



A novel method for the preparation of porous zirconia ceramics with multimodal pore size distribution

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Abstract

This work presents a new route of processing porous ceramic materials by vacuum induction melting of metallic ternary alloys from the system Ni–Zr–Y. Following internal oxidation results in an interpenetrating network of nickel and oxide phase consisting of yttria and zirconia. After dissolution of the metallic nickel matrix the oxide phase remains as a stable porous ceramic material with a multimodal pore size distribution. The porosity, pore size distribution and specific surface area can be controlled by alloy composition, solidification conditions and oxidation parameters. © 2013 Elsevier Ltd. All rights reserved.

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1. Introduction

Porous materials are used in a wide range of applications for example as filter materials, heat insulator or catalyst support material. Porous ceramics in particular are used for those purposes as they withstand corrosion even at high temperatures. According to Hirschfeld,¹ porous structures can be classified into fibrous, open or closed celled and membranes. They can be produced by sintering of ceramic powders together with pore forming additives. Such additives can be organic materials or graphite which is pyrolyzed during the sintering process.² Alternatively the pore forming material can be dissolved for example by leaching after the sintering process.³ Another possibility especially for the production of open celled structures is the use of porous preforms like wood⁴ or filter paper.⁵ After infiltration with a preceramic solution such as zirconium-oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$)⁴ the preform is dried, then pyrolyzed and subsequently sintered in order to guarantee structural integrity. The open porosity of the initial preform is directly transferred into a ceramic skeleton. Thus the microstructure of the porous ceramic depends on the pore morphology of the preform. It is also possible to form mixed oxides with this process by using

different solutions for the infiltration process. Alternative production routes are gelcasting⁶ or tape casting methods.⁷

The present work discusses a completely new approach that uses internal oxidation for the production of an oxide structure inside a metallic material.⁸ Internal oxidation as the crucial process step is a well investigated phenomenon described by Wagner in 1959⁹ for binary alloys. He also gave a mathematical description for the internal oxidation of such alloys. He assumed that oxygen diffuses through the metallic matrix into the material where the reaction with the more oxygen affine element takes place. Wagner's theory was successfully applied to a broad variety of binary alloys however it was not able to describe fast internal oxidation of Ni–Al^{10,11} and Ni–Zr¹² alloys. Fast oxygen diffusion along the metal/oxide phase boundaries has to be taken into account in these particular binary systems.

The internal oxidation of ternary alloys is even more complex because interactions between the oxygen affine elements have to be considered. Gesmundo and Niu¹³ as well as Guan et al.¹⁴ predicted the rates of internal oxidation in ternary alloys like Ni–Si–Al. But their models fail to explain the extremely high rates of internal oxidation in Ni–Zr–Y alloys found by Kloss et al.¹⁵ Konrad et al.¹⁶ showed that a continuous oxide network of yttria stabilized zirconia (YSZ) forms during internal oxidation of Ni–Zr–Y alloys. The very high oxygen ion conductivity¹⁷ of the continuous YSZ phase is meant to be the cause for extremely high internal oxidation rates of Ni–Zr–Y alloys. The continuous, interpenetrating YSZ phase is the major path for the oxygen

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diffusion in this system. The amount of Y has a big influence on the oxidation rate and can accelerate the oxidation even if only 0.1 at% are present in an alloy. This correlation is used as basis for the present work.

2. Experimental

2.1. Casting

Ni-alloys with additions of Zr and Y were produced by vacuum induction melting. Purities of the elements were 99.9% for Ni, 99.9% for Y and 99.8% for Zr. For a first casting campaign alloy melts were poured under vacuum into a rectangular copper mold at 25 °C to ingots of about 250 g.

In a second casting series alloy melts were poured under vacuum into ceramic shell molds or a copper mold with the same size. The cylindrical ceramic molds had an inner diameter of 10 mm and were preheated to 300 °C and 1000 °C respectively as described in.¹⁸ Pouring in the cylindrical copper mold was intended to increase cooling and hence solidification rates compared to the ceramic shell molds. Highest cooling rates were obtained by splat cooling of a melt drop between two copper plates. Cooling rates and solidification times were measured with thermocouples with the exception of splat cooling. Splat cooling rates were estimated numerically assuming cooling of a 500 µm nickel plate initially at melting temperature between two copper plates at room temperature. Parameters heat capacities, heat conductivities, heat transfer coefficients, etc. were taken from literature. The numerical calculations were done with Simulation Multiphysics 2012 (Autodesk; San Rafael, USA) and Comsol Multiphysics Version 4.0a (COMSOL; Stockholm, Sweden).

