New Bond Coat Materials for Thermal Barrier Coating Systems Processed Via Different Routes

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Abstract. This paper aims at describing the development of new Ru-based Bond Coats (BC) as part of Thermal Barrier Coatings. The challenge of this research was to obtain an adherent and uniform layer of alumina protective layer after high temperature exposure. We have prepared a RuAl 50/50 at% alloy in an induction furnace which was subsequently subjected to oxidation in an electric furnace, in air, at 1100°C, for 10h and 100h. Mechanical alloying of Ru and Al powders was another processing route used in an attempt to obtain a stoichiometric RuAl. The alloy was sintered by Spark Plasma Sintering (SPS) and then oxidized at 1100°C for 1 and 10h. The alloys obtained as such were analysed before and after oxidation using advanced microscopy techniques (SEM and TEM). The encouraging results in case of RuAl alloys prepared by induction melting reveal that we obtained an adherent and uniform layer of alumina, free of delta-Ru. The results for the samples processed by powder metallurgy were positive but need to be further investigated. We should note here the novelty of this method for this particular type of application – as a BC part of a TBC system.

1. Introduction
A Thermal Barrier Coating (TBC) system is presented in figure 1 and consists of: superalloy, bond coat (BC), thermally grown oxide (TGO) and thermal barrier coating (TBC).

Figure 1. Thermal Barrier Coating System [1].
The main component of the system is the Ni-based superalloy representing the base for the TBC. The role of the TBC is to provide protection against corrosion and high temperature developed in the gas turbine working environment.

The upper layer, the thermal barrier coating, has a low thermal conductivity [2,3] meaning a low heat flux from the combustion gases to the main component of the system (the superalloy) resulting in a decrease of temperature of over 100°C [3,4].

This layer (TBC) is usually yttria-stabilised zirconia (YSZ – 7wt% Yttria), has a certain porosity degree and has a thickness ranging between 100 and 500µm. Microcracks and aligned porosity are induced in these layers during the coating process, to accommodate the of thermal expansion effects.

The main function of the bond coat (BC), the layer between the superalloy and the TBC, is to protect the superalloy from oxidation and to act as a bond between the TBC and the superalloy. During high temperature exposures, a thermally grown oxide (TGO) layer forms between the BC and the TBC. BC plays a very important role as being the promoter of the thermally grown oxide and the layer provided should be a uniform, dense, stable. α-Al2O3 is the preferred oxide as TGO because it is thermodynamically stable, it is compatible with YSZ, has an oxygen low diffusivity and it is a very good thermal insulator [5,6].

The bond coat processing techniques including noble metals with favourable properties have been already described in the literature. Pd layers have a very good oxidation resistance at high temperature [7] and Ir layers form in fact two layers: one containing Ni and a lower Ir-rich layer [8,9].

Over the years, the most used BC alloys have been platinum-modified nickel aluminate (Ni-Pt)Al (37,44) and McrAlY (M, metal) [11,12].

Systems containing Ru have also been the subject of many studies but their mechanism of oxidation was not fully understood. The main goal of this research was to obtain a RuAl alloy which forms a uniform and adherent alumina layer after high temperature exposures.

The work focused on preparation and microstructural characterisation of RuAl alloys subjected to oxidation.

2. Materials and methods
Two processing routes were used for producing RuAl50/50 at%. First route was processing in liquid state, in a levitation induction furnace at 2400°C for 25 minutes. The second route was processing in solid state, using powder metallurgy technique.

The elemental powders were milled together in a planetary ball mill PM 400 RETSCH, in stainless steel vials and balls, at 300rpm for 25h. The process control agent (PCA) used was stearic acid in percentage of 1at%. The PCA was used to prevent the welding of the particles during mechanical alloying process and improving the alloying behavior of RuAl. For sintering we used Spark Plasma Sintering (SPS) technique in the following conditions: 1060°C, 80MP and 9kN.

The consolidated and as cast samples were subjected to oxidation at 1100°C for 10 hours, in an electric furnace. The samples were introduced in the furnace when the heating started.

The samples were investigated before and after oxidation. The SEM images were obtained with a Field Emission Gun (EG) Variable Pressure (VP) SEM equipped with WDX and EDX spectrometer.

