

The equilibria in the AlN–Al₂O₃–Y₂O₃ system – thermodynamics and neutron diffraction

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Abstract. The importance of aluminum nitride (AlN) stems from its application in microelectronics as a substrate material. Ytria (Y₂O₃) is the best additive for AlN sintering, and it has been shown that AlN densifies by a liquid-phase mechanism, where the surface oxide, Al₂O₃, reacts with the oxide additive, Y₂O₃, to form a Y–Al–O–N liquid that promotes particle rearrangement and densification. Construction of the phase relations in this multicomponent system is becoming essential for further development of AlN. The ternary phase diagram of AlN–Al₂O₃–Y₂O₃ was thermodynamically modeled and verified experimentally using in situ high-temperature neutron diffractometry. The ternary phase diagram of AlN–Al₂O₃–Y₂O₃ has been constructed for the first time in this work.

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Sintering of AlN with the addition of Y₂O₃ occurs in the presence of a liquid phase [1]. The amount of liquid and the phase evolution at a selected sintering temperature can be predicted using equilibrium diagrams.

To date, there is little information on the ternary AlN–Al₂O₃–sintering additives system [2]. To calculate reliable ternary, quaternary, and higher order metallic and ceramic phase diagrams, a thermodynamic description of the binary phase diagrams is needed and a thermodynamic model that can extrapolate binary data reliably into ternary and higher-order systems [3]. This is commonly done for metals where the thermodynamic data are more readily available. For ceramic systems, thermodynamic data are very sparse. Furthermore, measurements are very difficult considering the high temperatures involved.

A system is at equilibrium when its Gibbs energy is at a minimum. If we could calculate the Gibbs energy of all the possible phases of a system at a specified temperature as a function of composition it would be a simple matter to

select the combination of phases, which provides the lowest value of Gibbs energy. By definition these would be the equilibrium phases for the system at that temperature. By repetition of these calculations for the number of temperatures, the phase boundaries of the system can be determined and the phase diagram can be constructed. Once the binary subsystems have been analyzed by a coupled thermodynamic/phase diagram analysis, the phase diagram of a ternary or a quaternary systems can usually be calculated [5]. Binary diagrams of Al₂O₃–Y₂O₃, AlN–Al₂O₃, and AlN–Y₂O₃ were thermodynamically modeled. The obtained Gibbs free energies of components, stoichiometric phases and solution parameters were used for the calculation of isothermal sections and liquidus surface of AlN–Al₂O₃–Y₂O₃ system.

1 Experimental procedure

To determine the phase evolution in AlN–Al₂O₃–Y₂O₃ system, the neutron diffraction patterns were monitored in situ at elevated temperature using the DUALSPEC high-resolution powder diffractometer, C2, at the NRU reactor of Atomic Energy of Canada Limited (AECL), Chalk River Laboratories. The diffractometer is an 800-channel position sensitive detector that spans 80° in scattering angle, 2 θ . The wavelength, λ , of the neutron beam was calibrated by measuring the diffraction pattern of a standard powder of alumina obtained from the National Institute of Standards and Technology. $\lambda = 1.33(1)$ Å and 2 θ range from 8° to 88° were used in this experiment. The diffractometer was equipped with a tantalum-element vacuum furnace capable of reaching temperatures as high as 2000 °C.

AlN (grade F), Y₂O₃ (grade 5600) and Al₂O₃ powder, (grade A16-SG), were mixed in various stoichiometric amounts. Table 1 and Fig. 1 show the composition of these samples. It can be seen from this figure that these compositions were selected carefully to be close to the phase boundaries in order to critically verify the thermodynamic findings. In situ neutron diffraction was performed during heating and cooling of these samples by monitoring the changes in the