Nominal and measured chemical compositions of the alloys in this investigation are listed in Table 1. The materials used are different hypo- or near eutectic alloys. Earlier investigations show that hypereutectic alloys are very brittle due to their high volume fraction of intermetallic phases. The chosen alloys show good machinability in every state and an oxide volume fraction after internal oxidation of 6–25%. The chemical analysis of the specimens was carried out by energy dispersive X-ray analysis (EDX) in a scanning electron microscope (SEM). To get reliable quantitative EDX data by the ZAF method,¹⁹ compositions of reference samples with various Ni, Zr and Y

Table 1
Composition of alloys ingots from different melting campaigns.

| Nominal (at.%) | Measured | | |
|-------------------|------------|-----------|-----------|
| | Ni (at.%) | Zr (at.%) | Y (at.%) |
| Ni–2Zr–0.1Y | 98.0 ± 0.4 | 1.9 ± 0.4 | 0.1 ± 0.1 |
| Ni–2Zr–0.2Y | 97.4 ± 0.3 | 2.4 ± 0.1 | 0.2 ± 0.1 |
| Ni–5Zr–0.5Y | 93.8 ± 0.4 | 5.7 ± 0.4 | 0.5 ± 0.1 |
| Ni–8Zr–0.2Y | 91.7 ± 0.4 | 8.1 ± 0.3 | 0.2 ± 0.1 |
| Ni–7.7Zr–1.1Y | 91.5 ± 0.4 | 7.5 ± 0.4 | 1.0 ± 0.1 |
| Ni–8.8Zr–0.88Y | 90.4 ± 0.4 | 8.7 ± 0.4 | 0.9 ± 0.1 |
| Ni–8.8Zr–0.2Y | 90.8 ± 0.3 | 9.0 ± 0.2 | 0.2 ± 0.1 |

Table 2
Oxygen partial pressure at different annealing temperatures [20].

| | 800 °C | 1000 °C | 1100 °C |
|-----------------------|-----------------------|-----------------------|----------------------|
| $p(\text{O}_2)$ in Pa | 1.2×10^{-13} | 7.1×10^{-10} | 2.1×10^{-8} |

concentrations were measured with inductive coupled plasma-optical emission spectroscopy (ICP-OES) and glow discharge optical spectroscopy (GDOES). Throughout this work the nominal composition of the initial alloy is used for denomination of specimen cut from the ingot. Losses of the oxygen affine alloying elements Zr and Y during melting and pouring were small.

2.2. Internal oxidation

Bulk samples were cut into pieces, ground with SiC paper grit 1200 and cleaned in ethanol before conducting isothermal oxidation experiments at 800–1100 °C for various times in air and a specially designed quartz tube furnace²⁰ respectively. The oxygen partial pressure in the quartz tube furnace was adjusted by the temperature dependent dissociation of water into a H₂ and O₂. The amount of water vapour is set by an Ar/H₂ as carrier gas flowing through a temperature controlled water bubbler. The furnace permits to vary the oxygen partial pressure $p(\text{O}_2)$ in-between 10^{-6} and 10^{-17} mbar. The oxygen partial pressures for the internal oxidation annealing treatments applied in this work are listed in Table 2. The formation of an external nickel oxide scale can be suppressed by adjusting the oxygen partial pressure below the equilibrium partial pressure for the oxidation of nickel as it is described for example in.²⁰

Sample cross sections of as-cast and internally oxidized specimens were embedded in phenolic resin with carbon filler and ground and polished with diamond paste down to 1 µm grain size. Microstructural investigations were performed with optical microscopy and SEM (1540 EsB Cross-Beam, Zeiss, Oberkochen, Germany).

2.3. Acid leaching

In a third step samples were immersed in acid solutions for various times in order to dissolve nickel and retain a bulk porous ceramic. Dissolution of nickel was investigated on internally oxidized samples of the alloy Ni–7.7–1.1Y poured into a rectangular copper mold to accelerate solidification. Before acid leaching samples were internally oxidized at 1000 °C in air. Leaching experiments were carried out at 70 °C with different diluted acid solutions (HNO₃ with 4, 5.5, and 7 mol/l; HCl with 10 mol/l; HNO₃ + H₅IO₆ mixture with 100 ml 5.5 mol/l HNO₃ + 1.5 ml 50% H₅IO₆ adopted from Nelson^[21]).

Mercury porosimetry was done with a micromeritics auto-pore III in order to measure porosity, specific surface area and pore size distribution of porous ceramics. Additionally water immersion tests were carried out with the porous samples as it is described by Kim et al.³

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