P/M Processing of ODS Cr- and FeCr-based alloys for Solid Oxide Fuel Cell Applications

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Summary

Fuel cells in general are considered as one of the most promising future power engineering technologies. In particular, high temperature Solid Oxide Fuels Cells (SOFC) are candidates for various applications in mobile and stationary heat and power generation due to their high flexibility in gaseous or liquid fuel operation. The present work reviews Plansee´s development and powdermetallurgical (P/M) processing activities of high performance metallic SOFC interconnect materials based on ODS Cr- and FeCr-alloys. Several P/M processing routes, i.e. thermomechanical treatment of precompacts, net-shape pressing/sintering and tape casting of metal powders are outlined. The typical property profile of these materials is described in accordance to the operation requirements in SOFC environments and examples of components and applications in pre-series SOFC systems are given. Whereas the Cr-based Ducrolloy CRF has proven to be a metallic benchmark material in high temperature SOFC (900-1000°C) interconnect performance, emphasis is also laid on the development of advanced ODS ferritic P/M alloys ("IT-alloys") for intermediate-temperature SOFC (700-900°C) applications. The results of long-term (5.000h) corrosion tests of these alloys in air and fuel gas atmospheres at 800°C, CTE measurements, as well as contact resistance measurements in air at 800°C for several thousand hours are summarized. It is shown that P/M processing has multiple benefits with regard to alloy design and performance as well as to the potential of cost efficient volume production of components for SOFC applications.

Keywords

Power Engineering, SOFC, Interconnects, ODS Chromium, ODS FeCr alloys

1. Introduction

The requirements for suitable interconnect components of planar SOFC are challenging due to the influence of corrosive atmospheres at high temperatures ranging from 700-1000°C in combination with stresses induced during thermal cycling for e.g. APU applications or creep phenomenons caused by life cycles exceeding 40.000 hours for e.g. stationary applications. Compared to advanced ceramics, metallic interconnects offer a portfolio of attractive features such as processing reliability, robustness during service and maintenance as well as cost competitiveness.

Since more than one decade, PLANSEE is actively pursueing the development and production of metallic interconnect materials and components suitable for planar SOFC. In this context, PLANSEE is able to utilize sucessfully its core know-how of advanced P/M processing of high performance materials on industrial scale [1,2,3,4,5]. P/M ODS Cr-alloy, i.e. Ducrolloy CRF or similar alloys are introduced as a technology applicable for high temperature SOFC systems as well as P/M ODS ferritic FeCr-alloys to apply as interconnect to intermediate temperature SOFC. A current overview of the industrial base at PLANSEE is given to reveal that the chosen approach of P/M processing technology combined with high performance materials is most adequate to gain suitable metallic SOFC interconnects at competitive costs and with the perspective of industrially available quantities.

2. Background

P/M technology offers a wide range of processing to generate sound bulk material and components from high performance materials. Alloys which can not be processed adequately by ingot metallurgy (I/M) due to their reactivity with crucible materials or which have functional compositions or complex consolidation paths which are difficult or impossible to be adjusted by I/M processes can advantageously be processed by P/M technologies. Exemplarily, Fig. 1 reveals schematically 3 basic P/M processing routes which PLANSEE is pursueing on an industrial scale for the fabrication of mill products and components for SOFC interconnects made of ODS Cr- and FeCr-alloys.

Beside the classical process of P/M mill product and component fabrication via thermo-mechanical treatment and subsequent machining, PLANSEE was able to transfer its knowledge about volume production of P/M components, derived e.g. from automotive industry, to SOFC interconnects in succesfully applying a net-shape (NS) pressing and sintering approach [6]. In this context presents Fig. 2 an example of NS processed Cr-based interconnects for the SOFC pre-series systems HXS1000 Premiere of the Sulzer Hexis AG (CH) [7].

