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Effects of cerium on the microstructures and grain sizes of cast TiAl alloys

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The rare earth element cerium (Ce) was added to cast binary Ti-44 at.% Al alloys by arc melting in the range of 0.05 to 0.3 atomic percent. It was observed that the as-cast structures of the ingots consisted of the usual three zones of fine equiaxed grains near the mould wall, columnar grains growing away from the mould wall and coarse equiaxed grains near the center. Ce greatly promoted the growth of columnar grains and reduced their diameters. The ingots were subsequently heat treated to obtain well-defined fully lamellar structures. The material containing no rare earth displayed large equiaxed lamellar colonies of average size of >1400 μm; the material with 0.05 at.% addition of Ce consisted of lamellar colonies of as fine as ~ 440 μm. The finest grain size of this material was 320 μm at the top position in the ingot. © *2000 Kluwer Academic Publishers*

1. Introduction

Two-phase gamma TiAl based intermetallic alloys have been under intensive research and development during the last ten to fifteen years in an effort to improve their mechanical properties and to bring about their commercial use in manufacturing structural components for such applications at high temperatures as in turbine and automotive engines [1]. The most important microstructures are the fully lamellar (FL) structure consisting completely of colonies of alternating γ and α_2 plates, and the duplex structure consisting of equiaxed gamma grains and lamellar colonies of similar sizes and volume fractions. The materials with the FL structure exhibit high fracture toughness and creep resistance but lower ductility and strength at room temperature; on the other hand, the materials with the duplex structure show better ductility and strength at room temperature but low fracture toughness and creep strength [2, 3]. It is desirable to find ways of balancing the tensile properties at lower temperatures and the fracture and creep properties.

It has been found that reducing the lamellar colony sizes in the FL structure is effective in enhancing ductility at room temperature and strength at both room and elevated temperatures [4]. The coarse as-cast lamellar colonies can be refined by hot deformation. The colony sizes after isothermal forging and recrystallisation treatment would still be at least 500 to 1000 μm. It is possible to refine the lamellar colonies further by novel heat treatment (down to $\sim$200–300 μm), as high as 0.8 at.% addition of boron ($\sim$100 μm), and extrusion at high temperatures ($\sim$65 μm) [1]. For casting TiAl alloys, boron or TiB_2 additions have been shown to refine the microstructures considerably [5–7], and this is attributed to the presence of TiB_2 particles which act as nucleants as well as reinforcement phases in some cases.

Rare earth (RE) elements have been used for many years to purify and to refine the microstructures of such materials as steels, cast irons, aluminium alloys, titanium alloys and magnesium alloys [8]. Addition of RE elements to FeAl [9] and TiAl [10] alloys were shown to improve ductility and strength at room temperature. However, the use of REs in refining TiAl based alloys and the effects on mechanical properties have not been seriously investigated. In the present study RE element Ce was added to Ti-44 at.% Al alloys to refine the lamellar colonies in the fully lamellar structured materials. The results of effects of Ce on the macro- and microstructures and the grain sizes in casting ingots of the alloys are presented here.

2. Experimental materials and procedures

The form and purity of the metals used were as follow: cut bars and 99.9 wt.% of Ti, cut ingot and 99.99 wt.% of Al, and chips and 95.5 wt.% of Ce. The amounts of Ce added were 0.05, 0.1, 0.2, and 0.3 at.%.

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The alloys were prepared by arc melting and drop casting in a vacuum chamber back filled with Ar. For a particular alloy, the metals were placed in a banana shaped trough in a copper hearth which was water cooled during arc melting and casting. The ingots were remelted for five times, turned upside down with each melting, to ensure the uniformity of composition. The ingot was then drop cast into a square cavity of 15 mm in depth, 25 mm in length and 20 mm in width in the copper hearth. Chemical analysis and electronic diffraction of X-ray analysis (EDX) indicated that actual compositions were fairly close to the nominal ones.

For heat treatment samples of cast ingots were wrapped in Ta foil and sealed in quarts tubs filled with Ar. The sealed samples were heated and kept at 1350 °C in the single α region for one hour to cause the recrystallisation of α grains. This was followed by a controlled furnace cooling at $\sim$5.8 °C/min to 1000 °C and then at $\sim$1.8 °C/min to room temperature.

