DESIGN AND PRODUCTION OF COARSE-GRAINED AGGREGATES FOR (Nb/Ta)-Al_2O_3 REFRACTORY COMPOSITES

P. Gehre*, T. Zienert, D. Endler, J. Hubálková, E. Storti and C.G. Aneziris
Technical University Bergakademie Freiberg, Germany

ABSTRACT

Modern high-temperature processes require smart refractories with e.g. electric properties beside superior thermo-mechanical behavior. Refractory composites based on refractory metals and refractory oxides are a promising new class of smart materials for high-temperature applications. Here, electrically and thermally conductive and ductile refractory metals such as niobium and tantalum were combined with fine- and coarse-grained oxide ceramic aggregates such as corundum to develop refractories combining functional properties with low shrinkage during sintering, creep resistance at high temperatures, and an improved thermal shock behavior. The shaping of such smart refractories was performed by using ceramic technologies such as castables and pressure slip casting. The first step in developing this new type of refractory materials was the production of pre-sintered coarse-grained (Nb/Ta)-Al_2O_3 refractory composite aggregates. As the aggregate's properties are a function of chemical composition and morphology, they were influenced by the chemistry (type and purity) of the raw materials, the portion of refractory metal (60, 65, and 95 vol.%), sintering temperature, and process technology (extrusion and alginate gelation).

INTRODUCTION

For refractories in general, a wide range of properties such as mechanical strength, thermal shock and corrosion resistance, as well as thermal conductivity must be considered. Additionally, depending on the application, toughness and electrical conductivity are of importance in the case of metal-ceramic composites[1]. In contrast to technologies based on fine powders (fine-ceramic industry or powder metallurgy) which generally present high shrinkage, refractories require coarse grains (aggregates) to produce large components with high resistance against thermal shock, corrosion, and creep.

The properties of the coarse aggregates such as chemistry, morphology, and porosity have a substantial impact on the refractories properties[2]. Also, the applied particle size distribution and water content play an important role in the flowability of castables during the manufacturing process and hence affect the porosity of the final refractory product after sintering.

The combination of a ceramic refractory such as alumina (Al_2O_3) with refractory metals such as tantalum (Ta) or niobium (Nb) produced with refractory technologies opens new fields of applications for refractory composites. The coarse-grained metal-ceramic composites provide electrical and thermal conductivity with low shrinkage during sintering as well as high thermal shock and creep resistance[3].

The production of refractories with coarse grains up to e.g. 5 mm based on metals or metal-ceramic composites requires adequate technology to produce the aggregates. There are different technologies to produce coarse aggregates based on fine raw materials (Fig. 1), e.g. crushing of sintered castables[3] or extruded materials, buildup of aggregates by 3D-printing, gelation of alginates in chloride-containing solutions[4], or granulation by pelletizing[5].

The following work focuses on the production of coarse Ta-/ Nb-Al_2O_3 aggregates by casting and crushing and alginate route, respectively. The influence of the different production routes on the grain size, morphology, and porosity of the resulting aggregates will be investigated.

EXPERIMENTAL

Metal-ceramic aggregates were synthesized using the following routes. (i) Fine powders were wet-mixed and cast into forms, set, dried at 120 °C for 24 h, sintered at 1,600 °C under argon for 2 h, and finally crushed and sieved[5]. (ii) Fine powders were mixed into a slurry with the addition of gelation agents and were added dropwise into an aqueous solution with a solidifying agent. The resulting beads were dried at 50 °C for 24 h, debinded up to 300 °C in air, and sintered at 1,600 °C for 2 h under argon atmosphere[6].

The alumina powder CT9FG (Almatis, Germany) with a d_{90} of 28 µm, niobium powder (99.95 %, EWG Sondermetalle GmbH, Germany) with a d_{90} of 67 µm, and tantalum powder (99.95 %, Haines&Maassen, Germany) with a d_{90} of 68 µm were used for all mixtures. For the castable route, CL370 alumina powder (Almatis, Germany) and the hydratable alumina Alphabond 300 (Almatis, Germany) were used as binders. For the gelation process, sodium alginate as a gelation agent and calcium chloride as a solidifying agent were used.

