Research Journal of Applied Sciences 8 (5): 271-277, 2013
ISSN: 1815-932X

Experimental Study of Phase Relations in the ZrO_2-Nd_2O_3-Y_2O_3 System

L. Kastrati, N. Syla, G. Nafezi and N. Hasi
Departament of Physics, University of Prishtina, Nena Tereze Nr 5,10000 Prishtina, Kosova

Abstract: The aim of this study is to investigate phase equilibria in the ZrO_2-Nd_2O_3-Y_2O_3 System in the temperature range 1250-1600°C for the Nd_2O_3 rich compositions and to study transformations of three phase assemblage consisting of the Nd_2O_3 hexagonal phase A, monoclinic phase B and pyrochlore under increasing temperature. The samples were characterized by means of X-Ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM/EDX) and Differential Thermal Analysis (DTA). The results of XRD show that at 1250 and 1400°C the equilibrium phases are B+Pyr and probably Nd_2O_3-A is also present in small amount (~1%). At 1600°C equilibrium phases are Flu+Nd_2O_3-A. Therefore, two phase transformations occur in the range 1400-1600°C. DTA experiment was performed in range 25-1700°C and two phase transformations have been found: Pyr →Flu at ~1471°C and B→A at ~1608°C. This was confirmed by XRD and SEM/EDX.

Key words: ZrO_2-Nd_2O_3-Y_2O_3 System, phase equilibria, XRD, DTA, X-rays

INTRODUCTION

In the second half of the last century nickel based superalloys were found to be reliable materials for high temperature applications, especially for blades in gas turbines. To increase thermal conversion efficiency, advanced gas-turbines are developed for high operation-temperatures. Hot section components working within the combustion system of gas turbines are designed so that they can survive under elevated temperatures, thermal stress, thermal shock and severe corrosion. To extend the temperature range they have to be protected by a ceramic layer which creates temperature gradient between hot gas and surface of superalloy. This ceramic layer is called Thermal Barrier Coating (TBC). The use of TBC makes it possible to increase significantly the gas temperature without increasing temperature of the alloy thus resulting in improvement of engine efficiency. A substantial number of reviews on various aspects of TBCs are found in the recent literature (Evans *et al*., 2002; Padture *et al*., 2002; Clarke and Levi, 2003; Nicholls, 2003; Schulz *et al*., 2003; Cao *et al*., 2004; Levi, 2004).

The generic constituents of a Thermal Barrier System for superalloy component are illustrated in Fig. 1, along with summary of required properties for performance and durability (Levi, 2004). The baseline thermal barrier or top coat is a 125-250 μm layer of porous ZrO_2 partially stabilized with 7±1 wt. % Y_2O_3 (7YSZ), applied by either Air-Plasma Spray (APS) or Electron-Beam Physical Vapour Deposition (EB-PVD). The material of TBC presents metastable phase with tetragonal structure containing more Y_2O_3 than the equilibrium composition. Environmental protection relies primarily on a thin (<10 μm), dense Al_2O_3 layer of Thermally Grown Oxide (TGO), formed during service by thermal oxidation of the underlying metal. Concepts for additional environmental barriers exist, e.g. for protection against the attack of molten deposits but none has become part of the baseline system so far. Because superalloys are optimized for mechanical performance, their surfaces must be modified chemically to promote the formation of a stable, adherent TGO. These modified surfaces or Bond Coats (BCs) are classified into two major groups: single phase β-(Ni, Pt)Al (B2), applied by electrodeposition of Pt and subsequent aluminizing by some form of Chemical Vapour Deposition (CVD) with concurrent interdiffusion and overlay two-phase (γ+β/γ) MCrAlY's, applied by Low Pressure Plasma Spray (LPPS) or by EB-PVD (Levi, 2004).