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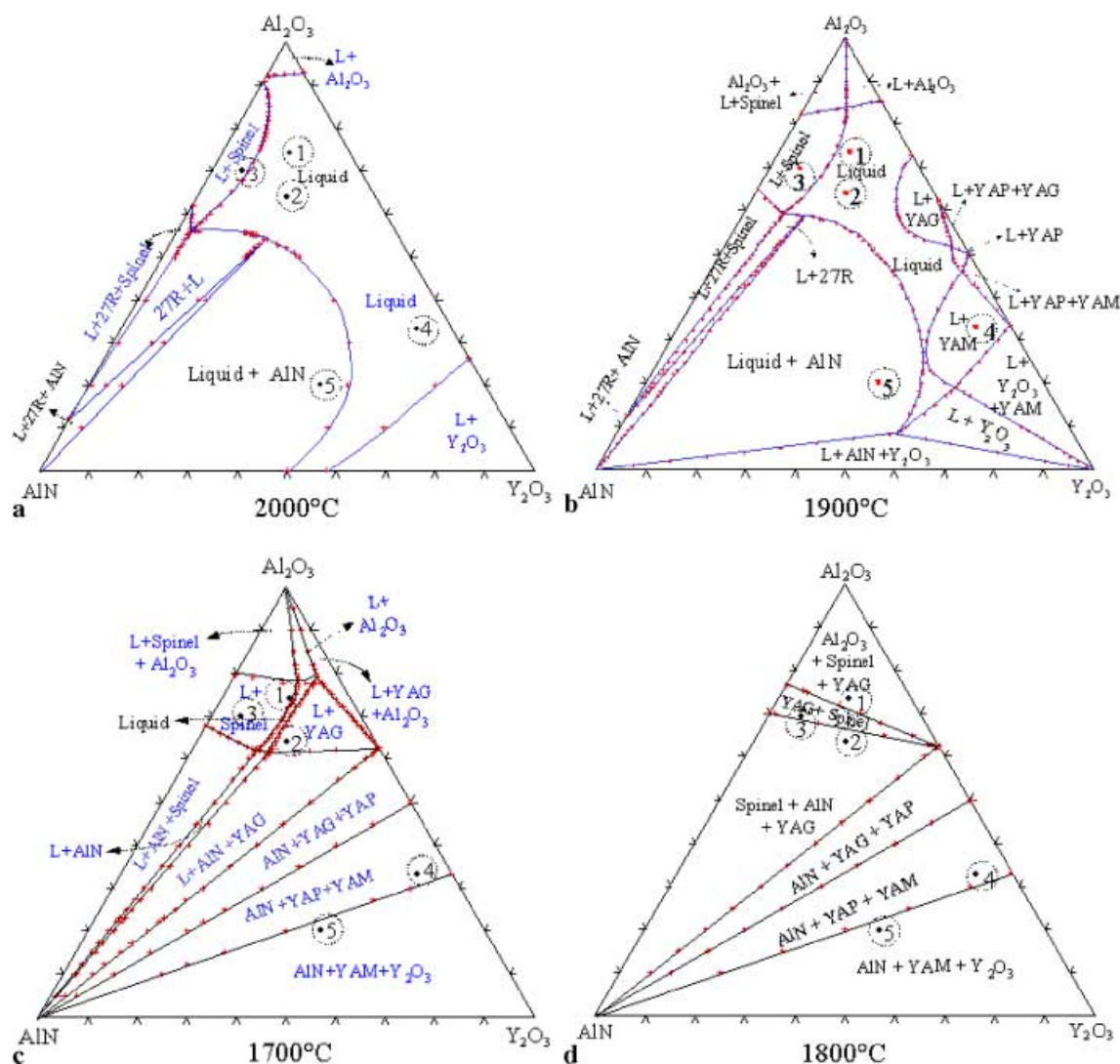


Fig. 1. AlN-Al₂O₃-Y₂O₃ isothermal sections at different temperatures with the five investigated ternary compositions. Where YAG: Y₃Al₅O₁₂, YAP: YAlO₃, YAM: Y₄Al₂O₉, 27R: Al₃O₃N₇ and spinel is γ -alonn

Table 1. The chemical composition of the studied samples

Composition	AlN (mol%)	Al ₂ O ₃ (mol%)	Y ₂ O ₃ (mol%)
1	12	74	14
2	17.5	64	18.5
3	24	70	6
4	7	33	60
5	33	20	47

diffraction peaks and the diffraction angles. In this paper composition 1, only, will be discussed.

A neutron diffraction spectrum for each sample was collected at room temperature to form the reference for any reactions taking place upon heating. The evolution of the reactions was followed by increasing the temperature in steps, and maintaining it for 120 min to ensure that the reaction was complete. Also cooling was carried out incrementally to detect the crystallization as well as the stability of each phase. Heating and cooling profiles were determined for each sample according to critical points, which were predicted by

the thermodynamic calculations. The samples were heated in flowing nitrogen gas to prevent the decomposition of AlN.

