Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 607–612

DIFFERENTIAL BAROTHERMAL ANALYSIS IN THE COURSE OF REACTIVE POWDER BAROTHERMAL PROCESSING OF RuAl ALLOYS

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Thermostable high-temperature structural alloys based on the refractory (melting temperature T_m=2060°C) RuAl intermetallic (IM) with an ordered B2 crystal structure (CsCl type) are developed. This IM surpass other aluminides (NiAl, TiAl and Ni_3Al) used as the base for the development of high-temperature alloys and matrices of high-temperature composites (CM) intended for hot parts of supersonic engines, which serve at the temperatures exceeding operation temperatures of modern nickel-base superalloys. The differential barothermal analysis was used to develop the basic technological process of barothermal reaction sintering to produce near-net shape billets from RuAl-based structural materials.

Keywords: *alloy, barothermal analysis, exothermic reaction, porosity, powder metallurgy, reaction sintering, RuAl*

Introduction

Refractory, high-temperature (oxidation-resistant) monoaluminide of ruthenium (RuAl) with the bbc B2 structure (T_m=2062°C, the density 7.97 g cm^{-3}) is promising material for hot parts of hypersonic flight vehicles and, in particular, hypersonic ramjet engines, which work with the high temperatures (>1500°C) in the high-speed (>5 M) gas oxidizing flows (23% O_2). The study of theoretical and practical aspects of production of the RuAl-based alloys by the method of powder metallurgy (PM) is of interest. The advantage of the PM method is the initially uniform distribution of components (Ru and Al powders, alloying elements) in the charge, which is especially important if to take into account the difference in the charge, which is especially important, taking into account the difference in the melting points of aluminum (T_m=660°C) and ruthenium (T_m=2250°C) and the densities Al (ρ_{Al}= 2.698 g cm^{-3} ρ_{Ru}=12.6 g cm^{-3}). In the paper [1] dense samples were produced by hot isostatic pressing (HIP), but they had non-equilibrium composition (RuAl, Ru, $RuAl_2$, Ru_4Al_{13}). The authors of [2] attempted to obtain the compact samples of stoichiometric ($Ru_{50}Al_{50}$) and hyperstoichiometric ($Ru_{52}Al_{48}$) alloys from the cold-pressed (CP) blends of Ru and Al powders during the subsequent heating by the method of reaction sintering (RS). It was shown that the interaction between Ru and Al occurs according to the exothermic reaction Ru+Al→RuAl at temperatures <700°C. After RS of cold-pressed billets the high porosity remains in the sintered specimens (ρ_{exp}~0.72ρ_{theor}). The subsequent sintering at 1400°C does not increase the density of (CP+RS) billets (ρ_{exp}~0.74ρ_{theor}) of the mixtures of powders Ru and Al (density~0.74% from the theoretical). The samples of single- phase RuAl with a residual porosity of 1.9% were produced by CP at 900°C; then they were axially hot pressed (HP) in high vacuum (10^{-5} mbar) at 500°C and 264 MPa for 0.5 h and further at 700°C and 264 MPa for 1 h; the final annealing was performed at 1600°C for 12 h in a vacuum of 10^{-5} mbar [3]. In the study [4], the characteristic features of the formation of RuAl-alloys by RS with the use of three scheme of consolidation were investigated: (I) RS of the blend of Ru and Al powders upon heating at a rate of 2–5 K min^{-1} in the adiabatic scanning calorimeter in argon atmosphere at 200–1000°C; (II) RS in the evacuated quartz ampoules at temperatures of 250–1200°C for 1 h at a heating rate of 5 K min^{-1}; (III) RS of CP-billets at 700°C under a pressure of 850±50 kg cm^{-3} for 1–2 h at a heating rate of 8 K min^{-1}. RuAl-based compact material with a density at 0.8–0.9ρ_{theor} was obtained.

This work was aimed at the study of the special features of RS-producted RuAl-based compositions under the pressure in the course of barothermal process, using HIP and differential barothermic analysis simultaneously to obtain the thermal characteristics of exothermic reaction Ru+Al→RuAl. As a rule thermal

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1388–6150/$20.00

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analysis (in particular, the differential thermal analysis), is an initial stage of the study aimed at the development of new materials, especially those prepared by reaction sintering [5].