The ZrO_2-Nd_2O_3-Y_2O_3 System is of interest because of various industrial applications of Yttria Stabilized Zirconia (YSZ) such as Thermal Barrier Coatings (TBC) and fixation of radioactive wastes. It has been shown that RE_2O_3 (RE = Rare Earth Elements) additives decrease the thermal conductivity and resistance to sintering of YSZ making it a promising material for TBC (Levi, 2004). Nd_2O_3 has been studied in several works (Khor and Yang, 1997; Rebollo *et al*., 2003; Xu *et al*., 2006a, b) as a possible stabilizer of tetragonal ZrO_2 YSZ. The compound $Nd_2Zr_2O_7$ with pyrochlore structure that is stable up to ~2300°C is also a promising candidate for TBC due to its low thermal conductivity (Xu *et al*., 2006a, b). The stabilized ZrO_2 with fluorite structure is a possible

Corresponding Author: L. Kastrati, Department of Physics, University of Prishtina, Nena Tereze Nr 5,10000 Prishtina, Kosova

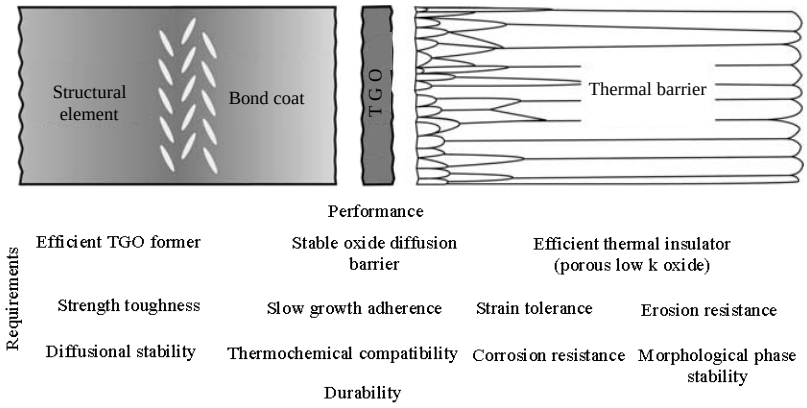

Fig. 1: Schematic of Thermal Barrier System showing constituent elements and major requirements for performance and durability (Levi, 2004)

candidate material for fixation of nuclear wastes. It should be mentioned that the amount of Nd_2O_3 in the fission products is relatively high (Hinatsu and Muromura, 1986). Therefore, the solubility of Nd_2O_3 in fluorite phase and phase relations in the ZrO_2-Nd_2O_3-Y_2O_3 System are important issue for nuclear waste fixation. According to Xu *et al.* (2004, 2006a, b) tetragonal YSZ co-doped with Nd_2O_3 has excellent mechanical properties in combination with high phase stability and interesting as advanced structural ceramic.

Phase equilibria in the ZrO_2-Nd_2O_3-Y_2O_3 System were experimentally studied by Hinatsu and Muromura (1986) at 1600°C. However, researchers concentrated on the determination of stability of fluorite phase while other equilibria were not studied in detail. Phase equlibria in the ZrO_2 rich corner at Y_2O_3 content 0.5-1.5 mol % and Nd_2O_3 content 0.5-2 mol % at 1450°C were investigated by Xu *et al.* (2004, 2006a, b). A more detailed investigation of phase diagram was undertaken by Fabrichnaya *et al.* (2011) in the range 1250-1600°C. The aim of this study is to investigate the phase relations in the ZrO_2-Nd_2O_3-Y_2O_3 system in the temperature range 1250-1600°C for the Nd_2O_3 rich compositions and to study transformations of three phase assemblage consisting of the Nd_2O_3 hexagonal phase A, monoclinic phase B and pyrochlore under increasing temperature.

MATERIALS AND METHODS

Sample preparation: Sample were synthesized from precursor solution in a similar way to that described by Fabrichnaya *et al.* (2011). The zirconium acetate solution in acetic acid, $Zr(CH_3COO)_4$, $Nd(NO_3)_3$. $6H_2O$ and $Y(NO_3)_3$. $6H_2O$ were adopted as the starting chemicals. In the first step, the $Nd(NO_3)_3.6H_2O$ and $Y(NO_3)_3.6H_2O$ were dissolved in distilled water and the initial zirconium acetate solution was diluted. After the determination of the oxide yield of the prepared solutions, they were mixed according to the selected rations to obtain ~3 g of sample. The concentrations were 1.14 mol L^{-1} for ZrO_2, 0.4 mol L^{-1} for $YO_{1.5}$ and 0.4 mol L^{-1} for $NdO_{1.5}$. The resultant precursor solution was dropped from the buret at a low speed (around 1 mL min^{-1}) into a big beaker containing about 500 mL of deionised water. To maintain the pH value above 9.0 ammonium hydrate was added. The precipitation occurred during dropping and stirring. The process occurring during co-precipitation is formation of hydroxides according to reactions:

$$Zr^{4+} + 4OH^- \rightarrow Zr(OH)_4$$

$$Y^{3+} + 3OH^- \rightarrow Y(OH)_3$$

$$Nd^{3+} + 3OH^- \rightarrow Nd(OH)_3$$

The obtained suspension was heated for 1-2 h at 60°C. The precipitate was then filtered and dried at 80°C. After drying of the sample, small part of it was dissolved in H_2SO_4 and concentration was determined by method of Inductively Coupled Plasma (ICP). The composition of filtrates was also determined by ICP with an accuracy of ±2%. The ICP analysis of filtrate shows that co-precipitation was successful because filtrate contain very small amount of Zr^{4+}, Y^{3+} and Nd^{3+} cat ions, respectively 7.7 10^{-7}, 2.2 10^{-7} and 5.5 10^{-6} mol L^{-1}.

During pyrolysis at 800°C proceeding for 3 h in air, hydroxides transform to oxides releasing water according to reactions:

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

$$2Y(OH)_3 \rightarrow Y_2O_3 + 3H_2O$$

$$2Nd(OH)_3 \rightarrow Nd_2O_3 + 3H_2O$$

Sample treatment and characterisation: The pyrolysed powder was pressed into cylindrical pellets and sintered in air at temperatures of 1250, 1400 and 1600°C in Pt-crucibles to obtain the equilibrium microstructure. The duration of heat treatments was 336 h at 1250°C, 192 h at 1400°C and 96 h at 1600°C. The samples were than analyzed by XRD, SEM/EDX and DTA.

The XRD patterns of powdered specimen were recorded using Cu-K radiation. Lattice parameters for phases, their volume fractions and grain size were calculated by Rietveld refinement. The microstructure of sintered samples was examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) spectroscopy was employed to obtain the compositions of the phases in the equilibrium state. Differential Thermal Analysis (DTA) was used to investigate the phase transformation up to temperature of 1700°C.

RESULTS AND DISCUSSION

The composition of sample studied in present research is shown on phase diagram calculated in research of Fabrichnaya *et al.* (2011) (Fig. 2).

The results of XRD investigations of sample heat treated at 1250, 1400 and 1600°C are shown in Fig. 3-5, respectively. At 1250 and 1400°C the equilibrium phases are B+Pyr and probably Nd_2O_3-A is also present in small amount (~1%). At 1600°C equilibrium phases are Flu+Nd_2O_3-A. Therefore, two phase transformations occur in the range 1400-1600°C.

The results of DTA investigations are presented in Fig. 6. DTA experiment was performed in range 25-1700°C and indicated two heat effects at 1471 and 1608°C. XRD after DTA indicated two phases A and F. Therefore, there are two transformations occurring in 1400-1700°C: Pyr→F and B→A. XRD after DTA and after heat treatment at 1600°C indicated the same phases F+A. Therefore, transformations are completed already at 1600°C; small difference with result of DTA (1608°C) is due to overheating effect and it is within uncertainly of method. To attribute transformations to heat effects observed in DTA study, additional DTA experiment was performed by heating sample up to 1500°C followed by keeping of isothermal regime at 1500°C for 2 h and then cooling. XRD of sample after this DTA experiments is shown in Fig. 7. XRD indicated phases B and F (A~1%). Therefore, the first heat effect at 1471°C is due to transformation of Pyrochlore to Fluorite and the second one at ~1600°C due to transformation of B to A.