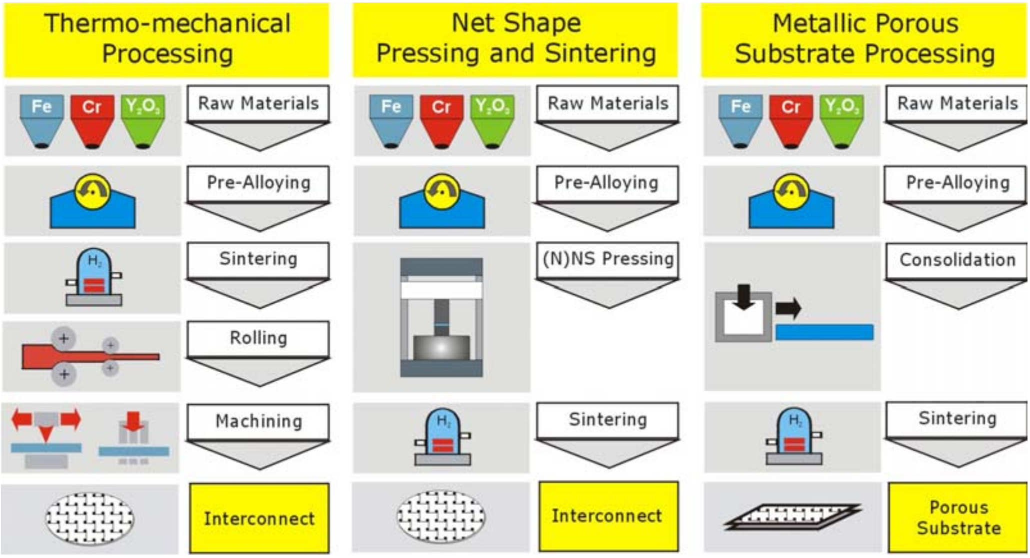

Fig. 1 Industrial P/M processing technologies for the manufacture of metallic interconnects and porous substrates for SOFCs.

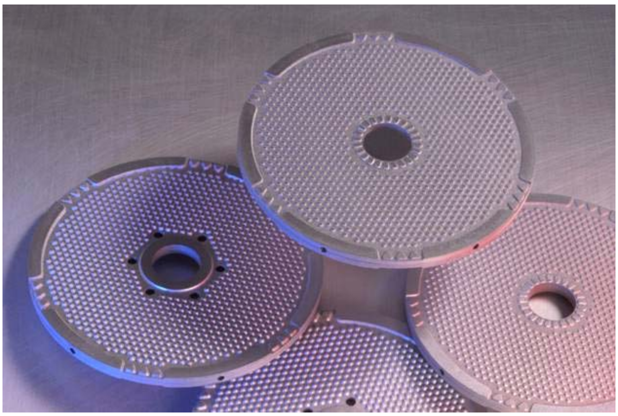

Fig. 2 Example of Cr-based metallic interconnects processed via NS pressing and sintering on industrial scale equipment for the Sulzer Hexis AG (CH) pre-series SOFC systems HXS1000Premiere.

Furthermore, P/M processing of ODS FeCr pre-alloyed powders enables the preparation of metallic porous substrates which are applicable to metal supported cell concepts of intermediate temperature SOFCs (Fig. 3) [8].

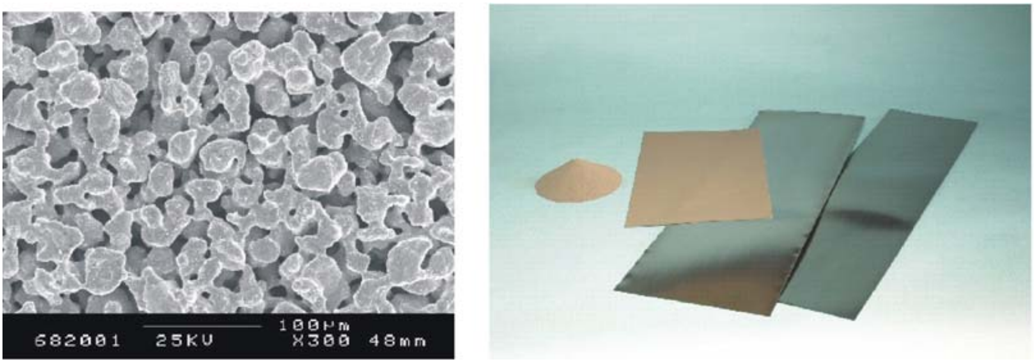

Fig. 3 Morphology of a metallic porous P/M substrate based on a FeCr-alloy (left) and example of foil material processed from P/M FeCr-alloy (right).

