Reaction hot-pressing and property-composition relationships of modified sialon – boron nitride hetero-modulus ceramics

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Abstract. Hetero-modulus ceramics (HMC) present the combination of a ceramic matrix with inclusions of a dispersed phase with considerably lower values of Young's modulus, resulting in a material with significantly advanced properties. Densified ´-$Si_{6-x}Al_xO_xN_{8-x}$ based HMC materials, with various volume contents of low-modulus α-BN phase and modifiers such as TiN or ZrO_2 in sialon matrix, were prepared by high-temperature reaction hot-pressing in nitrogen atmosphere. The pristine blend composition for reaction hot-pressing consisted of mixed fine powders of Si, Al, B, Ti nitrides and Al, Zr oxides. Statistical design of 2^{5-2} fractional factorial and third-order simplex-grid types was used for the experimental studies to estimate the effects of some technological factors on the densification of hot-pressed products and the property-composition relationships of modified HMC materials.

1. Introduction

Hetero-modulus ceramics (HMC) present an opportunity to combine a ceramic matrix having high Young's modulus (250–600 GPa) with inclusions of a dispersed phase having considerably lower values of Young's modulus (15–50 GPa). The damage tolerance of brittle refractory chemical compounds (oxides, nitrides, carbides, borides etc) under severe thermo-mechanical loads can be greatly enhanced by the addition of low-modulus phases such as graphite or graphite-like α-boron nitride. This materials design approach resulted in the development of the special materials termed "high-*E* – low-*E* composites" [1-3] or "hetero-modulus ceramics" [4-9], which were successfully applied in defence sector industry. The HMC are also known as "soft ceramics", with reference to its another significant advantage, namely the remarkable machinability by conventional tools with a high grade of accuracy that is normally unfeasible with conventional technical ceramics [4, 10].

The materials based on silicon nitride – α-BN compositions became attractive to high-tech designers from the 1960s [11]. The experience gained through the application of the HMC materials was subsequently transferred from spacecraft production (e.g. insulation in electric propulsion thrusters) [6] to metallurgy and machinery (diaphragms for continuous casting, highly loaded brake-shoes, etc) [12]. The high performance and excellent mechanical, thermal and electrical properties of Si_3N_4- and sialon-containing HMC were confirmed by various researchers [13-20].

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High-temperature hot-pressing technique has practically unlimited possibilities for the preparation and modification of HMC in the wide range of high- and low-modulus constituents ratios, including the manufacture of various sialon – BN compositions. However, the fabrication of modified sialon-based HMC by employing one-stage hot-pressing process, which includes the chemical synthesis of sialon phase and physical densification of sintering powder composition in the presence of low-modulus α-BN and transition-metal containing modifiers, has been undertaken for the first time. Therefore, the goal of the present work was to study the particularities of the conjugated physico-chemical processes of synthesis and densification for the ´-$Si_{6-x}Al_xO_xN_{8-x}$-generating compositions during HMC hot-pressing fabrication.

2. Experimental

Commercially available, fine powders of Si_3N_4 (-$Si_3N_4 > 95$, -$Si_3N_4 < 3$, $Si_2ON_2 < 3$ wt.%), AlN (> 99 wt.%) and Al_2O_3 (-$Al_2O_3 > 98$ wt.%) to form ´-sialon matrix, BN (-BN • 97.2, B_2O_3 • 0.1, C • 0.4 wt.%) as a low-modulus constituent, ZrO_2 (-$ZrO_2 > 98.5$ wt.%) and TiN (>99 wt.%) as modifiers were used in this study. The details of high-temperature hot-pressing procedures and measurements of shrinkage, microstructure and physical properties applied to various ´-sialon based compositions were similar to the proceedings, which were described in our earlier works on HMC materials [7-9].

3. Results and discussion

The general phase analysis of sialon-forming Si_3N_4-AlN-Al_2O_3 compositions treated by hot-pressing in nitrogen atmosphere at various temperatures is shown in figure 1.

