CHARACTERISTICS OF OXIDATION
IN Ru-RuAl INTERMETALLIC EUTECTIC[*]

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ABSTRACT

Oxidation characteristics and changes in the microstructure of Ru-rich RuAl-base intermetallics oxidized in air at 1100 and 1300 °C up to 100 h were reported. Oxidation process results in the formation of the oxidation zone under the external alumina layer. Oxidation zone consists of discontinuous structure composed of α-Al_2O_3 and Ru-rich phase, which gives rise to internal oxidation. Between external alumina layer and oxidation zone numerous voids formed as a consequence of vacancy agglomeration. Oxidation behavior and stability of lamellar microstructure are strongly influenced at temperatures higher than 1100°C. The results were compared and discussed within the context of oxidation characteristics in RuAl and other B2 aluminides.

Keywords: ruthenium, aluminum, intermetallics, oxidation, microstructure

1. INTRODUCTION

RuAl intermetallic compound has attracted significant attention, because of its promising combination of mechanical, chemical and physical properties [1]. The most interesting property is its good room-temperature ductility and toughness compared to other intermetallic aluminides with B2 structure [2]. In Ru-rich side of the Ru-Al phase diagram, RuAl forms with Ru solid solution high temperature eutectic (α-Ru + β-RuAl) which possesses markedly higher ductility and strength than its constituent phases [3].

Besides room-temperature toughness and high-temperature strength, oxidation resistance is one of the most important properties that determines the high-

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temperature applicability of an intermetallic. The properties of the formed oxide scale are of the main importance in oxidation behavior. Continuous and compact protective oxide scale which ensures long-term oxidation protection is characterized by easy formation and re-formation, slow growing rate, high thermodynamic stability and good adherence to the substrate [4]. Oxides based on alumina are considered as the most protective scales and many B2 aluminides have benefited from the ability of aluminum to build protective scales. Protective scales were also observed to form on RuAl, where alloying additions of Cr and Y improved oxidation resistance up to 1250 °C [5]. Greater attention has not been paid to study the oxidation of Ru-rich RuAl-base intermetallics because the limiting factor at higher temperatures was found to be high volatility of ruthenium oxides.

Considering that Ru-rich intermetallic aluminides have a certain potential as candidates for high-temperature applications as structural intermetallic composites, the ways of improving microstructural stability and oxidation resistance are worth studying. The aim of this paper was to study the characteristics of oxidation in Ru-rich RuAl-base intermetallics.

2. EXPERIMENTAL

In this study Ru-RuAl intermetallic eutectic of composition $Ru_{74}Al_{26}$ was investigated. Chemical composition throughout the paper is given in at. %. Alloy was manufactured from high purity constituents by arc-melting in protective argon atmosphere. To ensure material homogeneity buttons were turned over and remelted for several times and afterward homogenized at 1100 °C for 24 h in argon. Samples for oxidation were machined by electro-erosion and grind through 1200 mesh silicon carbide paper. Investigated samples had cylindrical (∅ 3 x 2 mm) and rectangular (8 x 8 x 2 mm) shape. Prior to oxidation samples were ultrasonically cleaned in acetone and ethanol. Oxidation was conducted in still air at 1100 °C for 1, 25, 50, 75 and 100 h and at 1300°C for 100 h. Cross-sections of the oxidized samples were used to study the characteristics of oxidation by means of scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS). The microstructure was observed mainly in back scattered electron mode (BSE) and elemental distribution was determined using X-ray elemental mapping. X-ray diffraction (XRD) with Cu K_α radiation was used to determine the type of the oxides formed. Weight change before and after oxidation was measured by precision electronic balance.