3. Experimental

The different P/M manufacturing routes illustrated in Fig. 1 depend on carefully pre-treated and pre-alloyed powders in order to achieve an adequate processing behavior within the specific manufacturing technology and adequate component properties. In regard to metallic SOFC interconnects, PLANSEE utilizes two different P/M alloy technologies which both feature an oxide dispersion strengthening (ODS) effect. On the one hand, Cr-based alloy $Cr\text{-}5Fe\text{-}1Y_2O_3$ for temperatures above 850 ^{o}C, on the other hand ferritic FeCr-based alloys which are modified by Mo, Ti, Mn and miscellaenous alloying additions for temperature up to 850 ^{o}C. This in order to comply with all main physical and chemical requirements of a SOFC interconnect. Main emphasis on the development of FeCr-alloys was laid on improved corrosion properties in intermediate temperature SOFC relevant atmospheres compared to ferritic steels including the formation of thin and well adherent corrosion scales with excellent contact resistance characteristics. As reference alloys in terms of property investigation, three commercially available ingot metallurgical (I/M) processed ferritic steels, ZMG 232 (trademark of Hitachi Metals), Crofer 22 APU (trademark of Thyssen Krupp VDM) and steel 446 were chosen for comparison.

Alloys	Fe	Cr	Mn	Ti	Al	Si	Others
ITM	Bal.	26.0			<0.03	<0.03	(Mo)x, (Ti)y, (Y)xy
ITM 14	Bal.	26.0			<0.03	<0.03	(Mo)x, (Ti)y, (Mn)z, (Y)xy
RA 446	Bal.	26.3	0.78	< 0.05	n.a.	0,16	Mo 0.05
ZMG232	Bal.	22.1	0.51	n.a.	0.19	0.40	Zr 0.22, La 0.044
Crofer22APU	Bal.	22.0	0.42	0.08	0.12	0.11	La (0,08)

Table 1 Compositions of various P/M and I/M FeCr-alloys.

4. Results of materials characterization

As a first SOFC-stack relevant physical property, Fig. 4 illustrates the behaviour of CTE vs. temperature of P/M FeCr-alloys as well as Cr-alloy. The CTE of the FeCr-alloys is similar, but rather somewhat lower than those of typical ferritic steels. Compared to the CTE of Cr-5Fe-1Y_2O_3 the CTE of the Fe-26Cr-based IT-alloys is about 1,6 x 10^{-6} K^{-1} higher in the temperature range of 700°C to 1000°C. The discontinuation of the relatively linear increase of the CTE around 600°C is related to the Curie transition temperature.

The data of the mechanical properties in Fig. 5 and Fig. 6 derived from tensile tests on sheet material with about 1 mm thickness. In comparison to sheet material made of ferritic I/M steel, the ODS P/M FeCr-alloy ITM exhibit significantly higher 0,2%-yield strength (0,2%-YS) and ultimate tensile strength (UTS) at temperatures which are typical for the operation of intermediate temperature SOFC interconnects.

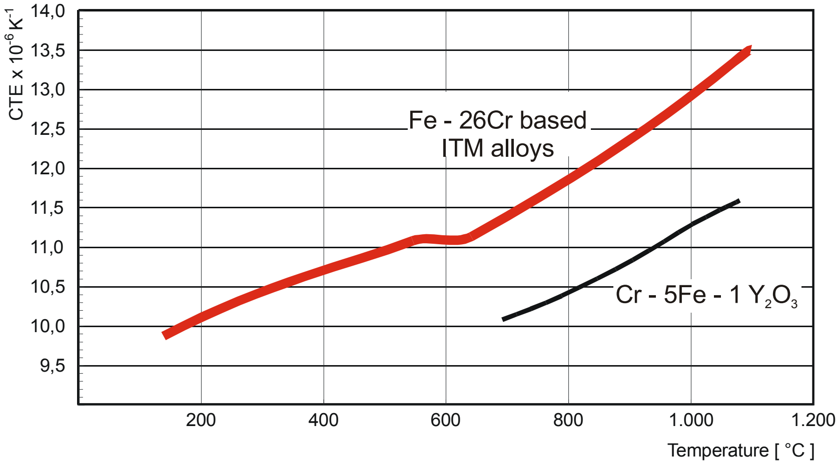

Fig. 4 CTE vs. temperature of P/M FeCr-alloy and Cr-alloy.