Samples from different locations were prepared for examination of both macro- and micro-structures. The standard procedures of metallography including polishing the samples were performed. The polished surfaces were etched in a modified Kroll's reagent of 10 vol % HF, 4 vol % HNO_3 and 86 vol % H_2O. The macrostructures were imaged by macro-photography and the microstructures were observed by optical microscopy. The oxides and aluminides of Ce were observed by scanning electron microscopy (SEM) and their compositions were analyzed by EDX-analysis. The lamellar colony sizes were measured using the circular intercept procedures as described in ASTM standard E112-95.

3. Experimental results

3.1. Macro- and microstructures of as-cast ingots

The ingots were cut in the middle along the height and length directions. Half of the ingot cross section examined is shown and the five locations where samples were taken for grain size measurements are indicated in Fig. 1.

The macrostructures of the binary Ti-44 at.% Al alloy are shown in Fig. 2, and those of Ti-44 at.% Al-0.05 at.% Ce and Ti-44 at.% Al-0.3 at.% Ce are shown in Figs 3 and 4, respectively. A thin surface layer of fine, equiaxed grains was observed in all three materials. The columnar grains can be seen to grow from the surface layer to the center in the opposite direction

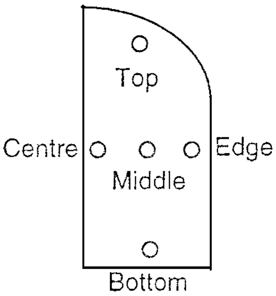

Figure 1 The positions of samples taken for macro/microstructure and grain size measurements.

Figure 2 Macrostructure of as-cast Ti-44 at.% Al alloy.

Figure 3 Macrostructure of as-cast Ti-44 at.% Al-0.05 at.% Ce alloy.

Figure 4 Macrostructure of as-cast Ti-44 at.% Al-0.3 at.% Ce alloy.

of heat flow, and the size of the columnar zone in the vertical direction is as small as ~2 mm in the binary alloy and the sizes in the alloys with 0.05 and 0.3 at.% Ce are about 10 mm. The central zone contains coarse equiaxed grains. It is obvious that the macrostructures of the materials are typical of the three zones observed in castings and Ce greatly changed the solidification behavior of the alloy.

Microstructural observations revealed that each "grain" is actually a lamellar colony as shown in Figs 5–7. Fig. 5 shows the columnar "grains" at the bottom of the ingot for binary alloy. Figs 6 and 7 show the columnar "grains" for Ti-44 at.% Al-0.05 at.% Ce and Ti-44 at.% Al-0.3 at.% Ce, respectively. The diameters of the columnar grains are 120–180 μm in the material without Ce, 70–150 μm in the material with 0.05 at.% Ce, and about 50–80 μm in the material with 0.3 at.% Ce. So, it is known that Ce does not only promote the length of the columnar grains but also reduces these diameters. The "grains" in the fine and coarse equiaxed regions are also lamellar colonies in all the three materials.

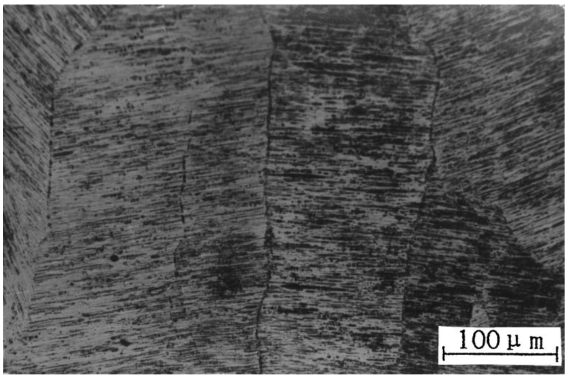

Figure 5 Columnar lamellar colonies at the bottom of the cast Ti-44 Al alloy.

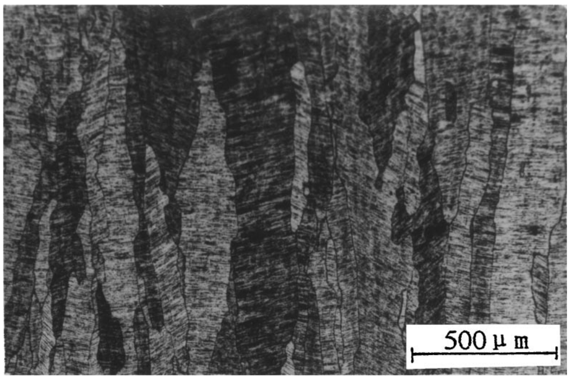

Figure 6 Columnar lamellar colonies at the bottom of the cast Ti-44 Al-0.05 Ce alloy.