3. RESULTS AND DISCUSSION

The initial microstructure of eutectic alloy consisted of Ru-RuAl lamellar or rod-like eutectic with few primary RuAl dendrites and is documented in a previous work [6]. After short oxidation at 1100 °C for 1h, porous island-like oxide scale formed

preferentially on α-Ru phase, although β-RuAl was also slightly affected. In this oxidation stage XRD investigations revealed weakening of RuAl reflections and that oxide scale consists of α-Al$_2$O$_3$ and RuO$_2$ [13]. The presence of α-Al$_2$O$_3$ indicates that oxidation process begins with the formation of the stable alumina modification. It should be pointed out that in NiAl, depending on the temperature of oxidation, growth of transient alumina (γ- or θ-Al$_2$O$_3$) precedes the formation of stable α-Al$_2$O$_3$ [7]. XRD studies in this and previous work [9] showed, however, that in early stages of oxidation only stable α-Al$_2$O$_3$ nucleates and grows during oxidation process. No coarsening of the eutectic microstructure has been observed even after prolonged oxidation (for 100 h at 1100°C).
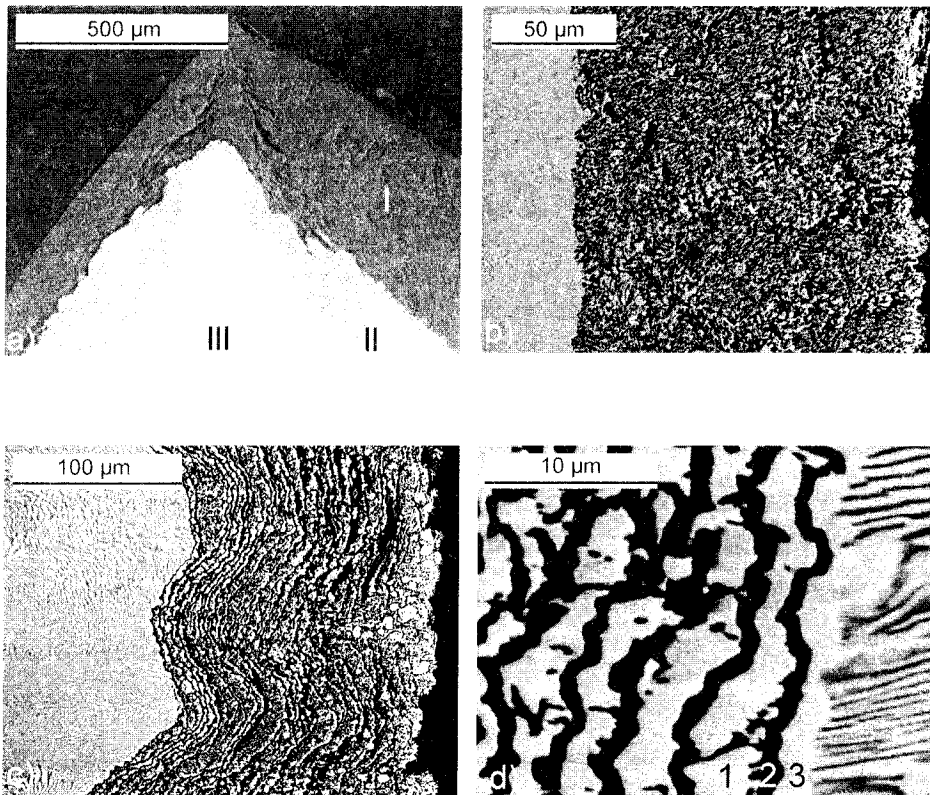

Figure 1a-d - General look (SEM; Back Scattered Electron-BSE image) of the cross-section of eutectic alloy after oxidation at 1100 °C ; a) external alumina layer (I), internal oxidation zone (II), and unaffected bulk material (III) in the center (after 100 h), b) irregular oxidation zone (after 50 h) , c) regular banded oxidation zone (after 50 h) and d) detail from c