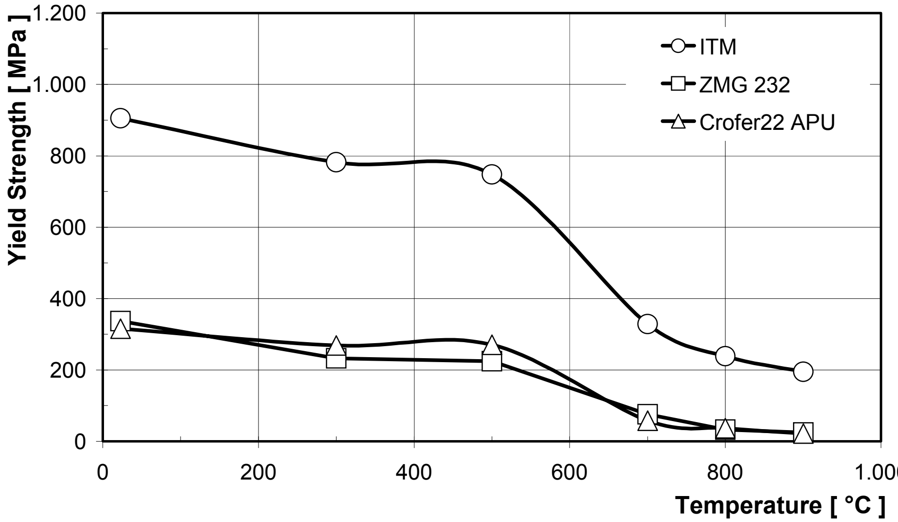

Fig. 5 0.2% YS vs. temperature of Plansee ITM alloy, ZMG232 and Crofer22APU.

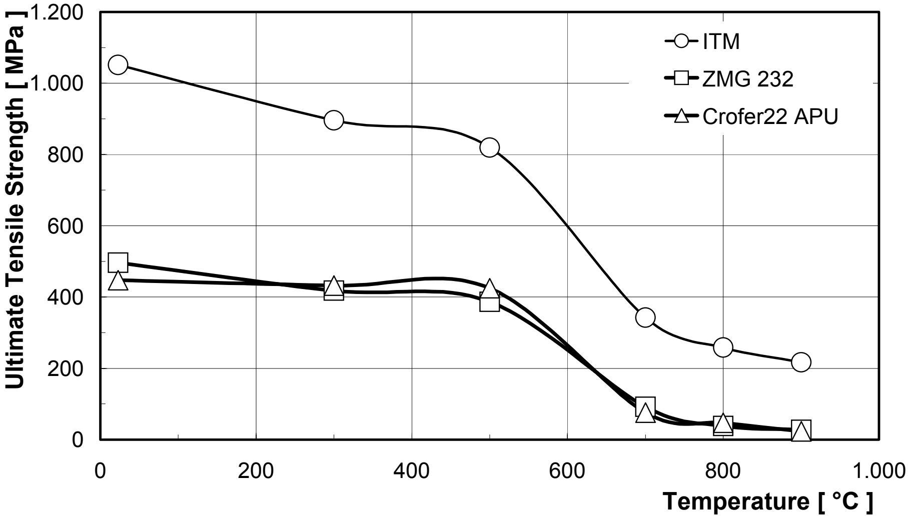

Fig. 6 UTS vs. temperature of Plansee ITM alloy, ZMG232 and Crofer22APU.

Although the creep properties have not yet been determined one can assume that the creep behaviour of the ODS P/M FeCr-alloy is superior to the I/M ferritic steels due to the elevated temperature strengthening effect of the oxide dispersoids. The higher strength characteristics might be of potential advantage in applications of thinner foil interconnects in terms of geometrical stability which might be impacted by stresses caused by thermal cycling or buckling due to corrosion scales formed over longer service times.