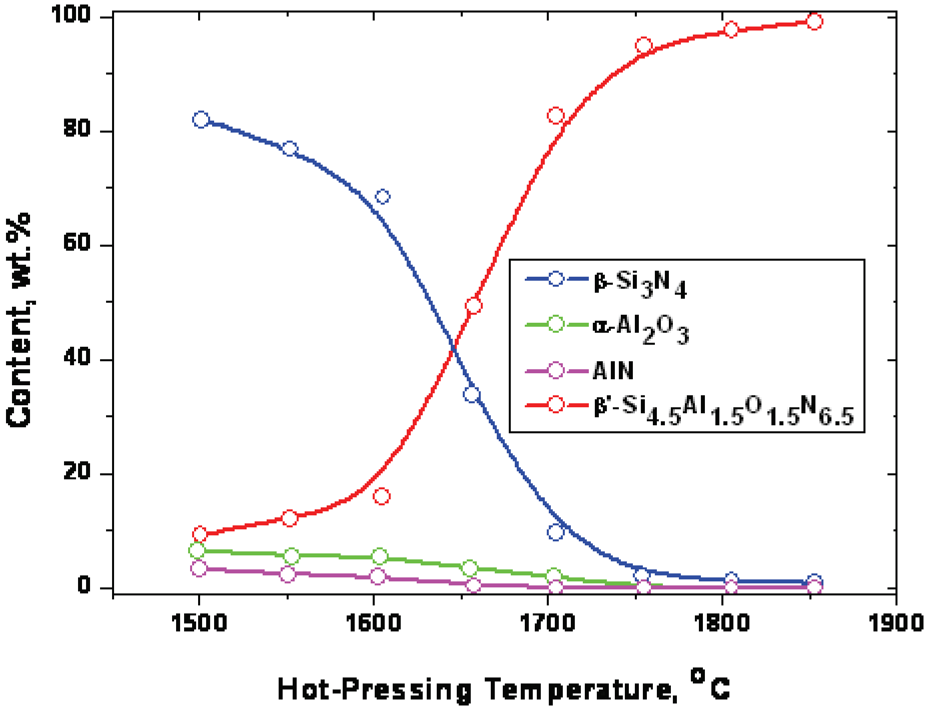

Figure 1. Phase contents vs. hot-pressing temperature for $(2 - x/3)Si_3N_4 + x/3AlN + x/3Al_2O_3$ ($x = 1.5$) reactive compositions (isothermal annealing time – 1 h).

Actually, in the reaction hot-pressed materials residual β-Si_3N_4 is presented by phase with some deviations from the lattice parameters in comparison with a starting material; at that β-Si_3N_4 content increased with increasing the volume fractions of low-modulus constituent α-BN and/or modifier TiN.

More likely, this phase is β'-$Si_{6-x}Al_xO_xN_{8-x}$ with very small value of x forming during hot-pressing operation by the solid state diffusion mechanism, which is acting concurrently with the predominant liquid phase (recrystallization) mechanism of the formation of β'-sialon matrix. In contrast to the effect of TiN, the addition of ZrO_2 results in the absence of β-Si_3N_4 phase in hot-pressed products because of larger amounts of oxinitride liquid melt formed in the treated compositions. In relation to the reaction of sialon synthesis, BN particles play a chemically inert body role contrasting sharply with the modifiers, which are partly transforming to oxinitride TiN_xO_y and N-stabilized cubic γ-ZrO_2 during the treatment.

To evaluate the effects and optimize the values of technological factors such as hot-pressing temperature (X_1) and pressure (X_2), isothermal annealing time (X_3), furnace gas (N_2) pressure (X_4) and blend milling time (X_5) on the densification of hot-pressed products, a 2^{5-2} fractional factorial statistical design [21] was applied. On the basis of regression statistical analysis of the gained experimental data, the following expression for the bulk density of hot-pressed products (Y_1) was estimated:

$$Y_1 = 3.23 - 0.036X_1 - 0.041X_3 - 0.019X_4 - 0.046X_5 - 0.024X_1X_3 - 0.026X_2X_3 \qquad (1)$$

One of the examples for the factorial correlation diagrams obtained from this expression with Design Expert 8 software is presented in figure 2.