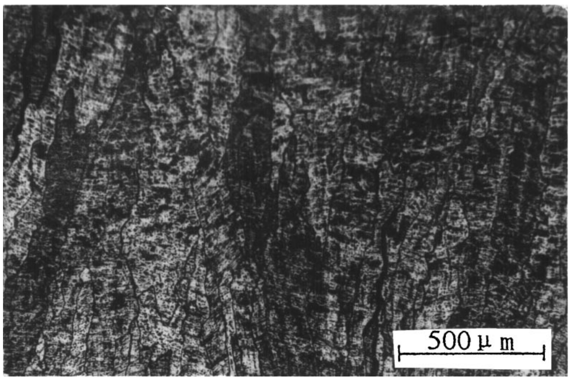

Figure 7 Columnar lamellar colonies at the bottom of the cast Ti-44 Al-0.3 Ce alloy.

3.2. Macro- and microstructures of ingots after heat treatment (HT)

The macrostructures of the binary alloy and the alloys with Ce additions after the heat treatment are shown in Fig. 8. Equiaxed grain structures were observed in the binary alloy and the alloys containing 0.05 and 0.1 at.% Ce, however, when compared with the binary alloy, the equiaxed grains are much finer in the Ce containing alloys. For the alloy with 0.1 at.% Ce, the grains appear to be finer towards the top of the ingots and some reminiscence of the columnar grains can still be seen near the bottom of the ingots and for the alloy with 0.05 at.% Ce, the finest and most uniform grains were observed. However, for the alloy with 0.2 at.% Ce, the columnar grains were apparently broken up into three or four segments from bottom to center and some reminiscences of coarse columnar grains were obtained in the middle part of the ingot except the very fine equiaxed grains at the top position. The shape of the columnar grains was practically not changed after heat treatment for the alloy with 0.3 at.% Ce. This means that the additions of Ce had apparently stabilized the structures of the columnar grains.

By heat treatment in the Ce containing alloy, the fully lamellar (FL) structure was obtained in the alloys as shown in Figs 9–11. However, some boundary phases and ladder-like fully lamellar structure were observed in materials with the higher Ce contents ($\geq$0.2 at.%) as shown in Figs 10 and 11, respectively. The black areas in ladder-like structure in Fig. 11 is very fine fully lamellar structure observed by SEM, as shown in Fig. 12. It is deduced that Ce atoms in the grains changed the recrystalization behavior during the heat treatment.

The lamellar colony sizes were measured for materials with different Ce contents at the five locations illustrated in Fig. 1, and the results are shown in Fig. 13. It can be seen that addition of 0.05 at.% Ce produces the finest colonies and the most uniform distribution of colony sizes in the ingots. The average colony sizes of the binary alloy and the Ti-44 at.% Al-0.05 at.% Ce alloy are ~1425 and 440 μm, respectively. The finest colonies were found to be 320 μm near the top of the ingots with 0.05 at.% Ce. The average colony sizes in the materials with different additions of Ce are 1424 μm (undoped binary alloy), 440 μm (0.05 at.%), 676 μm (0.1 at.%) and 995 μm (0.2 at.%), respectively.

3.3. Appearances and distributions of oxides and aluminides of Ce

Fig. 14 displays the distributions of oxides of Ce in the ingot with 0.1 at.% Ce. Fig. 15 shows the distributions of oxides of Ce in the matrix and aluminides of Ce along