Compositions of alloys, the regimes of barothermal treatment and the methods of study. As a subject of this study the alloys were selected, which are located in the two-phase region β+γ of phase diagrams, that adjoin the boundary β/(β+γ) where β-solid solution based on β-RuAl, γ-solid solution based on ruthenium (γ-Ru). In the alloys enriched in Ru, the eutectic L↔β-RuAl+γ-Ru (T_{eut}=1920°C) is formed, which usually has the form of the degenerated eutectic in the alloys with 45–50 at% Al, i.e., Ru-based solid solution with disordered hcp crystal lattice [4, 6]. The eutectic composition RuAl–Ru is at 25 at% Al [7] and 30 at% Al [8, 9]. The alloying elements (AE) were introduced into the alloys (at%), which replaced Ru (2% Ni, 1, 3 and 5% Re) or Al (2% Si, 1% W, 1% Mo), and also the refractory interstitial phases (vol%): 2% HfC, HfN, HfB_2, 2.5% Y_2O_3).

Particles of Ru powder (Fig. 1a) with the size of 1–2 μm are connected into the conglomerations of irregular shape (5–20 μm) with the developed surface. The oxygen content in the powder, determined using LECO TC-436 Analyzer, was ~0.075 mass%, oxygen was predominantly adsorbed on the surface of the particles. The granules of Al (5–20 urn) (Fig. 1b) were covered with the thin dense film Al_2O_3, oxygen content was 0.335 mass%. Powders of some AE are shown in Figs 1c, d. Powders were mixed for 6 h in a Turbula eccentric mixer. Initial compact billets were obtained by uniaxial CP of the powder blends. The temperature intervals exothermic effects of not alloyed RuAl and its alloys were determined using Setaram-device at a rate of heating of 2 K $\min^{-1}$. The BTT was performed by with an HIP on ‘Abra’ press.

The CP (Ru+Al) billets and CP billets after preliminary RS without any pressure application were used. Temperature interval RS was determined for different compositions. The billets were placed into the stainless steel ampoules, soldered in the vacuum with the titanium getter. Temperatures of samples and W reference specimen were measured by W/Re thermocouples. Temperature interval RS under the BTT was determined. For further work the billets of two types were used, i.e., CP-billet and CP-billet heated to the temperature of the end of exothermic reaction without any pressure application and under pressure. After the I$^{\mathrm{st}}$ BTT (heating to 1200°C at a rate of 5–7 K $\min^{-1}$ with a gradual increase in pressure to 160 MPa, holding for 3 h), samples (without am-