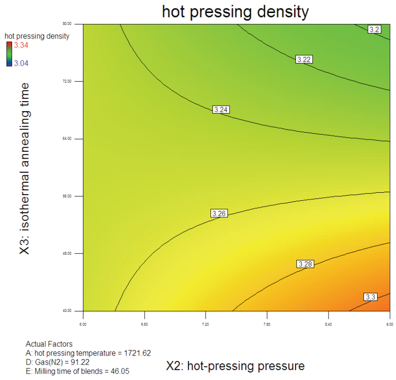

Figure 2. 2D-diagram for the density of 80 vol% ´-$Si_{6-x}Al_xO_xN_{8-x}$ (x = 1.5) – 20 vol% -BN HMC hot-pressed materials vs. hot-pressing pressure – isothermal annealing time factorial correlation.

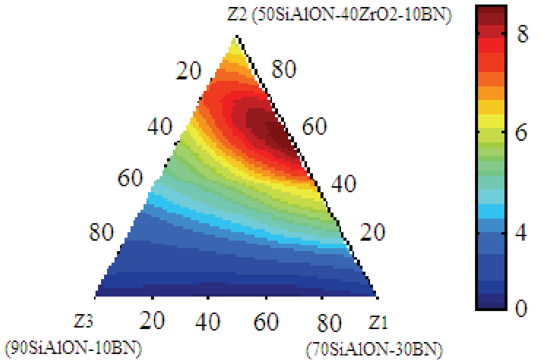

Figure 3. Porosity (in percents) – composition correlations for 90-50 vol% :´-$Si_{6-x}Al_xO_xN_{8-x}$ (x = 1.5) – 0-40 vol% ZrO_2 – 10-30 vol% -BN HMC materials.

Plotting the property-composition relationships $Y_2 = f\,(Z_1, Z_2, Z_3)$ for modified hot-pressed HMC materials, third-order simplex-grid statistical design was employed. The special compositions, in accordance to the design requests, were prepared by hot-pressing at the optimal values of technological factors in two quazi-ternary HMC materials systems (90-70 vol% ´-$Si_{6-x}Al_xO_xN_{8-x}$ (x = 1.5) – 0-40 vol% ZrO_2 – 10-30 vol% -BN and 47.5-77.5 vol% ´-$Si_{6-x}Al_xO_xN_{8-x}$ (x = 1.5) – 2.5-10 vol% TiN – 20-50 vol% -BN) for the calculations of the regression equations

$$Y_2 = \sum_{1\le i\le 3} b_i Z_i + \sum_{1\le i<j\le 3} b_{ij} Z_i Z_j + \sum_{1\le i<j\le 3} g_{ij} Z_i Z_j (Z_i - Z_j) + b_{123} Z_1 Z_2 Z_3\,, \qquad (2)$$

which describe the relationships between the physical properties (Y_2) and values of 3 relative (extreme) ingredient contents (Z_1, Z_2, Z_3) in the materials. The Si_3N_4-AlN-Al_2O_3 mixtures were input to the starting compositions jointly with BN and ZrO_2 (or BN and TiN), taking into account the stoichiometry of fully accomplished sialon formation reaction, to obtain the predetermined matrix volume fraction in a treated material. An example of property-composition diagram plotted for porosity of sialon-BN HMC modified by ZrO_2 is given in figure 3. On the basis of obtained experimental data for ZrO_2 and TiN modified materials, the diagrams on heat capacity, thermal conductivity, electric resistance, bending and compression strengths, Young's and shear modulus in different directions to the axis of hot-pressing were plotted.

These diagrams can be used in HMC design for materials engineering analysis, optimization of physical properties and manufacture of compositions with predetermined high-performance characteristics.

4. Conclusions

One-stage hot-pressing process to manufacture modified sialon-BN HMC materials was realized practically. The synthesis of ´-$Si_{6-x}Al_xO_xN_{8-x}$ by reaction hot-pressing in the presence of low-modulus constituent α-BN and modifiers such as ZrO_2 and TiN was studied. To fabricate the densified products of HMC, hot-pressing technological factors were optimized by applying a 2^{5-2} fractional factorial statistical design. On the basis of 3-component simplex-grid statistical design, some property-composition diagrams for the modified sialon-BN HMC were plotted and analyzed.

5. References

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