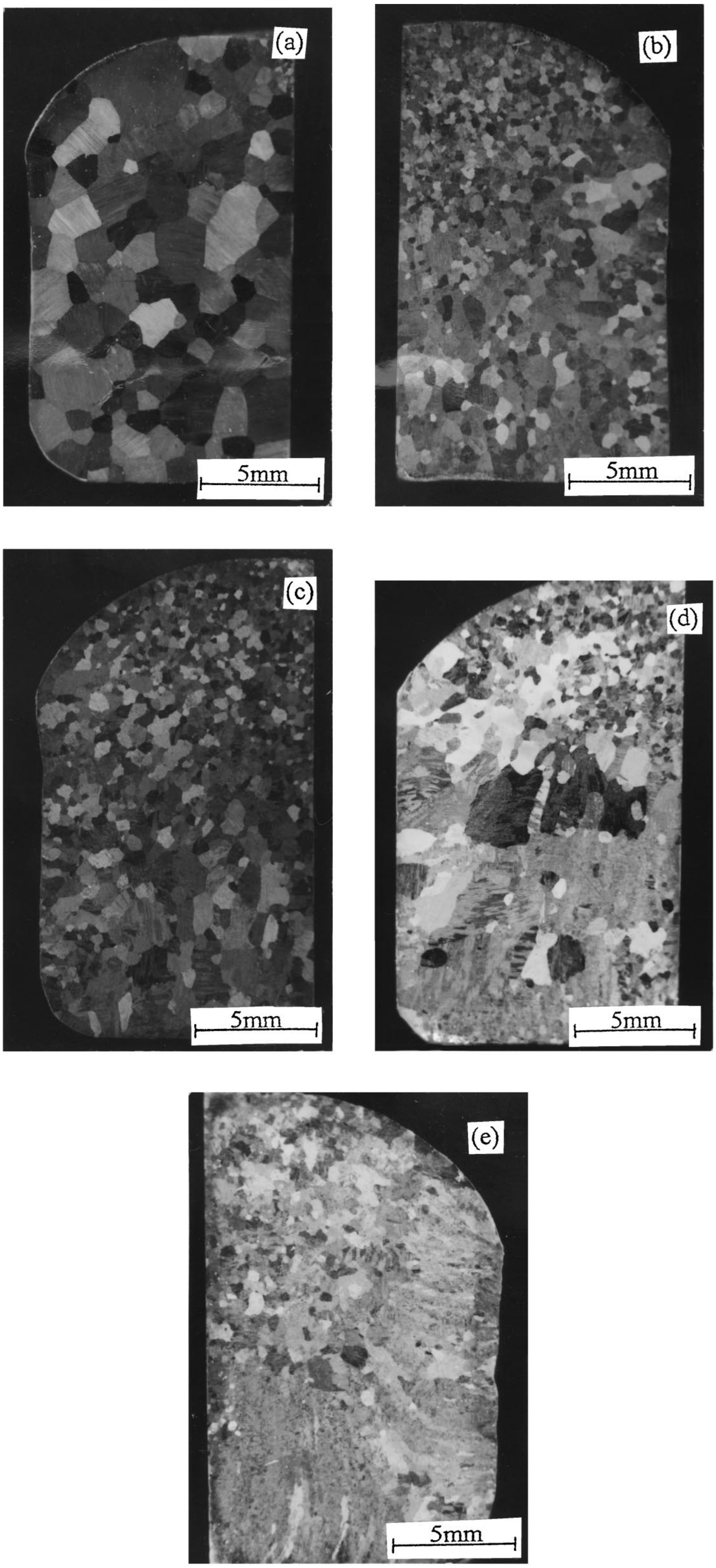

Figure 8 The macrostrucures of the cast Ti-44 at.% Al alloys after heat treatment (a) binary alloy; (b) 0.05 at.% Ce; (c) 0.1 at.% Ce; (d) 0.2 at.% Ce and (e) 0.3 at.% Ce.

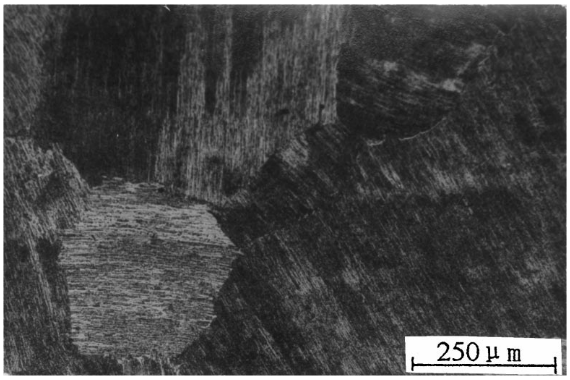

Figure 9 FL structure in alloy containing 0.1 at.% Ce after HT.