2 Results

Diffraction patterns obtained during heating and cooling of composition 1 are shown in the following figures. The patterns are shifted by a suitable offset for better comparison. The peaks are identified by markers as given in legend of each figure, and will be discussed and compared with the thermodynamic findings in this section. The effect of thermal expansion was observed in all the samples when the peaks shifted to lower and higher diffraction angles due to heating and cooling, respectively.

The reaction of this composition (12 mol % AlN, 74 mol % Al₂O₃ and 14 mol % Y₂O₃) during heating the sample from room temperature until 1900 °C is illustrated in Fig. 2. AlN peaks were identified as a hexagonal unit-cell (space group $P6_3mc$, $a = 3.112(0)$ Å and $c = 4.978(0)$ Å), while Al₂O₃ peaks and Y₂O₃ peaks were identified using a Rhombo-

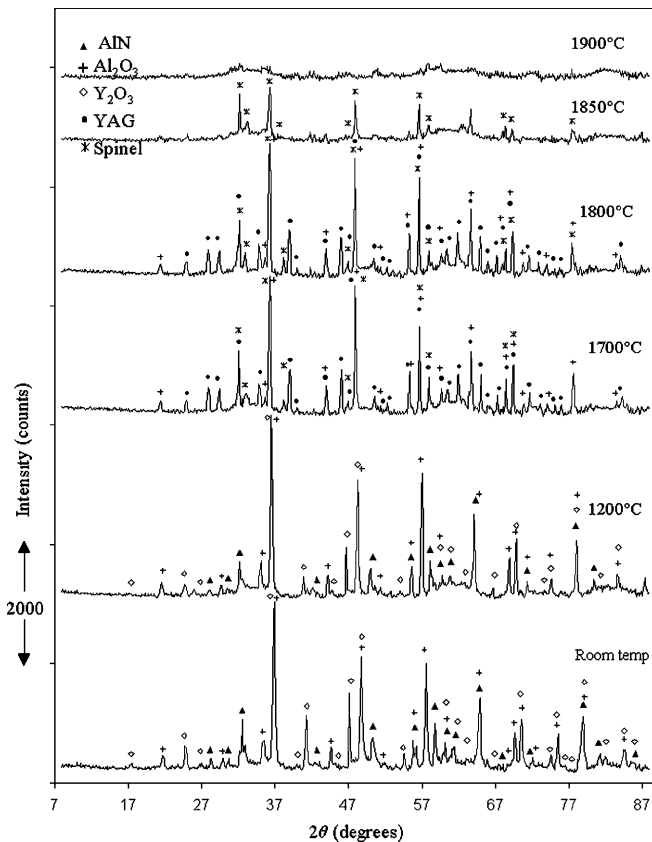


Fig. 2. Neutron patterns during heating of composition 1

hedral unit-cell (space group $R3c$, $a = 4.759(0)$ Å and $c = 12.992(0)$ Å) and cubic unit-cell (space group $Ia3$, $a = 10.608(7)$ Å) respectively.

Increasing the temperature to 1200 °C did not introduce any change in the neutron diffraction pattern collected at this temperature. This indicates no reaction took place in this temperature range. The first changes are visible when comparing the neutron diffraction patterns at 1200 °C and that at 1700 °C, where additional peaks appear. The new peaks were found to belong to YAG and spinel phases. YAG peaks were indexed as a cubic unit-cell (space group $Ia3d$, $a = 12.016(3)$ Å) [4] and spinel peaks were indexed as a cubic unit-cell (space group $Fd3m$, $a = 7.9435(2)$ Å) [6]. Unlike Al_2O_3 diffraction peaks, Y_2O_3 peaks were not observed at 1700 °C, this means that all the 14 mol% Y_2O_3 reacted to produce YAG phase, whereas residual Al_2O_3 shows incomplete reaction to form spinel. This is consistent with the ternary phase diagram shown in Fig. 1d where composition 1 lies in the three-phase-region of Al_2O_3 , spinel and YAG. Cheng et al. also observed incomplete reaction between Al_2O_3 and AlN at 1650 °C for 6 h. They noticed an increase in the amount of spinel with increasing time from 60 min to 6 h [7] Moreover, Yawei et al. [8] concluded that it is difficult to produce spinel by reaction sintering below 1650 °C. Upon heating from 1700 °C to 1800 °C, no difference in the diffraction patterns was observed. Neutron diffraction patterns were acquired at higher temperatures to detect the liquid formation and melting of this sample. At 1850 °C YAG peaks were not observed, whereas spinel peaks were present. Since no other peaks were present at this temperature, thus it can be