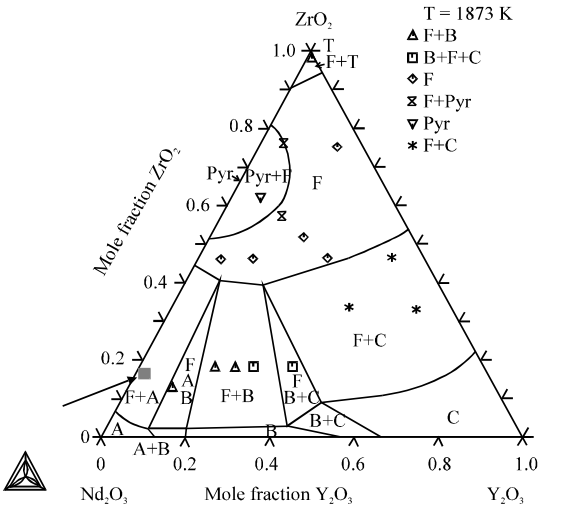

Fig. 2: Phase diagram of ZrO_2-Nd_2O_3-Y_2O_3 System at 1600°C with composition studied in present research 18.18 mol % ZrO_2, 79.09 mol % Nd_2O_3 and 2.73 mol % Y_2O_3

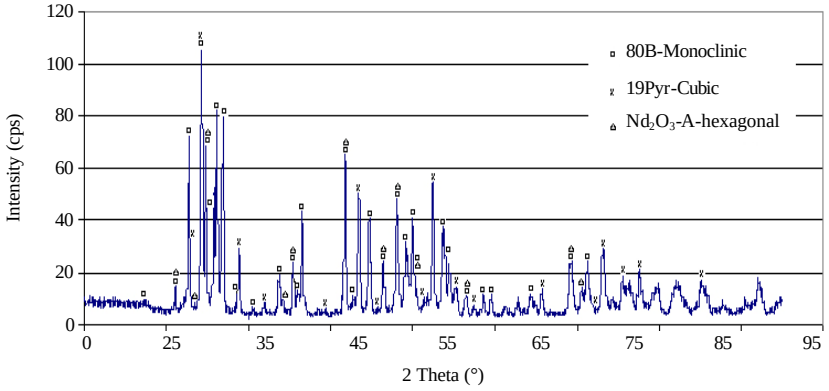

Fig. 3: XRD results at 1250°C

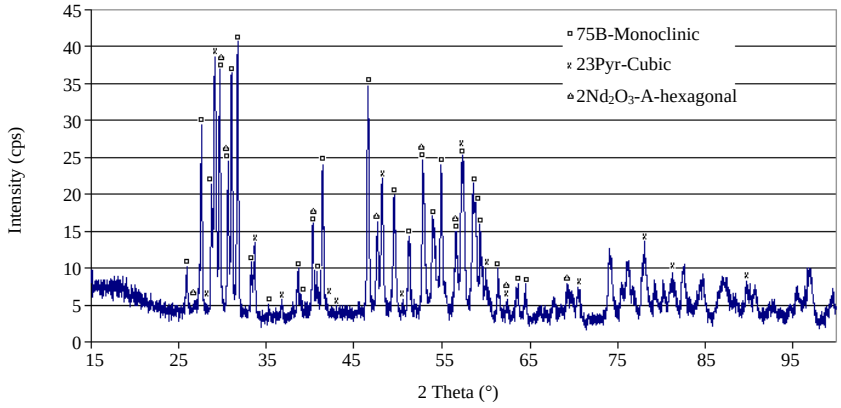

Fig. 4: XRD results at 1400°C