3. Results and discussions
The SEM images obtained for RuAl 50/50 before oxidation are presented in the figure 2 a and b. Figure 2 reveals the microstructure of the RuAl50/50 at% presenting the backscattered image revealing three different phases in the alloy (a) and in figure 2b a detail of the Ru-RuAl eutectic is presented.

To prepare a stoichiometric RuAl alloy is the main challenge of this work due to the high difference between Ru and Al melting points: Ru has the melting point at 2334°C and Al at 660°C. In the phase diagram presented in figure 3 the narrow stoichiometry interval proves that processing RuAl 50/50 at% could be difficult. The narrow stoichiometry gap is also a matter to be taken into consideration when processing this alloy. The alloy obtained indicates the presence of more phases of RuAl compound due to the Al leaving the melt resulting in secondary phase formation.
Figure 2. Microstructure of the RuAl processed in liquid state before oxidation: a) three phases present in RuAl alloy and b) detailed image of Ru-RuAl eutectic.

Figure 3. Ru-Al phase diagram.

In figure 4 a SEM image of the solid state processed samples is shown.

Figure 4. The SEM image of SPS sample (processed in solid state).

Figure 5 and 6 present the EDX result analyses for the as cast and SPS consolidated samples.

The oxidation process is important for assessing the new alloy capabilities. The ability of the bond coat to resist formation of the thermally grown oxide depends on the method of surface preparation and the thermal cycles in the corrosive environment where the chemical composition is constantly changing due to interdiffusion and oxidation. The most important part of the TGO is to act as a diffusion barrier between the oxidant atmosphere and by oxygen diffusion inhibiting in the sublayers and rapid diffusions towards the oxidant atmosphere. This layer is essential for the chemical and mechanical compatibility of the super alloy with the thermal barrier system. The oxidation time is important in order to evaluate the behavior of Ru phase. The chosen time for this set of experiments was 10h.
Figure 5. The EDX analyses results for as cast sample.

Figure 6. The EDX analyses results for SPS consolidated sample.

Figure 7. Acicular growth of the Al2O3 oxide on the RuAl surface.

Figure 8. SEM image of the oxide grown on the RuAl SPS consolidated sample.

In figure 7 and 8 the microstructures of the as cast and SPS consolidated samples after 10 h oxidation in the furnace are shown.

The thermally grown oxide obtained after 10h oxidation time seem to be dens and uniform and the most important is the absence of the delta – Ru phase which is very good indicator of the successful oxidation of RuAl 50/50at%.

4. Conclusions

RuAl 50/50at% was processed using two different routes: liquid state processing and solid state processing. The RuAl alloy was not reported yet to be processed by powder metallurgy and the results obtained after oxidation process encourage further investigation for this processing route. The alloy processed in liquid state grew an oxide layer dense and uniform, without delta-Ru phase indicating a very good behavior as a bond coat.

References
[1] Tryon B, Feng Q, Pollock T M, et al. 2006 Metall and Mat Trans A 37 33 - 47
[2] Wright P K, Evans A G 1999 Current Opinion in Solid State and Materials Science 4 255
[3] DeMasi-Marcin J T, Gupta D K 2000, Surface and Coatings Technology 68/69 1 - 7
[4] Nicholls J R 1994, Journal of Metals 28
[5] Clarke D R 2003 Acta Materialia 51 1393 - 6
[6] Levi C G 2004 Emerging materials and processes for thermal barrier systems. Curr. Opin. Sol.St&Mat.Sci. 8 77
[7] Angenete J, Stiller K, Langer V 2003, Oxidation of Metals 60 47
[8] Li M J, Sun X F, Guan H R, Jiang X X, Hu Z Q 2003, *Surface and Coatings Technology* 167 106
[9] Datta P K, Burnell-Gray J S, Natesan K 2002 *Intermetallic Compounds, Westbrook, J.H. and Fleischer, R.L. New York: John Wiley & Sons, Ltd.* pp. 561.
[10] Fisher G, Datta P K, Burnell-Gray J S 1999b*Surface and Coatings Technology* 113 259
[11] Leyens C, Pint B A, Wright I G 2000, *Surface and Coatings Technology* 133-134 15

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