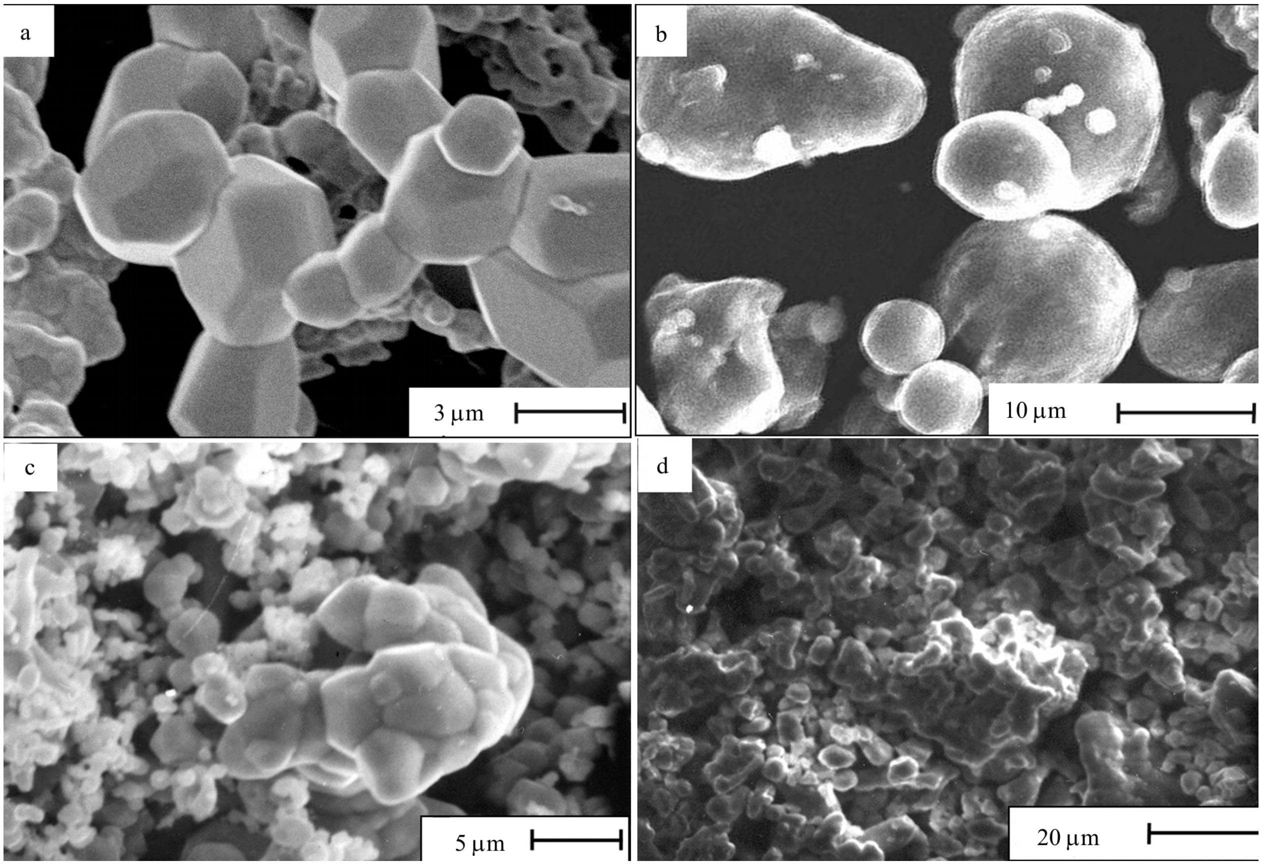

Fig. 1 Powders of a – Ru, b – Al, c – Mo, d – HfN

poules) were treated according to the following scheme: annealing in a vacuum 10^{-5} torr at 1400, 1500 and 1550°C for 5, 4.5 and 0.5 h, respectively; then IInd HIP at 1200°C and 180 MPa for 3, 5 h; then IIIrd HIP with 1500°C 170 MPa for 1 h. After each operation the density, structure, hardness and some other properties were studied. The determination of residual porosity was performed using Neophot-32 optical microscope (program 'Atlas'), the structural-phase state of the sintered billets was studied with the help of LEO 430 scanning electron microscope equipped with the microanalyzer. The phase analysis was performed using a DRON-3 diffractometer.

Results and discussion

Characteristic exothermic effects, that take place upon heating without applied pressure and under BTT conditions are shown in Figs 2a and b. It was found that some factors (alloying, area and cleanliness of the contact surface between the particles in the blends, the presence of the internal and applied stresses, and the heating rate) effect on the temperature of he exothermic reaction of RuAl-formation from elements Ru+Al and the completeness of the reaction, the density and the structural-phase state of the RS material. It was established that the contact interface between the particles of powders and a pressure at the contact surface increase in going transfer from the initial mixtures of powders [2, 4] to CP initial mixtures and further to CP+RS mixtures of the powders, whose densification continues during RS [4]. In all cases weak contact interaction between Ru and Al during the exothermal reaction Ru+Al→RuAl begins in the solid phase without any fusion of Al. So for the CP-samples of RuAl during the heating without the application of pressure, the temperatures of beginning, peak and end of exothermic reaction are 586, 612, 635°C (Fig. 2a). When 2% Ni is added these temperatures decrease to 576, 609 and

