OXIDATION RESISTANCE & PERFORMANCE IN STACK TESTS
OF NEAR-NET-SHAPED CHROMIUM-BASED INTERCONNECTS

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ABSTRACT

The Cr-5Fe-1Y₂O₃ alloy, manufactured by Plansee Ltd., is a well-known material in the field of high-temperature planar solid oxide fuel cells (SOFC). Its thermal expansion compatibility with stabilised zirconia and its excellent oxidation resistance make it a viable candidate for metallic interconnects. During the last five years Sulzer HEXIS Ltd. has been integrating metallic interconnects, supplied by Plansee, in their stack and systems testing programme. Despite the excellent material characteristics of the Cr-5Fe-1Y₂O₃ alloy, projected manufacturing cost of the interconnects was found to be above the estimated target value for commercialisation. This was primarily due to the intricate design of the current collector, which requires extensive machining. For this reason, a new family of chromium based alloys was investigated by Plansee. The aim was to manufacture the HEXIS current collector through novel and cost-effective powder metallurgy routes. Chromium-based powder mixtures were pre-alloyed, pressed into structured plates and sintered. The microstructure, oxidation and contact resistances were evaluated. A selected number of powders were then pressed into current collectors and integrated in stack tests. Performance of stacks fitted with these new components was identical to that observed in stacks contacted with the conventional current collectors.

INTRODUCTION

The Cr-5Fe-1Y₂O₃ alloy, manufactured by Plansee Ltd., is well known in the field of planar high-temperature solid oxide fuel cells (SOFC). The characteristics offered by this material, as for example, thermal expansion compatibility with stabilised zirconia and excellent high temperature oxidation resistance are not satisfied by any other product on the market today. Because of these unique characteristics, the Cr-5Fe-1Y₂O₃ alloy is a viable candidate for metallic interconnects (1). However, when this material was first introduced in SOFC stack tests, some years ago, rapid electrochemical degradation was observed. Stack lifetime was limited to approximately 200 hours of service. This degradation was later found to be related to the evaporation of chromium from the surface of the current collector (2). Re-deposition by condensation on the cathode surface...
modified the structure and chemistry of the electrode and induced the electrochemical
degradation observed. By coating the surface of the interconnects with appropriate
protective layers, Sulzer HEXIS was able to demonstrate a significant increase in
electrochemical stability. Transport of chromium was inhibited and stability was extended
to more than ten thousand hours of service. This coating solution and the Cr-5Fe-1Y2O3
alloy have, since then, successfully been used in stack and system testing by HEXIS (3,4).

Unfortunately however, despite these encouraging results, projected manufacturing costs
of the HEXIS current collector were found to be above the estimated target value for
commercialisation. This was primarily due to the intricate design of the interconnect,
which requires extensive machining of Cr-5Fe-1Y2O3 plate material.

A new approach to the manufacturing of these current collectors had to be made, with the
aim to reach the estimated price objective of approximately $10/current collector. This
was only possible if machining efforts are reduced to a minimum and efficient use of the
chromium powder is made. A new family of chromium-based powders had to be
investigated, where in combination with all the material characteristics of the Cr-5Fe-
1Y2O3 plate material, these new powders had to satisfy the material requirements dictated
by near-net-shaping. The aim was to manufacture HEXIS current collectors by novel and
cost-effective powder metallurgy routes.

This report summarises the results obtained in an effort to achieve cost-effective current
collectors obtained by near-net-shaping.

**METHOD**

At Plansee Ltd., chromium-based powder mixtures were pre-alloyed, pressed into
structured plates and sintered. Three different powder grades were evaluated (grades I, II
and III). The difference between them was related to their level of pre-alloying, purity,
morphology and compaction additives. After sintering the microstructure and oxidation
resistance were evaluated. With the aim of optimising pressability, sinterability and
corrosion resistance, eighteen different compositions, based on Cr-5Fe and in the three
powder grades, were evaluated. Results related to this work are reported in another paper
in this symposium (5). After this preliminary materials selection phase, the identified
powder types were pressed into structured Ø30mm discs, 2.5 mm thick, and their
compatibility with the HEXIS protective coatings was tested.

**Thermal Spraying**

The standard HEXIS La0.8Sr0.2MnO3 protective coating is thermally sprayed on the outer
surfaces of the cathode side of the interconnect. Its function was to seal the metal surface
from chromium evaporation, as well as provide a highly conductive interface for current
collection. The HVOF (high velocity oxyfuel) thermal spray parameters were carefully
selected to achieve dense and chemically homogeneous coatings. The contact resistance
at 920°C was then evaluated according to standard procedures described elsewhere (3).
Enamelling

Chromium vapour enrichment may also occur in the air entering the heat exchanger volume of the HEXIS current collector. Therefore, to avoid chromium induced electrochemical degradation, the internal surfaces of the interconnect are sealed, eliminating any risk of chromium transport. However, contrary to the thermally sprayed perovskite seal, this coating must not be electrically conducting. The composition of an alumino-silicate enamel was adjusted to fit the thermal expansion of the chromium-based alloys selected. Furthermore, the composition was carefully selected to prevent crystallisation of the glass during prolonged exposure at 920°C.