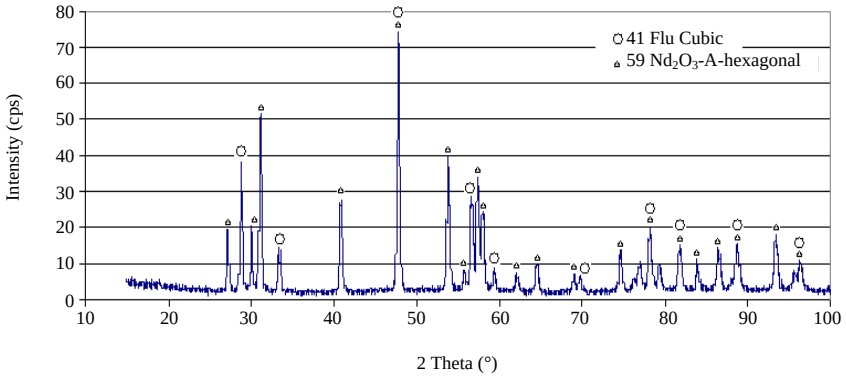

Fig. 5: XRD results at 1600°C

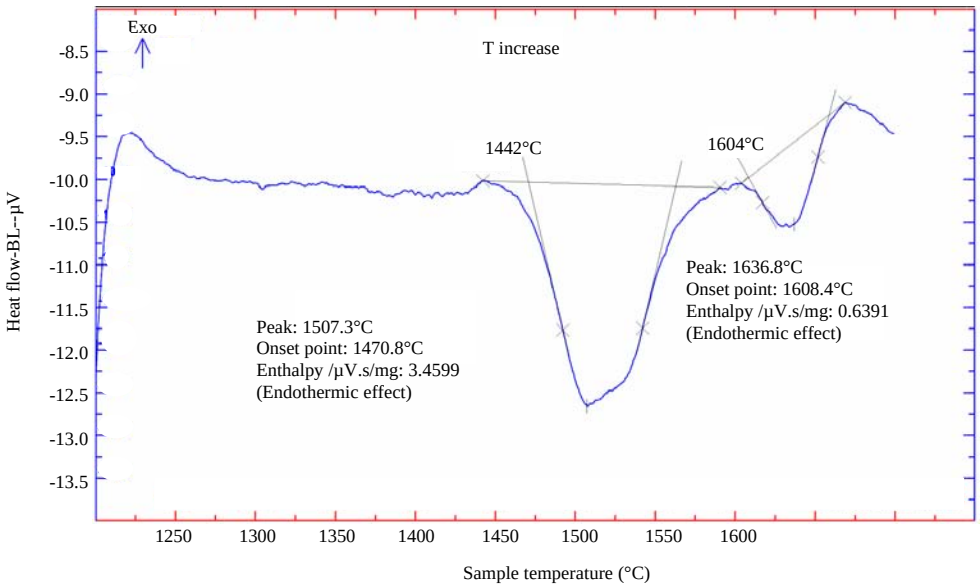

Fig. 6: Result of DTA investigation in the range 25-1700°C

The results of SEM investigation of samples are presented in the Fig. 8 and 9. In Fig. 8, bright and dark areas are observed. Bright areas present B (Monoclinic) phase and dark areas present Pyrochlore phase. In the

