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The comparison of effects of four rare earth elements additions on structures and grain sizes of Ti-44Al alloy

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By vacuum arc melting, four kinds of rare earth (RE) elements, Ce, La, Nd and Gd, were added in the range from 0.05% to 0.5% (mole fraction) to binary Ti-44% Al alloy to refine its grains of structures for high ductility. Effects of RE elements on structures and grain sizes of the alloy were investigated and compared. It was observed that Ce had the strongest effect on promoting growth of columnar colonies and Gd had the weakest one, while the other RE elements obviously promoted this growth in as-cast structures of the ingots. It was seen that the four RE elements initially reacted with oxygen to form oxides in the melt, the RE aluminides occur at boundaries during heat treatment, and sometimes the aluminide co-existed with oxide at boundaries or in grains. Results of measurement of grain sizes showed that the grains in the ingots heat-treated were effectively refined by properly adding the four RE elements, and the average grain size in the ingot with 0.15% Gd is finer and more uniform than that with Ce, La and Nd. The results of comparison verified that the sequence of effects of the four RE elements is Ce, La, Nd and Gd from strong to weak, which means that the alloy is sensitive to a small amount of Ce addition and is comparatively dull to a larger amount of Gd.

1. Introduction

TiAl based intermetallic alloys have been expected as a new kind of aircraft and aerospace materials to substitute for Ni_3Al and Fe_3Al alloys owing to their high toughness at elevated temperature and low density [1–3]. A great number of results from other researchers show that microstructure is the major factor affecting mechanical properties of the alloys [4–10]. It is stated that fine full lamellar grains perform an outstanding balance between fracture toughness and creep resistance at elevated temperature and ductility and strength at room temperature. In recent years, an untiring effort to refine grains has being carried out. For example, the grain sizes after isothermal forging would still be at least 500–1000 μm [7] and the grain sizes after reciprocating hot–mechanical process were as fine as 20–30 μm [11]. The alloying process to refine grains for improving ductility at room temperature was recently another main research topic [12–14]. The grain sizes were reduced to 100 μm by adding 0.8% boron into the alloy [15].

Rare earth elements have been used for many years to purify and refine the microstructures of such materials as steels, cast irons, aluminum alloys, titanium alloys and magnesium alloys [16, 17]. It is reported that rare earth element, Er, could change the behavior of solidification of TiAl alloy [18] and La could improve the ductility of TiAl alloy at room temperature [19]. However, the use of RE in refining TiAl based alloys and their effects on structures and grain sizes have not been seriously investigated. In this study RE element, Ce, La, Nd and Gd, were added to Ti-44% Al alloy to refine the grains in the fully lamellar structured materials. The effects of them on the macro- and micro-structures and the grain sizes in casting ingots of the alloys are present.

2. Experimental materials and procedures

2.1. Preparation of ingots

The raw materials of pure titanium, aluminum and one of the rare earth metals totally weighted to 30 grams were melt in a vacuum arc melting furnace and cast into an ingot with 23 mm in length, 19 mm in width and 19 mm in height. The purity of the metals used was as follows: 99.9% for Ti, 99.99% for Al, 99.5% for Ce, La, Nd and Gd. The amounts of rare earth additions were

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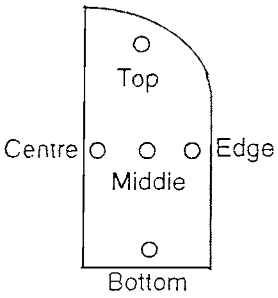

Figure 1 The positions of samples taken for macro/microstructures observations and grain size measurements.

0.05, 0.1, 0.2 and 0.3% for Ce, 0.05, 0.1, 0.2 and 0.3% for La, 0.05, 0.1, 0.15, 0.2 and 0.3% for Nd and 0.1, 0.15, 0.2, 0.3 and 0.5% for Gd. The results of chemical analysis for alloys indicated that actual compositions of the alloys were fairly close to their nominal ones.