Finally, based on the results of thermal spraying, contact conductivity and enamel compatibility, two powder types were selected and pressed into Ø120mm HEXIS interconnects at Plansee. The near-net-shaped components were then coated with the different protective layers and integrated in HEXIS 5-cell stack tests.

RESULTS

Thermal Spraying

Densities of approximately 80% were observed in pressed and sintered components made from powders of grade III. Because of their higher porosity, they showed excellent behaviour during thermal spraying. The high thermal stresses usually encountered with this process did not seem to affect these porous substrates. Neither did any cracking, nor coating spallation occur. Furthermore, because of their rougher surface, sandblasting was not necessary. Nevertheless, adhesion of the ceramic coating to the substrate was good.

![Figure 1](image_url)  
(a) (b)  
Figure 1. Thermally sprayed samples. (a) and (b) show scanning electron micrographs, back scattered electron contrast, of thermally sprayed coating (top) and substrate made from powder grades II and III, respectively.

Plates made from powders of grades I and II had higher sintered densities. However, they were susceptible to the stresses imposed during thermal spraying and substrate cracking was observed when the same thermal spray parameters were used as for samples of
powder grade III. Therefore, as used for the standard Cr-5Fe-1Y₂O₃ plate material, substrate cooling was introduced to avoid substrate damage and sandblasting to improve coating adherence.

These observations suggested that the performance of sintered substrates made from powders of grades I and II behave very much like the Cr-5Fe-1Y₂O₃ plate material. Figures 1a and 1b show scanning electron micrographs of thermally sprayed substrates with the same nominal powder composition made from powder grades I and III, respectively. The effects of sandblasting as well as the higher substrate density can clearly be seen in figure 1a.

**Enamelling**

Figures 2a and 2b show a cross section of enamelled samples made from powder grades II and III, respectively. The enamel had excellent wetability and penetrated the pores of the samples made from powder grade III. As can be seen in figure 2b, the glass enamel was fully consumed, filling the connected porosity of the metal. No crazing was detected, demonstrating the good thermal expansion fit between the sintered metal and the glass.

![Figure 2. Enamelled samples. (a) and (b) show scanning electron micrographs, back scattered electron contrast, of enamelled substrates made from powder grades II and III, respectively.](image)

**Contact Conductivity**

Contact conductivity measurements of the thermally sprayed substrates made from the different powder grades showed that the substrates with lower density decreased in conductivity with time. However, when samples of similar compositions were made from grade I powder, significantly better performance was observed, figure 3. The rapid increase in resistance was related to the formation of oxides within the pores of the substrate.

Despite the simplified thermal spraying required for the porous samples made from grade III powders, the poor oxidation behaviour and contact conductivity limit their application as materials for HEXIS current collectors.
Figure 3 Contact resistance of pressed, sintered and thermally sprayed samples. The open symbols represent samples made from powder grade III, while the full represent powder grade II.

Scale-Up and Electrochemical Performance

From the extensive list of alloy compositions initially identified, two compositions were selected. They had the best combination of forming characteristics, corrosion resistance and compatibility with the HEXIS protective coatings. Powders of grade II were used and structured plates Ø120 were pressed at Plansee. This first attempt to fabricate the HEXIS current collector by near-net-shaping demonstrated that better use of the chromium powder and significant reduction of machining time was possible.

After thermal spraying the interconnect with the standard Laₐ₀.₈Sr₀.₂MnO₃ protective coating and enamelling the internal surfaces of the heat exchanger, the current collectors were prepared for testing. Figure 4 shows the average performance of a 5-cell stack fitted with near-net-shaped current collectors made from grade II powder. Electrochemical performance stability was identical to that observed in stacks contacted with the conventional Cr-5Fe-1Y₂O₃ plate material.

CONCLUSIONS

This study has demonstrated the feasibility of net shape manufacturing of chromium-based interconnects. The components manufactured by this cost-effective alternative could be integrated as current collectors in the HEXIS stack without any loss in performance. Slight modifications in composition of the conventional Cr-5Fe-1Y₂O₃ alloy were necessary to achieve the required powder pressability. An extensive materials selection effort enabled the identification of powder compositions offering the best combination in pressing and sintering characteristics, oxidation resistance, contact conductivity and compatibility with the different protective coatings involved.
Figure 4 Endurance test performed on a 5-cell stack with near-net-shaped chromium-based current collectors. Testing conditions: temperature=950°C, steam reformed natural gas, steam to carbon ratio=2.5, lambda=3.0, and operating electrical efficiency =35%

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