Castables mixtures with 60/40 vol.% and 65/35 vol.% of niobium/alumina were investigated. Gelation beads with metal contents (niobium and tantalum, respectively) of 60 vol.% and 95 vol.% were synthesized.

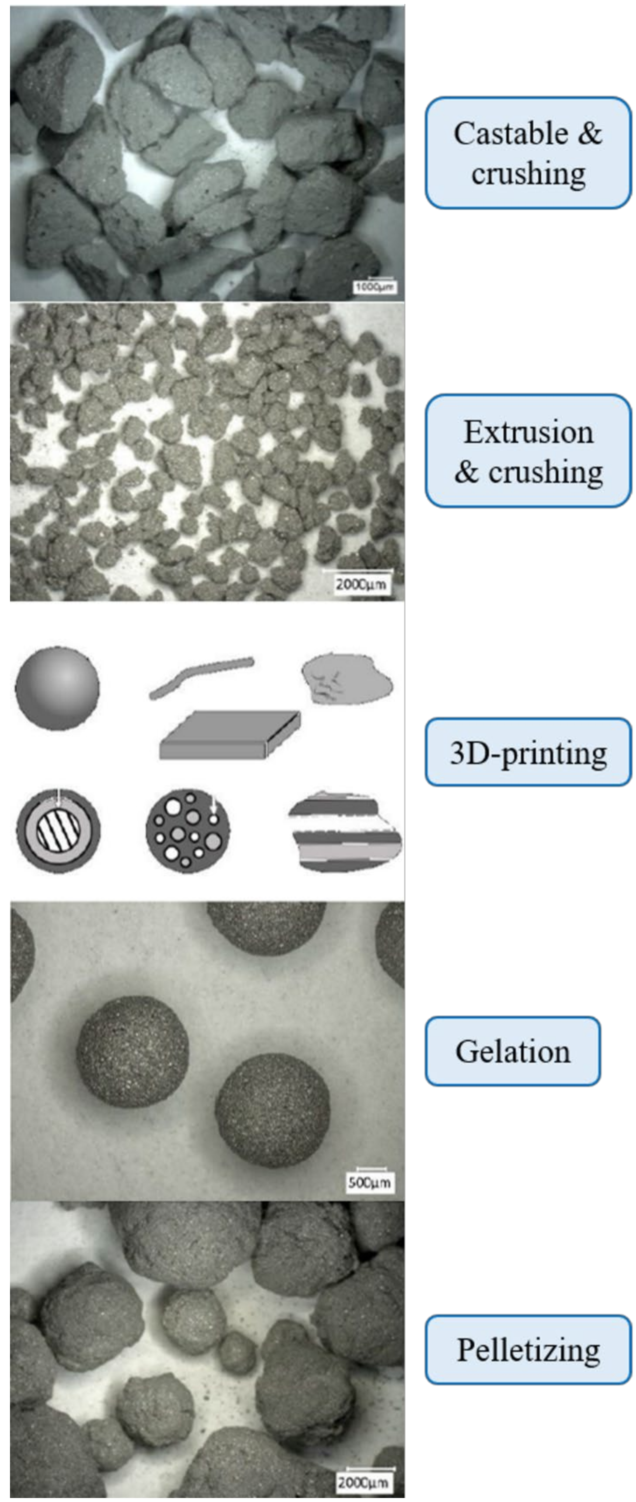

Fig. 1. Technologies to produce coarse aggregates based on fine-grained mixtures

The phase assemblage and the microstructure of the produced aggregates were analyzed using X-ray diffraction, SEM/EDS, and SEM/EBSD. The porosity of the aggregates was investigated by mercury intrusion porosimetry. In addition, the particle size distributions of the obtained sieve fractions (route i) were determined by laser granulometry and the particle's morphology using laser-scanning microscopy.

RESULTS AND DISCUSSION

The typical morphology of an aggregate produced by the casting route and after crushing (i) can be seen in Fig. 2. This image was obtained using a laser-scanning microscope and shows the particle morphology in all three dimensions, which can be described as a typical splintered one.