Figure 1a shows a typical cross-section of the eutectic alloy after 100 h of high-temperature oxidation. Going from specimen free surface towards the center, cross-section consists of : I) dark external layer of porous sponge-like α-Al_2O_3, II) light gray layer called internal oxidation zone, and III) unaffected bulk material in the center. At higher magnifications it can be resolved that internal oxidation zone can have an irregular structure made up of intertwined white and dark regions (Fig.1b) and regular periodic structure composed of alternate white and dark bands (Fig. 1c). Detailed view of periodic structure and neighboring bulk eutectic is shown in Fig 1d. EDS analysis revealed that white bands are rich in Ru (83 % Ru, 1 % Al, 16 % O; point 1 on Fig. 1d), while dark bands are α-Al_2O_3 with small content of Ru remained (6 % Ru, 33 % Al, 61% O; point 2 on Fig. 1d). When compared to other Ru-rich bands, the Ru-rich band closest to the bulk material is slightly enriched in Ru (85.4% Ru, 0.9% Al 13.7% O; point 3 on Fig. 1d) and is named "oxidation affected band", similar to notification given by Chou who studied oxidation in IrAl [8]. The periodic bands are discontinuous with the average thickness of 2- 3 μm for Ru-rich bands, while α-Al_2O_3 bands are somewhat thinner. The same band thickness (2-3 μm) could be also observed in RuAl-base alloys oxidized at 1300 °C for 50 h [9] and 1350 °C for 20 h [10], whereas in IrAl (at 1300 °C for 8-100 h) bands were about 13 μm thick. This indicates inherent characteristics of different material systems which will be mentioned later as influencing parameters. Common for both Ru-RuAl eutectic alloy and IrAl is the porosity in Ru-rich or Ir-rich bands respectively. In this work it is not clearly observed that the thickness of α-Al_2O_3 bands increases as their distance approaches the bulk material as was the case in IrAl.

In the study of oxidation in IrAl, Chou observed that regular periodic structure in oxidation zone was replaced by irregular structure when the oxidation temperature was raised from 1300 to 1600 °C, and explained this as a change in oxidation kinetics [8]. In this work both regular and irregular structure are observed after oxidation at 1100 °C, suggesting that approximately at this temperature change of oxidation kinetics occurs. After oxidation of eutectic alloy at 1300 °C only irregular structure was observed.

The formation of periodic structure in RuAl-base alloys was previously reported in the literature [9,10], but it was not studied in more detail. This phenomenon can be explained in the same way as in IrAl [8], i.e. due to strong affinity of aluminum to oxygen, outward diffusion of Al atoms and subsequent oxidation take place. Consequently, the formation of Al_2O_3 is accompanied with the Al-depleted regions which give rise to Ru-rich phase formation. The formation of periodic structure was shown to be a complex function of many parameters such as diffusion kinetics, nucleation and growth kinetics of the precipitate, solubility of precipitate in solution and supersaturation.

In RuAl-base alloys, bulk material is always separated from alumina scale by Ru-rich phase, opposed to NiAl, where different alumina modifications are in close contact with NiAl bulk [11]. Specific characteristic of oxidation in Ru-RuAl eutectic structure is dissolution of RuAl lamellae (Fig. 1d) due to outward diffusion of Al, which is enhanced by high density of phase boundaries and short diffusion paths. It is interesting to note that oxidation front propagates evenly through both α-Ru and β-RuAl phase and not preferentially along the α-Ru phase as in RuAl alloys with intergranular Ru-rich phase, where oxidation occurs intergranularly [12]. It is therefore obvious that phase and grain boundary diffusion have a significant effect on oxidation resistance.
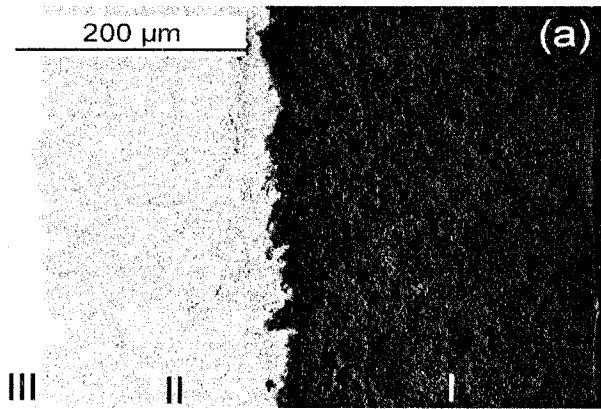