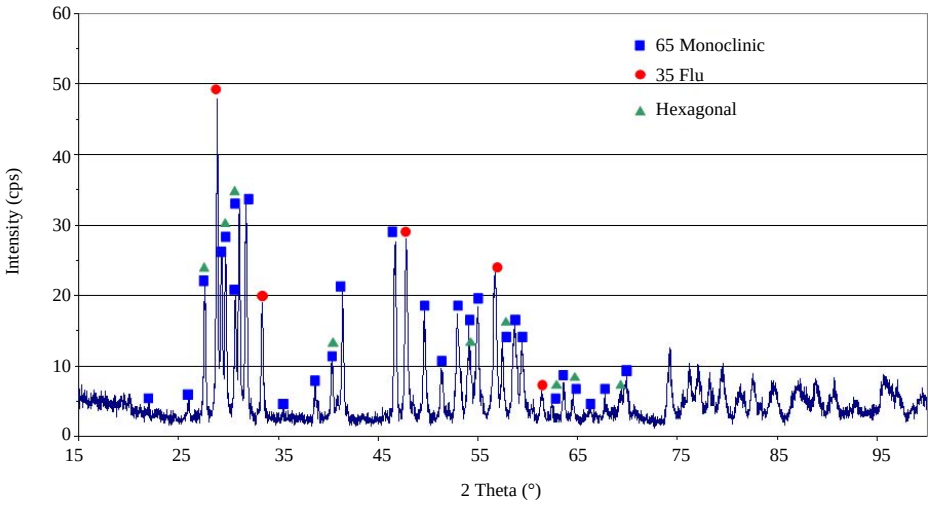

Fig. 7: XRD results for sample Nd23 after DTA heating up to 1500°C

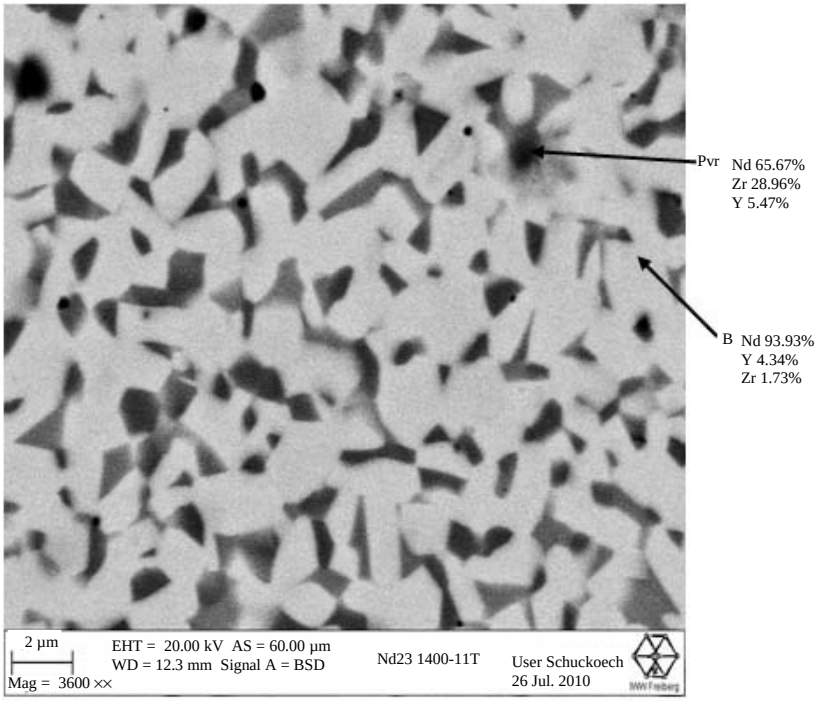

Fig. 8: SEM image sample heat treated at 1400°C; compositions are determined by EDX

Fig. 9 bright areas present A (hexagonal) phase and dark areas present Fluorite phase. Hexagonal phase A forms characteristic microstructure (needle like). Similar microstructure was observed by Wang (2006) for Nd_2O_3 rich sample in the ZrO_2-Nd_2O_3 System. It should be mentioned that similar microstructure was observed for the ZrO_2-La_2O_3-Y_2O_3 System (Fabrichnaya, personal communication). Changing temperature from 1400-1600°C Pyrochlore transformed to Fluorite (Pyr→F) and Monoclinic B phase transformed to Hexagonal structure (B→A). Compositions of phases determined by EDX are presented in the Fig. 7 and 8 and they are consistent with calculated phase diagram data of Fabrichnaya *et al.* (2011).

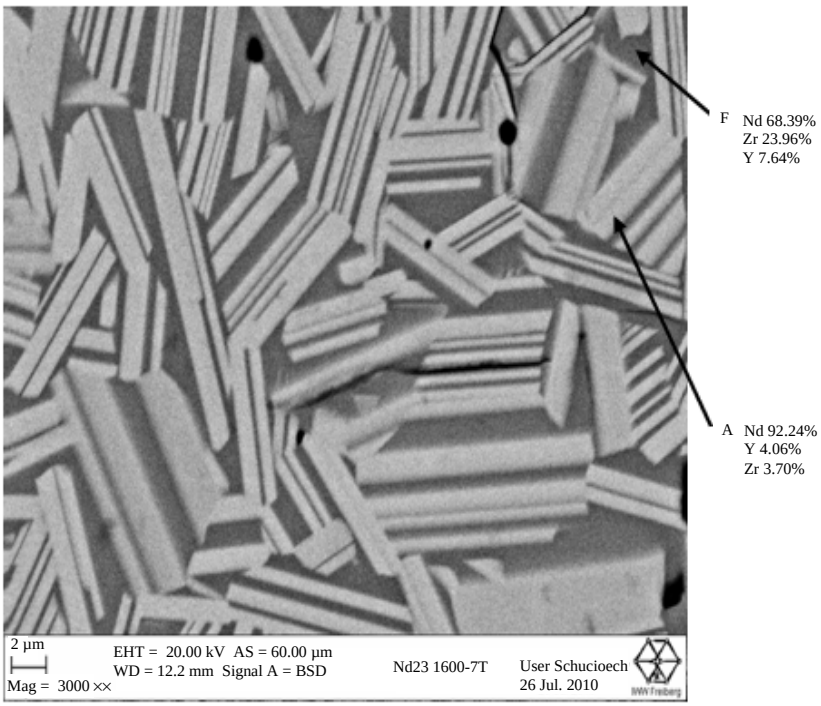

Fig. 9: SEM image of sample heat treated at 1600°C; compositions are determined by EDX