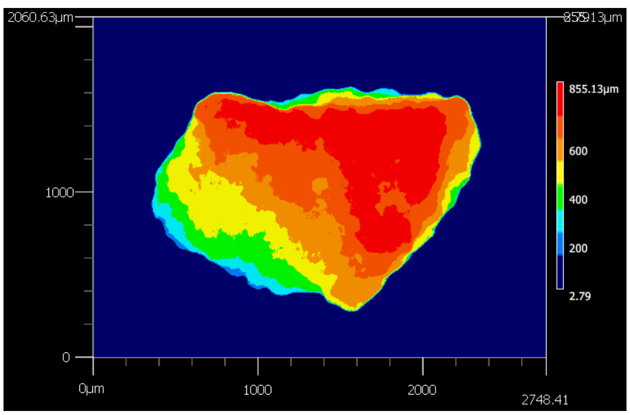

Fig. 2. Typical morphology of an aggregate produced by casting and subsequent crushing[6].

The particle size distributions of the obtained sieve fractions were almost the same for the two castable mixtures 60/40 and 65/35 $Nb-Al_2O_3$. Only the sieve fraction of 45–500 µm showed differences in the maximum particle sizes as can be seen in Fig. 3. The material with 65 vol.% Nb showed a d_{90} of 717 µm and the 60 vol.% one a d_{90} of 325 µm.

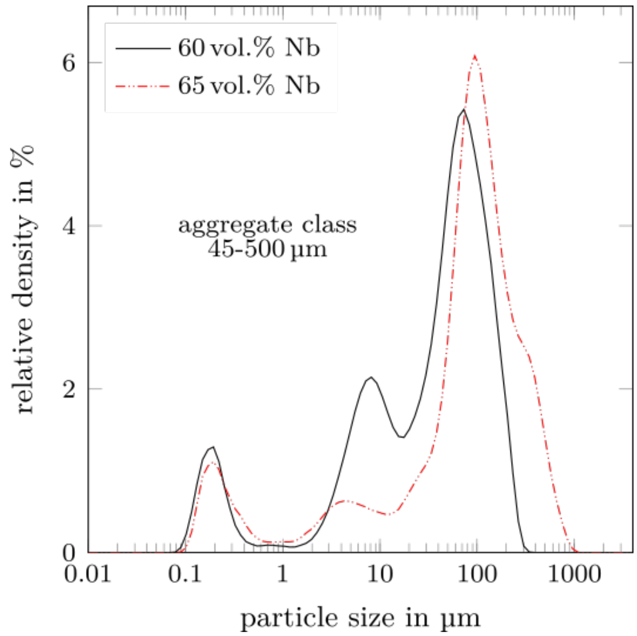

Fig. 3. Particle size distributions of the crushed fractures of the produced 60/40 vol.% and 65/35 vol.% $Nb-Al_2O_3$ castables.

For both materials, a typical open porosity of 15–20 % after sintering (route i) was determined, whereas the open porosity of the produced $Nb-Al_2O_3$ composite beads (route ii) was between 40 % and 47 %. For the latter, the porous surface is visible, as shown in Fig. 4 using the example of the 95 vol.% Nb composition.

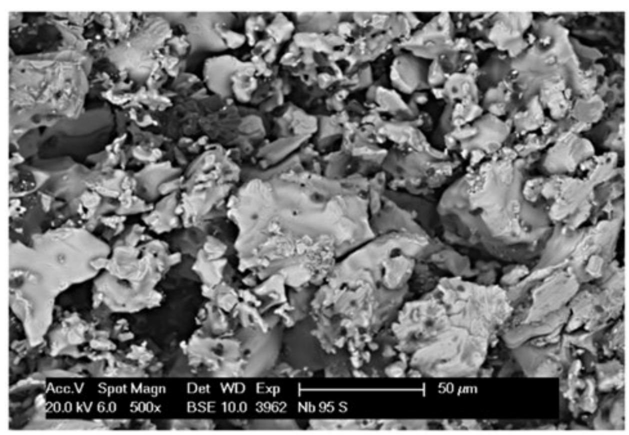

Fig. 4. SEM micrograph of the 95 vol.% Nb $Nb-Al_2O_3$ bead's surface after sintering[7].