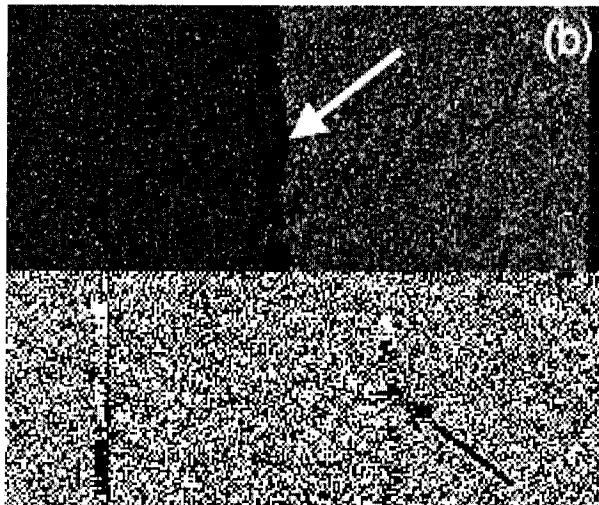Figure 2a - BSE of eutectic alloy oxidized 100 h at 1100°C.

Figure 2b - Al map (void formation is indicated with arrows).

Similar as in Fig. 1a, enlarged cross-section of eutectic alloy after 100 h of oxidation at 1100 °C is presented with BSE image and Al map additionally (Fig. 2a-b). The specimen free surface can be seen at the very right-hand side of Fig. 1a and the cross-section comprises of the same layers as already shown in Fig 1a. Distribution of present elements indicates that oxygen penetrates the oxidation zone and diffuses into a certain depth of the bulk eutectic material, as well as that certain amount of Ru remains in external alumina scale [13]. It was also found out that between external alumina scale and oxidation zone coalescence of vacancies takes place and they form agglomerates in form of large voids and cavities (shown with arrows on Fig. 2b). Voids and cavities decrease the area of coherence and lead to undesirable oxide scale spallation. Cavity formation under the Al_2O_3 scales formed on NiAl and FeAl was also observed [15]. This phenomenon is explained by the concentration gradients due to Al-depletion and inward diffusion of Ni and Fe. The porosity of both the external alumina scale (Fig. 1a) and internal oxidation zone, i.e. individual alumina and Ru-rich bands was also noticed. Porous oxide layers do not prevent material from further oxidation because of enhanced oxygen penetration. The porosity of oxide layers is the result of evaporation of ruthenium oxides. Solid $RuO_{2(s)}$ reacts with oxygen and forms gaseous $RuO_{3(g)}$ and $RuO_{4(g)}$ [16,17] which evaporate from the sample. At ambient pressure and above 1054 °C, $RuO_{3(g)}$ predominates in the gaseous phase [16], therefore being the major gaseous ruthenium oxide at 1100 °C.
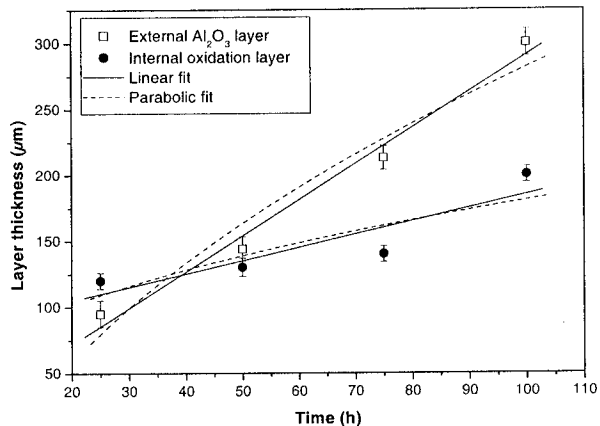

Figure 3 - Change of the layer thickness with the oxidation time at 1100 °C

Fig. 3 represents the change of the layer thickness with the oxidation time. In most of the samples the thickness of the formed layers was not uniform and resulted in data scattering. It was noticed that at shorter times, oxidation zone was thicker than external alumina layer, but this was significantly changed at

longer times in favor to external alumina layer, which was then almost twice as thicker. At the very beginning of the oxidation process, only oxidation zone covers the free surface of the material. As the time of oxidation increases, the oxidation zone grows thicker and advances towards the specimen center. After certain time, due to evaporation of Ru oxides in oxidation zone, an external alumina layer forms on the free surface of the material. Once formed, the external alumina layer grows faster than the oxidation zone and after approximately 40h (Fig. 3) reaches the thickness of the oxidation zone. Fitting of the data showed that the growth of the external alumina layer is better described with linear law (the linear rate constant, k_l, is determined to be 2.73), while the growth of the internal oxidation zone slightly deviates from both the linear and parabolic law. Oxidation behavior which obeys linear law is usually the indication of disability of one metallic material to give adequate protection against further oxidation starting from the initial stages [18], which is the case of Ru-RuAl eutectic alloy.