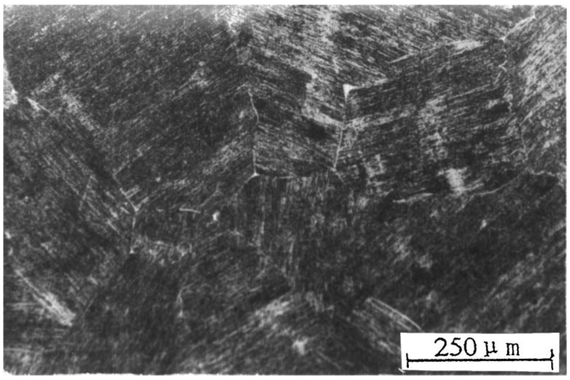

Figure 10 FL structure and boundary phase in alloy containing 0.3 at.% Ce after HT.

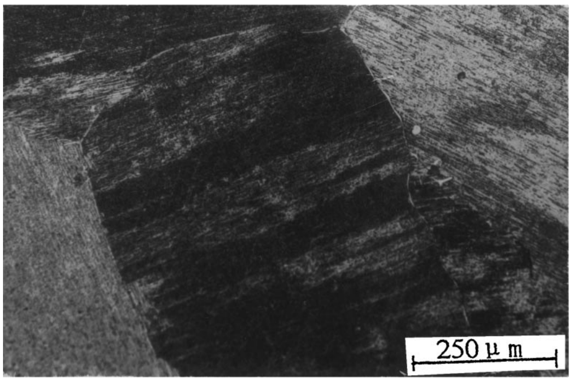

Figure 11 FL structure and ladder structure in alloy containing 0.3 at.% Ce after HT.

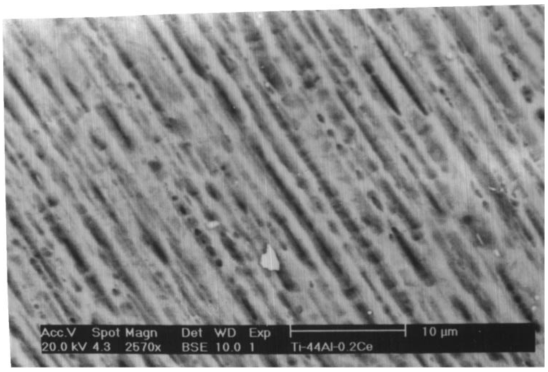

Figure 12 Appearance of ladder structure in high magnification in alloy containing 0.3 at.% Ce after HT (SEM).

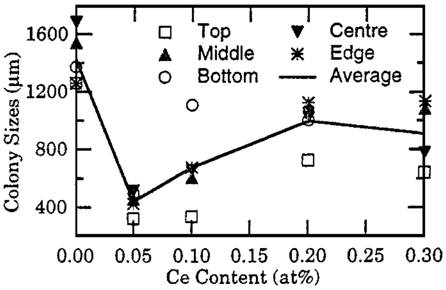

Figure 13 Grain sizes at different locations as a function of Ce content in Ti-44 at.% Al-Ce alloys.

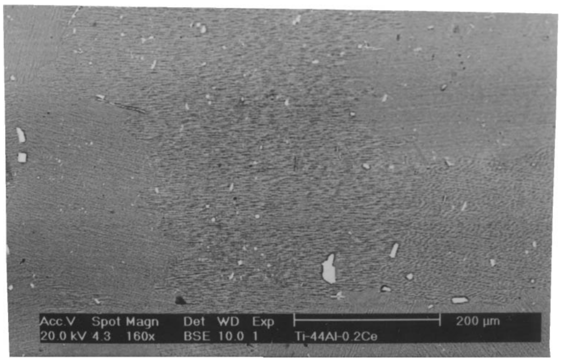

Figure 14 Distributions of Ce oxides in the matrix of Ti-44 Al-0.1 Ce alloy (SEM).

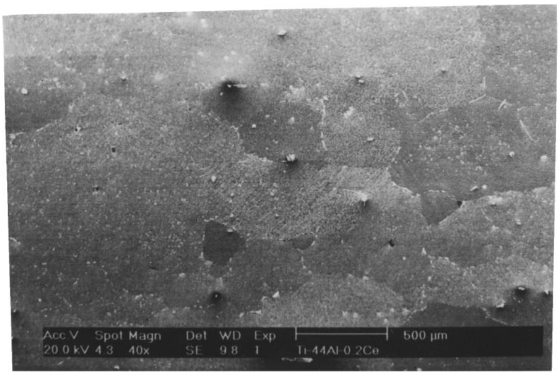

Figure 15 Distributions of Ce oxides and aluminides in Ti-44 Al-0.2 Ce alloy (SEM).