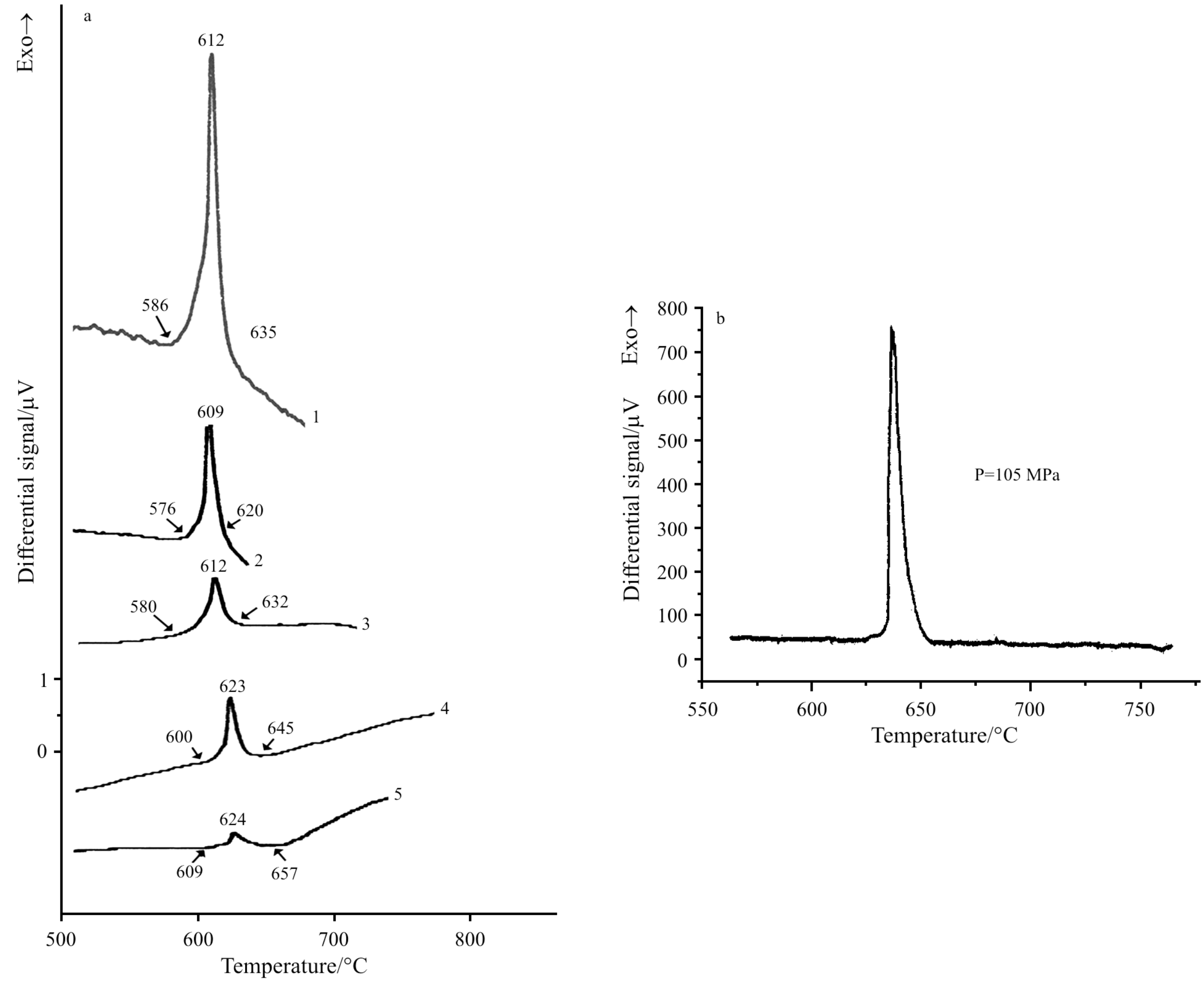

Fig. 2 Exothermic effects for RS of alloys a – without the application of pressure: 1 – RuAl; 2 – $Ru_{50}Al_{48}Ni_2$; 3 – $Ru_{52}Al_{48}$+2.5 vol% Y_2O_3; 4 – $Ru_{52}Al_{48}$+2 vol% HfC; 5 – $Ru_{47}Al_{48}Re_5$ and b – RuAl under BTT

620°C, respectively. The introduction of refractory AE and interstitial compounds (1–5 at% Re, W and 2 vol% HfC, HfN, HfB_2) increases the temperatures of beginning, peak and end of the exothermic reaction. So introduction of 2 vol% HfC or 5 at% Re increases them to 600–609, 623–624 and 645–657°C, respectively. The introduction of 2.5 vol% of inert oxide Y_2O_3 practically does not change them (580, 612 and 632°C). In all cases, already at ~580–600°C aluminum-rich Ru_4Al_{13}, $RuAl_2$ and traces RuAl are formed. Introduction of 2 vol% HfC, HfN, HfB_2 hampers the interaction of Ru and Al. In this connection, the reaction products contain 26–40 vol% residual Ru and the Al-rich ruthenium aluminides. The most complete interaction occurs in the Ru+Al powders, alloyed by the metals of the VIII group (Re and Ni). This alloys contain 83–91% RuAl and 5–15% (Ru) and the negligible traces of other ruthenium aluminides. As a result of the development of exothermic reaction, the temperature of RuAl sample rises to ≥700°C. Heating to ≥700°C allows one to obtain the practically equilibrium alloys (vol%): 90.5 RuAl and 9.5 (Ru) in alloy $Ru_{52}Al_{48}$.