The results of the oxidation tests performed in laboratory air at 800°C for 5.000h are illustrated in Fig. 7. Fig. 8 shows the mass gain of P/M FeCr alloy compared to I/M ferritic steels after a test in 15% H_2 / 85% H_2O atmosphere at 800°C for 2.000h. The respective oxide layers formed during oxidation and corrosion testing have been characterized in [9].

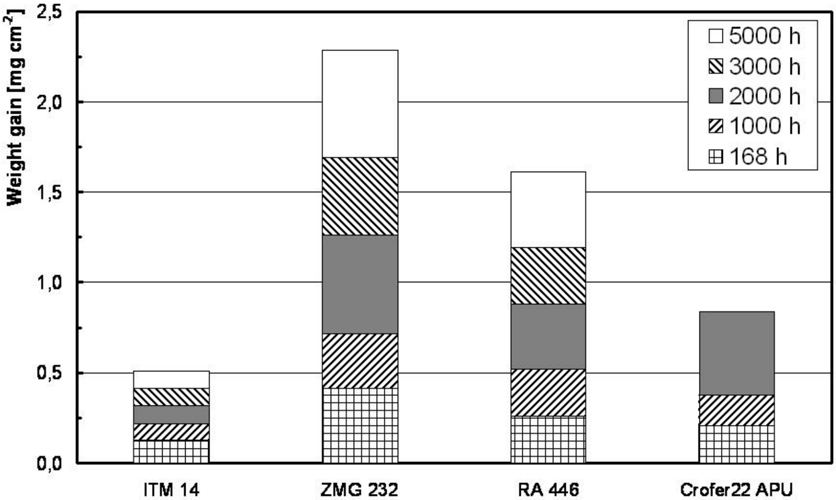

Fig. 7 Mass gain vs time derived from oxidation tests at 800°C in laboratory air for 5.000h. ITM 14 is shown in comparison to the reference sheet material ZMG232, RA 446 and Crofer22APU (oxidized in air only for 2.000 hours).

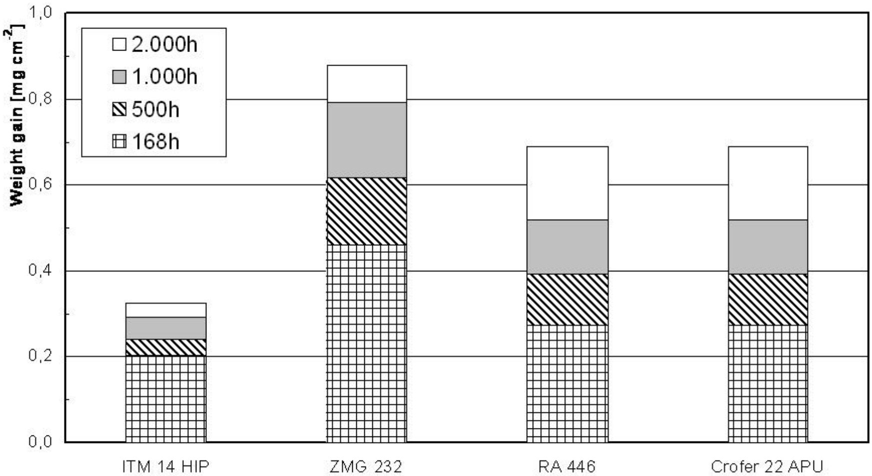

Fig. 8 Mass gain of ITM 14 compared to various I/M ferritic steel material after testing in 15% H_2 / 85% H_2O atmosphere at 800°C for 2000h.

The results of the contact resistance behaviour measured in-situ at 800°C in laboratory air for 4.800h are illustrated in Figs. 9 and 10. P/M FeCr-alloys point out superior contact resistance behaviour in comparison to the reference alloys ZMG232 and Crofer22APU also in terms of the trend of the slope (extrapolation) of the contact resistance towards the end of the test duration (see Fig. 10).