Synthesized $Ta-Al_2O_3$ beads with a metal content of 60 vol.% can be seen in Fig. 5. Similarly to the $Nb-Al_2O_3$ composite beads, an open porosity between 42 % and 47 % was determined for these samples.

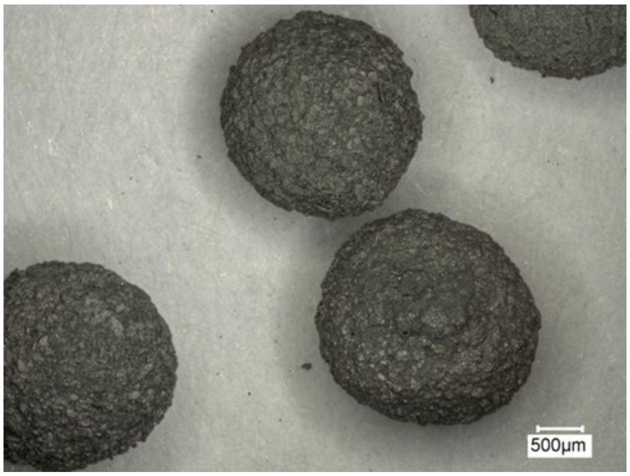

Fig. 5. Photograph of sintered $Ta-Al_2O_3$ composite beads with a tantalum content of 60 vol.%.

CONCLUSION

Two different kinds of aggregates of $Nb-Al_2O_3$ and $Ta-Al_2O_3$ composites with metal contents between 60 vol.% and 95 vol.% were produced: (i) crushed granules and (ii) beads based on an alginate gelation process.

As intended, the morphology of the two kinds of aggregates differs widely. While the crushed aggregates exhibit a splintered shape, the beads show a spherical morphology. Next to the shape, there are significant differences in the open porosity values. Using these aggregates as a coarse-grain fraction in castable mixtures will strongly influence the water demand for achieving sufficient flowability and will also affect the resulting porosity and mechanical strength of the coarse-grained composites. Moreover, such Ta- and $Nb-Al_2O_3$ aggregates can be used to improve the thermal shock resistance, to adjust the thermal conductivity, and to enable the production of coarse-grained refractories with functional properties such as electrical conductivity.

ACKNOWLEDGMENT

The investigation was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 416817512 – FOR 3010, Subprojects TP1 and TP2. The authors thankfully acknowledge the financial support.

REFERENCES

1. J.A. Yeomans, "Ductile particle ceramic matrix composites - Scientific curiosities or engineering materials?", J. Eur. Ceram. Soc., 28 [7] 1543-1550 (2008).

2. J. Fruhstorfer, C.G. Aneziris, "The influence of the coarse fraction on the porosity of refractory castables", J. Ceram. Sci. Tech., 05 [02] 155-166 (2014).

3. T. Zienert, M. Farhani, S. Dudczig, C.G. Aneziris, "Coarse-grained refractory composites based on $Nb-Al_2O_3$ and $Ta-Al_2O_3$ castables", Ceram. Int., 44 [14] 16809-16818 (2018).

4. T. Wetzig, A. Schmidt, S. Dudczig, G. Schmidt, N. Brachhold, C.G. Aneziris, "Carbon-bonded alumina spaghetti filters by alginate-based robo gel casting", Adv. Eng. Mater., 22 [2] 1900657 (2020).

5. M. Siebert, P. Gehre, W. Schärfl, D. Cölle, R. Radünz, C.G. Aneziris, "Processing and development of carbon containing alumosilicate composite materials", Proc. 53rd Int. Colloq. Refract., Aachen, Germany, pp. 233-235 (2010).

6. T. Zienert, E. Endler, J. Hubálková, G. Günay, A. Weidner, H. Biermann, B. Kraft, S. Wagner, C.G. Aneziris, "Synthesis of niobium-alumina composite aggregates and their application in coarse-grained refractory ceramic-metal castables", Materials, 14 [21] 6453 (2021).

7. E. Storti, M. Neumann, T. Zienert, J. Hubálková, C.G. Aneziris, "Metal-ceramic beads based on niobium and alumina produced by alginate gelation", Materials, 14 [19] 5483 (2021).