Oxidation of Ru-RuAl eutectic at 1300°C for 100 h, confirmed findings of Wolff and Sauthoff who pointed out the instability of eutectic microstructure at high temperatures [3]. Higher temperature did not only cause fine eutectic microstructure to coarsen, but it did change the oxidation kinetics also, which could be noticed on the cross-section of the oxidized sample (Fig. 4). External alumina layer (I on Fig. 4) was very porous due to extensive ruthenium oxide evaporation having thickness of about 1200 μm, while internal oxidation zone (II on Fig. 4) had irregular structure and thickness of only 25 μm.
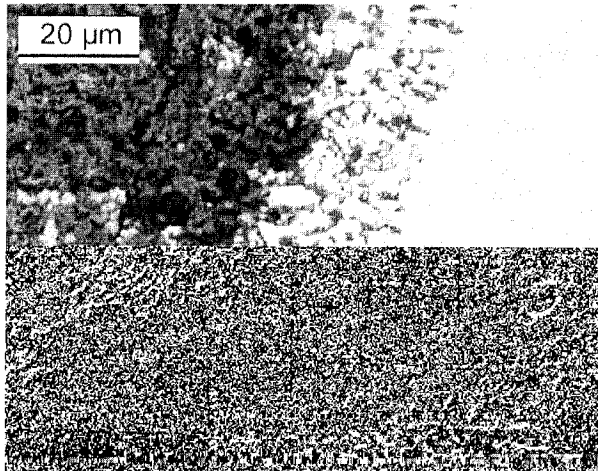

Figure 4 - Formation of different zones (I, II, and III) after oxidation of eutectic alloy at 1300 °C / 100 h (SEM, BSE). For description of zones refer to Fig. 1a

Internal oxidation of RuAl base alloys was reported to occur at 1300 °C [14], while in this work internal oxidation of Ru-RuAl alloys was already noticed at 1100 °C. Weight measurements after oxidation in all tested Ru-RuAl alloys showed weight loss which is attributed to extensive evaporation of Ru oxides. The same trend was observed in RuAl [10] and IrAl [8] after oxidation at high temperatures and is explained with the formation of volatile ruthenium and iridium oxides respectively. Thermogravimetric analysis during oxidation of RuAl at 1100 °C demonstrated weight gain with oxidation time [10], meaning that formation of alumina layer is a dominant mechanism. In the same work, approximately 70 μm thick external alumina scale was formed on $Ru_{51.5}Al_{48.5}$ alloy oxidized for 20 h at 1350°C. In Ru-RuAl eutectic alloy in this work, after 25 h at 1100 °C external alumina scale was 90 μm thick (Fig. 3), indicating higher oxidation tendency.

4. CONCLUSIONS

Oxidation of Ru-rich RuAl-base alloys produced by arc-melting, occurred by formation of discontinuous α-Al_2O_3 and Ru-rich phases which resulted in internal oxidation. Oxidation front propagates evenly through both α-Ru and β-RuAl phase, with characteristic dissolution of RuAl lamellae because of outward diffusion of Al. High density of phase boundaries and short diffusion paths enhanced oxidation in eutectic alloy when compared with near-single phase RuAl alloys.

Due to evaporation of ruthenium oxides external alumina scale that formed was very porous and did not prevent the alloy from further oxidation. Numerous voids formed between external alumina layer and oxidation zone as a consequence of vacancy agglomeration.

Temperatures higher than 1100°C have a strong influence on oxidation resistance and stability of eutectic microstructure. Increased oxidation kinetics, extensive evaporation of Ru oxides and coarsening of the microstructure were the consequences of oxidation at 1300°C.

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