the heat treatment boundaries in the ingot of Ti-44 at.% Al-0.2 at.% Ce alloy, and Fig. 16 shows the appearances of aluminides of Ce along the heat-treatment grain boundaries of the same ingot as mentioned above. As addition of Ce was over 0.1 at.%, there were some aluminides of Ce in the boundaries of the alloy, which were the boundary phases mentioned in the Fig. 10. Fig. 17 shows coexisting of oxides and aluminides at a boundary in the ingot with 0.3 at.% Ce, with the oxides being surrounded by aluminides. The characteristics of appearances and distributions of the oxides and the aluminides show that oxides of Ce were formed during solidification of the alloys and that aluminides of Ce were formed during cooling after heat treatment. It is verified by the examination using EDX-analysis that the oxides are Ce_2O_3 and the aluminides are Ce_2Al_3.

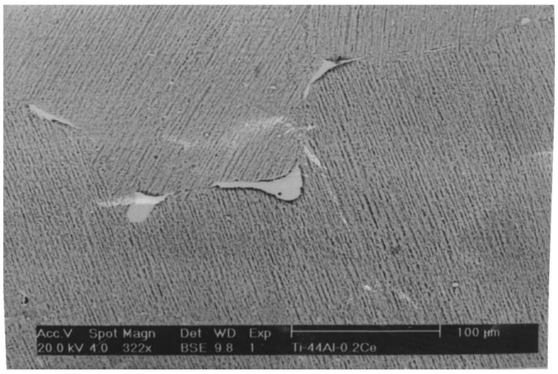

Figure 16 Appearances of Ce aluminides along boundaries in Ti-44 Al-0.2 Ce alloy (SEM).

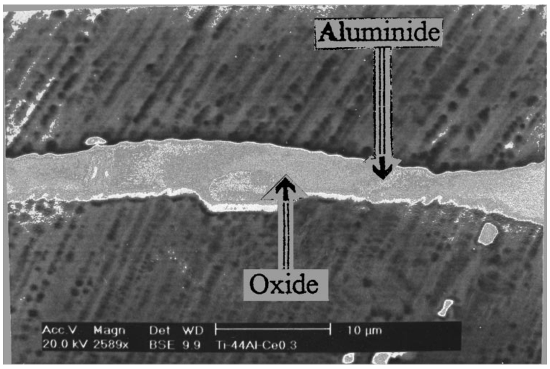

Figure 17 Appearances of co-existence of Ce oxides and aluminides in Ti-44 Al-0.3 Ce alloy (SEM).

4. Discussion

It has been shown in this investigation that grain structures are finer and more uniform in the alloys micro-alloyed with Ce. Oxides and aluminides of Ce have been observed using scanning electron microscopy (SEM). It is deduced that some of the oxides are too tiny to be seen by SEM and may act as nucleation clusters during solidification and recrystallisation. RE elements are known to segregate at grain boundaries in many alloy systems to retard the growth of grains during solidification and recrystallisation [8]. The existence of Ce aluminides at heat treated boundaries in this work is an indirect evidence of segregation of Ce atoms from matrix to boundaries. Ce aluminides were formed when Ce atoms react with Al atoms at boundaries as soon as certain concentration of Ce was reached.

The effect of refining seemed to decrease with increasing Ce contents above the optimum level and new phases and less-well-defined lamellar structures were observed in the alloys heat treated. It is likely that the high contents of Ce have changed the phases present at various temperatures although the ternary phase diagrams are not readily available.

5. Conclusions

Ce has obviously changed solidification behavior and promoted the growth of columnar colonies in the as-cast structure in Ti-44 at.% Al alloys. It is difficult to break the columnar colonies to get grain colonies during heat treatment when Ce additions were over 0.05 at.%.

Ce in the melt initially reacted with oxygen to form oxides. Ce aluminides occur in heat treatment boundaries as Ce additions were over 0.1 at.%. Sometimes aluminide co-existed with oxide.

The colonies in fully lamellar alloys were refined by proper additions of Ce amount. The average colony sizes in heat treated ingots were reduced from >1400 to ~ 440 μm with a proper addition of 0.05 at.% Ce, and the finest colony size is 320 μm in the top position of the ingot with 0.05 at.% Ce.

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