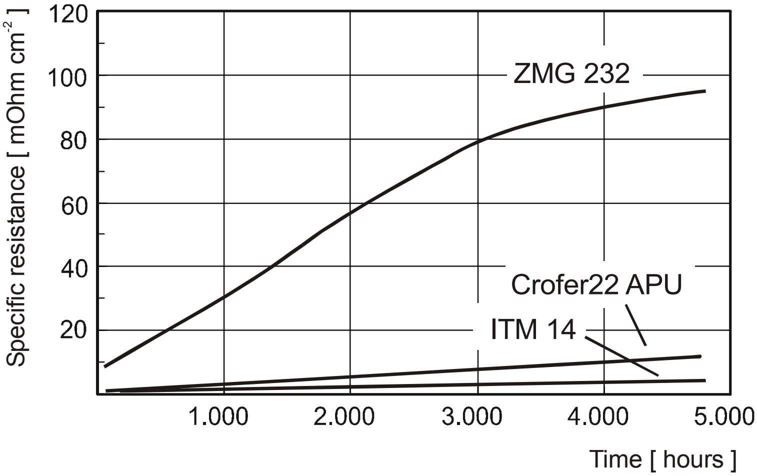

Fig. 9 Overview of the specific contact resistance vs time at 800°C in air for ITM 14 in comparison to the reference alloys.

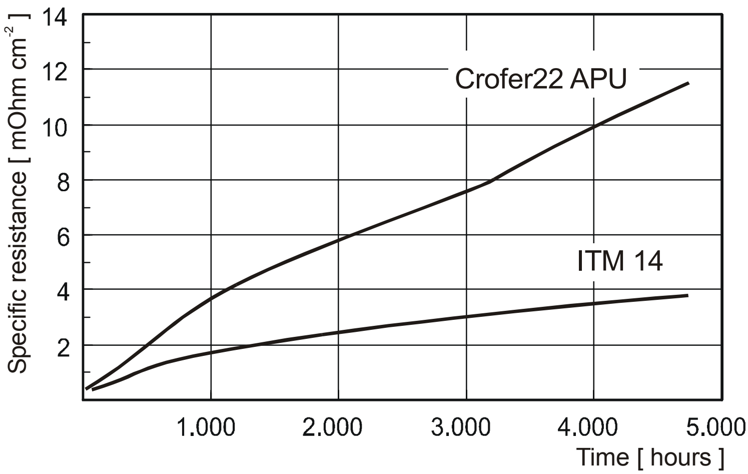

Fig. 10 Detail of the specific contact resistance vs time at 800°C in air for ITM 14 in comparison to I/M Crofer22APU.

5. Conclusions

Advanced P/M processing techniques have been established at PLANSEE and have shown their capability for the fabrication of high performance metallic interconnects and porous metallic substrates for planar SOFC applications. By utilizing these technologies a variety of significant advantages are achieved in terms of reliable processing as well as the capability of net-shape fabrication of interconnects, offering cost efficient production potential on an industrial scale.

On the other hand, P/M alloy technology enables the use of advanced ODS Cr- and FeCr alloys. Both exhibit a combination of properties which are well suited to comply with the challenging requirements for planar SOFC interconnects.

In particular, the achieved results on the P/M ODS metallic interconnect materials revealed advantages in terms of low contaminations with Al and Si, homogeneity of the microstructure and the oxide dispersoid additions and improved alloy design abilities by means of homoneneous implementation of functional alloying elements. These features are highly advantageous to achieve a range of superior properties in terms of CTE, corrosion resistance, contact resistance and mechanical strength which appear to be beneficial for SOFC applications at intermediate and high temperatures compared to commercially available I/M state-of-the-art ferritic steels.

PLANSEE will continue to pursue efforts in regard to its ODS P/M materials technology for SOFC interconnetcs to achieve a more detailed understanding of the processing-property-relationship, e.g Cr evaporation behavior or stability under electrochemical stack conditions. On the other hand, P/M processing technologies will be further improved to generate at PLANSEE a sound and competitive industrial base for the fabrication of interconnects made of flat mill products, porous substrates or net-shape pressed and sintered components. In summary, the recently established status revealed that it will remain an interesting challenge as well as an ambitious perspective for PLANSEE in collaboration with its partners and customers to further aim a balance of suitable materials, adequate P/M processing methods and sound stack performance at acceptable cost.

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