The density of CP billets and samples after RS without the applied pressure is 70–74 and 75–80% of the theoretical density, respectively. Annealing after RS at 1400°C does not decrease the residual porosity. The retention of high residual porosity (to 20–25 vol%) is caused by two reasons: (1) upon RS of Ru+Al powders without the application of pressure and with a slow rise in temperature, RS begins already in the solid phase; apparently, the preferred diffusion Al in Ru occurs, as it takes place in the Ni+Al samples, which causes the formation of pores (Kirkendall effect); (2) increase in the temperature to T_m Al causes the melting of aluminum unreacted in solid phase Al; remelted Al wets the particles of powder Ru and form RuAl, which are tightened local islands, which has a ~100% density, but they are divided by large pores. Based on the data obtained the conclusion was made about the need for application of BTT (RS with HIP) for compacting of the CP samples or the applications of BTT on the samples in the RS-process to determine a temperature interval and exothermic effects for the conditions of BTT of ampoule with the experimental CP-billets, they were heated to 750°C with a simultaneous increase in the pressure to 105 MPa. An intense exothermic peak was recorded upon heating at a rate of several K min^{-1} with the simultaneous rise in pressure up to 105 MPa. The peak could be divided into 3 stages. At the first stage, one can observe the start of the interaction at 625°C with a small (but sharp) elevation of the ampoule temperature. At the second stage beginning at 632°C, the temperature of the powder mixture in