CONCLUSION

Sample with composition 18.18 mol % ZrO_2, 2.73 mol % Y_2O_3 and 79.09 mol % Nd_2O_3 obtained by co-precipitation was heat treated at 1250, 1400 and 1600°C. Samples were characterized by XRD, SEM/EDX and DTA. Two phase transformations have been found by DTA investigation in the range 1400-1600°: Pyr→Flu at ~1471°C and B→A at ~1608°C. This was confirmed by XRD and SEM/EDX.

REFERENCES

Cao, X.Q., R. Vassen and D. Stover, 2004. Ceramic materials for thermal barrier coatings. J. Eur. Ceram. Soc., 24: 1-10.

Clarke, D.R. and C.G. Levi, 2003. Materials design for the next generation thermal barrier coatings. Ann. Rev. Mater. Res., 33: 383-417.

Evans, A.G., D.R. Mumm, J.W. Hutchinson, G.H. Meier and F.S. Petit, 2002. Mechanisms controlling the durability of thermal barrier coatings. Prog. Mater. Sci., 46: 505-553.

Fabrichnaya, O., G. Savinykh, G. Schreiber and H.J. Seifert, 2011. Phase Relations in the ZrO_2-Nd_2O_3-Y_2O_3 System: Experimental study and advanced thermodynamic modeling. J. Phase Equilib. Diffus., 32: 284-297.

Hinatsu, Y. and T. Muromura, 1986. Phase relations in the systems ZrO_2-Y_2O_3-Nd_2O_3 and ZrO_2-Y_2O_3-CeO_2. Mater. Res. Bull., 21: 1343-1349.

Khor, K.A. and J. Yang, 1997. Rapidly solidified neodymia-stabilised zirconia coatings prepared by DC plasma spraying. Surf. Coat. Technol., 96: 313-322.

Levi, C.G., 2004. Emerging materials and processes for thermal barrier systems. Curr. Opin. Solid State Mater. Sci., 8: 77-91.

Nicholls, J.R., 2003. Advances in coating design for high-performance gas turbines. MRS Bull., 28: 659-670.

Padture, N.P., M. Gell and E.H. Jordan, 2002. Thermal barrier coatings for gas-turbine engine applications. Science, 296: 280-284.

Rebollo N.R., A.S. Gandhi and C.G. Levi, 2003. Phase Stability Issues in Emerging TBC Systems. In: High Temperature Corrosion and Materials Chemistry IV, Opila, E.J., P. Hou, T. Maruyamma, B. Pieraggi, M. McNallan, D. Shifler and E. Wuchina (Eds.). The Electrochemical Society, USA., ISBN-13: 9781566773997, pp: 431-442.

Schulz, U., C. Leyens, K. Fritscher, M. Peters and B. Saruhan-Brings *et al*., 2003. Some recent trends in research and technology of advanced thermal barrier coatings. Aerospace Sci. Technol., 7: 73-80.

Wang, C., 2006. Experimental and computational phase studies of the ZrO_2-based systems for thermal barrier coatings. Ph.D. Thesis, University of Stuttgart, Germany.

Xu, T., J. Vleugeis, O. Van der Biest and P. Wang, 2004. Mechanical properties of Nd_2O_3/Y_2O_3-Coated zirconia ceramics. Mater. Sci. Eng. A, 374: 239-243.

Xu, Q., W. Pan, J. Wang, C. Wan and L. Qi *et al*., 2006a. Rare-earth zirconate ceramics with fluorite structure for thermal barrier coatings. J. Am. Ceram. Soc., 89: 340-342.

Xu, T., J. Vleugeis, O. Van der Biest, Y. Kann and P. Wang, 2006b. Phase stability and mechanical properties of TZP with a low mixed Nd_2O_3/Y_2O_3 stabiliser content. J. Eur. Ceram. Soc., 26: 1205-1211.