concluded that liquid formation started between 1800 °C and 1850 °C. This is consistent with the isothermal section calculated at 1800 °C and shown in Fig. 1c. It can be seen from Fig. 2 that this composition lost crystallinity in the diffraction pattern acquired at 1900 °C. This shows that the sample melted between 1850 °C and 1900 °C, which is consistent with the calculated isothermal section at 1900 °C and shown in Fig. 1b.

Figure 3 shows the cooling cycle for composition 1. It can be seen that spinel was fully crystallized at 1850 °C, confirming that the liquidus point is in the temperature range of 1850 °C to 1900 °C. However the diffraction pattern collected at 1800 °C did not show YAG peaks as in the 1800 °C pattern collected during heating. In general, it was noticed that the peaks in the cooling cycle are weaker than those collected during heating, due to shrinkage of the sample because of melting, also, the background of the patterns collected during cooling was higher than those collected during the heating cycle. In any case, YAG peaks were noticed to have lower counts than those of the spinel phase. This may have contributed to the loss of YAG peaks in the background of the pattern at 1800 °C. By cooling to 1400 °C, decomposition of the spinel phase had occurred. This is evident by the new peaks of AlN and Al_2O_3 detected at this temperature. YAG peaks were also observed in the diffraction pattern collected at 1400 °C. The same phases were found in the diffraction patterns collected at 1000 °C with higher counts of AlN and Al_2O_3 peaks indicating more decomposition of spinel phase upon cooling. Comparing the patterns of 1000 °C and that collected at room temperature reveals that they are similar.

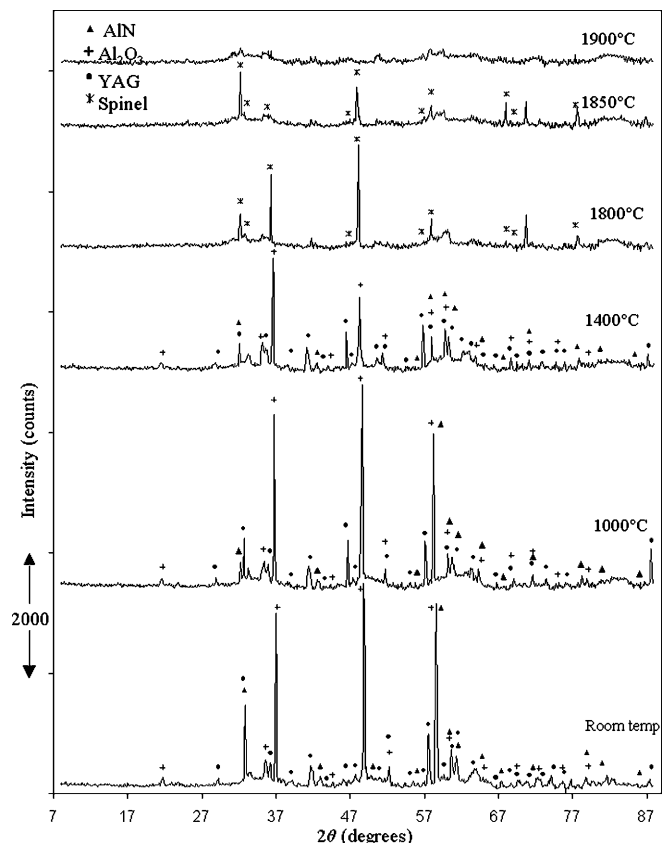


Fig. 3. Neutron patterns during cooling of composition 1

This sample is composed of AlN, YAG and Al₂O₃ at room temperature.

3 Conclusions

- High temperature neutron diffractometry has permitted real time measurement of the reactions involved in AlN-Al₂O₃-Y₂O₃ ternary system, especially to determine the temperature range for each reaction, which would have been impossible to establish ex situ.
- Thermodynamic calculations of AlN-Al₂O₃-Y₂O₃ agree with the in situ neutron diffraction results.
- There is no reaction between AlN and YAG, YAP, YAM or Y₂O₃ which supports the thermodynamic findings.

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