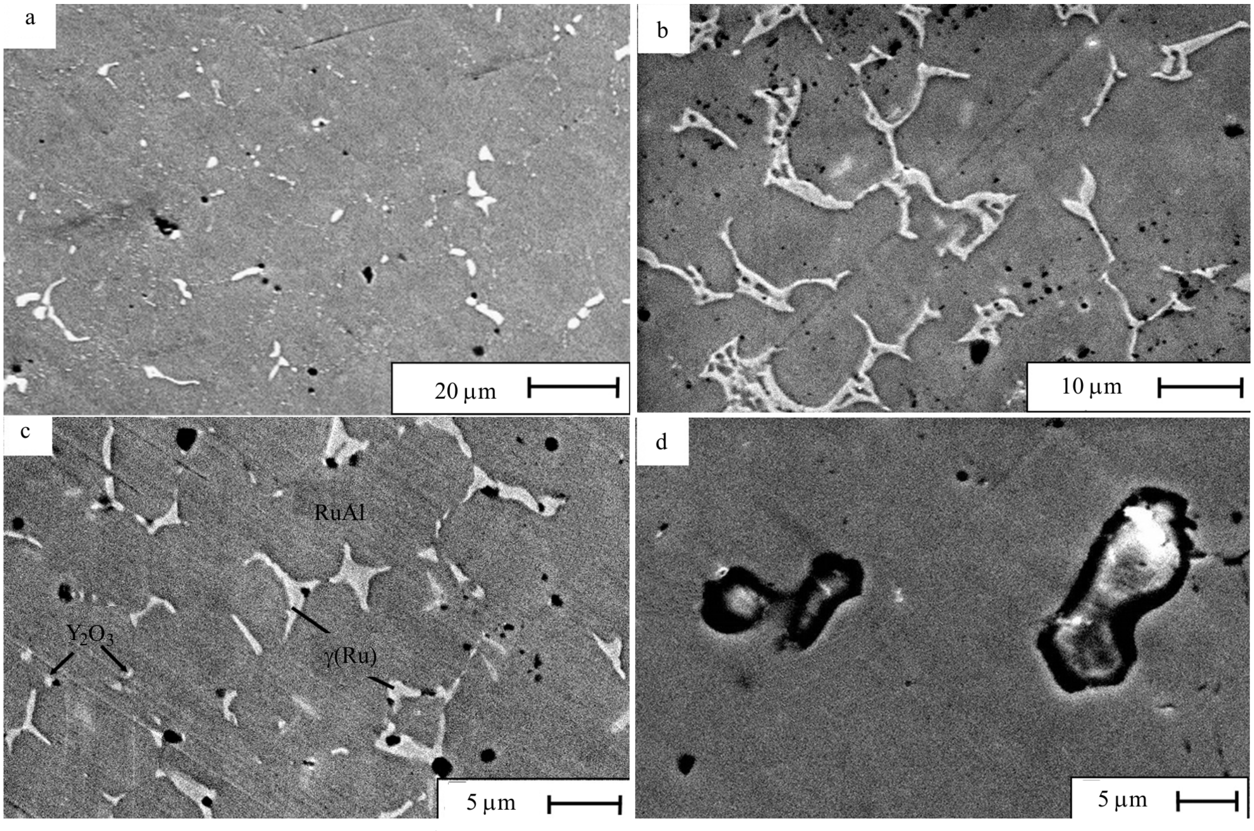

Fig. 3 Microstructures of RuAl alloys after I^{st} BTT+RS (at%): a – 52% Ru–48% Al; b – 52% Ru–47% Al–1% Mo; c, d – 97.5 vol% $Ru_{52}Al_{48}$ – 2.5 vol% Y_2O_3

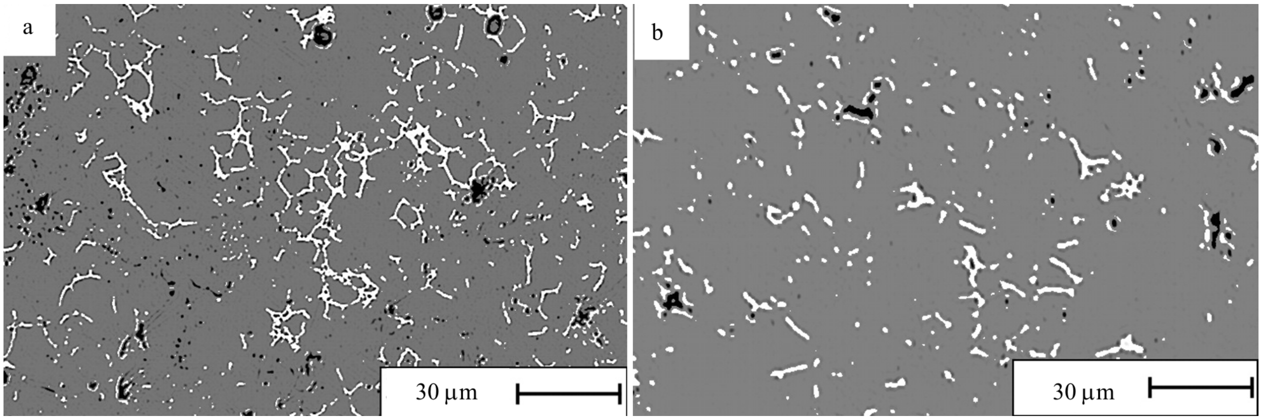

Fig. 4 Microstructures of RuAl alloys after Ist BTT+RS and homogenizing annealing at 1500°C for 10 h (at%): a – 47% Ru–48% Al–5% Re; b – 52% Ru–47% Al–l% Mo

the ampoule increases by 3 K at a rate of 9 K min^{-1}. At the third stage beginning at 635°C, the interaction between the components results in the heating of ampoule by 700°C at a rate of 430 K min^{-1}. When the reaction was finished, the ampoule was gradually cooled to media gas temperature. The consideration of differential barothermal data allows us to use the thermodynamic data to establish the mechanisms of the chemical interaction between Al and Ru at a pressure of 105 MPa. RS begins in solid phase at temperatures below the melting temperature of Al. The effect of pressure on the starting temperature of reaction, $\mathrm{d}T_{react}/\mathrm{d}P\sim -30$°C/100 MPa, was established.

After Ist barothermal RS (with HIP) of CP and (CP+RS)-billets, the phase composition of samples was practically equilibrium (Figs 3a, b): RuAl in different samples contained (at%): from ~53 to 56.5Ru with ~ 43.5–47Al; inclusions of eutectic type based on (Ru) contained from ~85.0 to 92.5Ru with ~7.0–13.5Al. Content of β-RuAl for the different alloys varies from 85 to 95%. Distribution AE between both phases corresponds to the concept of the higher AE solubility in γ-Ru with fcc disordered lattice as compared to bcc RuAl: so in the alloy with 1 at% Mo (W), ~1.85% AE are dissolved in γ-Ru and only 0.15% in RuAl. It is possible to assume that interstitial phases with participation of Hf interact with both basic phases of alloy. The more inert oxide Y_2O_3 forms the disperse inclusions (≤0.3–1 μm) of the predominantly rounded form in the alloys, obtained of both initial materials. The rarely arranged particles of irregular shape, which consist of 2–20 smaller particles of the initial powder Y_2O_3 are also met in the alloy (Figs 3c, d).

