

Route B
- Raw material
- Prealloying
- Pressing and sintering
- Canning and forming

Figure 2: Siemens design of a Ducrolloy bipolar plate.

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Figure 3: Hot isostatically pressed Ducrolloy cut by a multi-wire saw.

Figure 4: Expected development of costs for Ducrolloy bipolar plates.

- **R&D scale**: 5 t/y
- **Pilot plant scale**: 10-20 t/y
- **Small**: 100-500 t/y
- **Large**: >1000 t/y