After the homogenization annealing at ~1500°C for –10 h, when the diffusion rate increases, the phase composition of alloys with the non-equilibrium structure changes, approaching equilibrium. The content of (Ru)-solid solution is 5–8 vol% (Figs 4a, b).

Residual porosity in the alloys after the BTT (Table 1) with HIP sharply decreases in comparison with initial CP or (CP+RS) billets.

Table 1 Residual porosity (vol%) of RuAl alloys after RS during the barothermal treatment (HIP)

Composition/at%	Initial billet	HIP			Composition/vol%	Initial billet	HIP		
		Ist	IInd	IIIrd			Ist	IInd	IIIrd
52Ru–48Al	CP	2.0	1.7	1.1	98RuAl–2HfC	CP CP+RS	6 15	4.7 10.3	2.8 6.9
50Ru–50Al	CP CP+RS	1.9 3.6	– 3	– 1.7	98RuAl–2HfN	CP CP+RS	4.01 8.6	– 6.8	1.5 6.3
50Ru–48Al–2Ni	CP CP+RS	2.5 5.3	– 4.2	1.6 3.2	98RuAl–2HfB$_2$	CP CP+RS	6.7 –	– –	2.3 –
51Ru–48Al–1Re	CP CP+RS	4.3 7.5	– 5.2	2.4 4.7	98RuAl–2MoSi$_2$	CP CP+RS	4.1 9.9	– 8	1.9 7.3
47Ru–48Al–5Re	CP CP+RS	5.2 10.7	4.4 6.4	2.9 5.8	97.5Ru$_{52}$Al$_{48}$–2.5Y$_2$O$_3$	CP CP+RS	4.7 6.8	– –	2.2 3.1
52Ru–47Al–1W	CP CP+RS	5.1 5.8	– 5.2	3.8 4.8	97.5Ru$_{50}$Al$_{50}$–2.5Y$_2$O$_3$	CP CP+RS	4.8 7.3	–	2.8 3.5
52Ru–47Al–1Mo	CP CP+RS	4.8 7.8	– 7.1	3.6 5.6					

The residual porosity depends on two factors: (1) composition of alloy and, therefore, phase transformations in the process of preliminary RS or RS with BTT, and (2) the structure of billet, which is formed with preliminary RS without the application of pressure or RS with BTT, i.e. the presence of zones with open and closed porosity and their relationship. The fraction of the open porosity is maximum in the CP-billets after RS. This depends on the retention of high residual porosity in samples both after Ist BTT in the shells and after HIP (IInd and IIIrd BTT) already without the shells. A certain reduction in the porosity of these samples after IInd and IIIrd BTT in comparison with Ist BTT indicates the formation of the sections with closed porosity during Ist BTT, which were densified during the subsequent operations HIP. The closed porosity is most actively formed upon RS under the conditions of BTT of CP-billets, whose densification occurs under the conditions of three-dimensional compression at a high temperature. The samples of not alloyed RuAl and the alloy with 2% Ni obtained from CP billets demonstrate the minimum residual porosity after BIT (1.1 and 1.6 vol%, respectively). Maximum residual porosity is characteristic of the alloys from CP+RS of billets with $MoSi_2$, HfC, HfN, Re and Mo (from ≈7.3 to ≈1.5–3.6 vol%).

Conclusions

For all alloys, residual porosity after BIT of any samples, obtained from the CP-billets, (RS in the process BTT), is lower by a factor for of about 1.3–1.6, than that for the samples from CP+RS of the billets where RS preceded BTT. The homogenization at ~1400°C for –10 h leads to a certain decrease in the residual porosity, Ind and IIIrd BTT decrease in the residual porosity of all samples by ~1.5–2.5 times in comparison with the state after Ist BTT. Probably the temperature of homogenization is sufficiently high to reach the equilibrium phase composition but it is insufficient for the intense densification. For the best densification, temperatures ≥0.8–0.9 T_m of material are necessary [10]: this corresponds to ~1500–1700°C for the eutectic-containing alloys based on RuAl and ~1800–2000°C for the alloys, which do not practically contain eutectic. For further densification of the RuAl PM-alloys obtained in this work, it is possible to use high-temperature annealing at temperatures of ~0.82–0.9 T_m RuAl and/or additional deformation by hot extrusion.

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