Cast ingots were wrapped with Ta foil and sealed in quartz tubes filled with Ar for heat treatment. The sealed ingots were heated and kept at 1350°C in the single α region for 1 hour to cause the recrystallization of α grains. This was followed by a controlled furnace cooling at 6°C/min to 1000°C and then at 1.85°C/min to room temperature.

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

2.2. Processes of observations of structures and measurements of grain sizes

The standard procedures of metallography examination were followed in polishing ingots. The macrostructures were taken using a normal camera and the microstuctures were observed by optical microscopy. The oxides and aluminides of the RE in the alloy were observed by scanning electron microscopy (SEM) and their compositions were analyzed by electron spectrometer and pulsed NMR spectrometer. The grain sizes were measured using the circular intercept procedures as described in ASTM standard E112-95.

3. Experimental results

3.1. Effects of Ce, La, Nd ane Gd on structures

3.1.1. Effects of Ce, La, Nd and Gd on as-cast macrostructures

Effects of Ce, La, Nd and Gd on as-cast macrostructures of the alloy are shown in Fig. 2. A thin layer of fine equiaxed grains was observed under surface of ingots in all five materials. The columnar colonies can be seen to grow from the surface layer to the center in the opposite direction of heat flow during solidification. The lengths of the columnar zone without and with Ce, La, Nd and Gd in the vertical direction in ingots are presented in Table I.

It is known from Fig. 2 and Table I that the four RE elements have promoted the growth of columnars during solidification and the effects of Ce, La and Nd on promoting this growth are greater than that of Gd.

3.1.2. Effects of Ce, La, Nd and Gd on as-cast microstructure

Effects of Ce, La, Nd and Gd on microstructure of the ingots are shown in Fig. 3. The diameters of the columnar colonies were reduced from 180–250 μm in the ingot without RE to smaller ones in the ingots with different RE element additions. Reduced diameters can be seen from Fig. 3 and the sizes of them were shown in Table II.

It is known that the four RE elements can refine diameter of columnar colonies and the refinement effects increase with increasing the elements additions. An interesting difference between them is that the refinement effect of Gd is smaller than that of Ce, La and Nd. The effect of 0.15% Gd is smaller than that of 0.05% Ce, 0.05% La and 0.05% Nd, and 0.5% Gd has the same effect as 0.3% Ce, 0.3% La and 0.3% Nd have.

3.1.3. Effects of Ce, La, Nd and Gd on macrostructures after being heat treated

The macrostructures of the ingot of the binary alloy and the alloys with RE additions after being heat treated are shown in Fig. 4. From this figure, it is quite obvious that the columnar colonies disappeared and equiaxed grains occur in the binary alloy and the alloys with RE element additions—very coarse in the binary alloy and much refined in the alloys with RE element additions. The finest and most uniform grains were seen in the alloys with 0.05% Ce, 0.1% La, 0.1% Nd and 0.15% Gd for four RE elements additions, respectively. However, while amount of RE elements additions are greater, the RE elements enhanced the stabilization of the columnar colonies in the processing of heat treatment and some reminiscences of the columnar colonies could still be seen in the region of the bottoms of the ingots. The lengths of the reminiscences are about 8 mm for the alloy with 0.3% Ce (see Fig. 4b), 4–5 mm for the alloy with 0.3% La (see Fig. 4e), 7–8 mm for the alloy

TABLE I The lengths of the columnar zone in the vertical direction (mm)

Without RE	0.05%Ce	0.3%Ce	0.05%La	0.3%La	0.05%Nd	0.2%Nd	0.15%Nd	0.15%Gd
2	11	12	8	12	10	12	5	11

TABLE II The sizes of the diameters of the columnar colonies (μm)

No RE	0.05%Ce	0.3%Ce	0.05%La	0.3%La	0.05%Nd	0.2%Nd	0.15%Gd	0.5%Gd
180–250	70–150	50–80	100–180	50–60	50–90	20–50	120–170	20–50

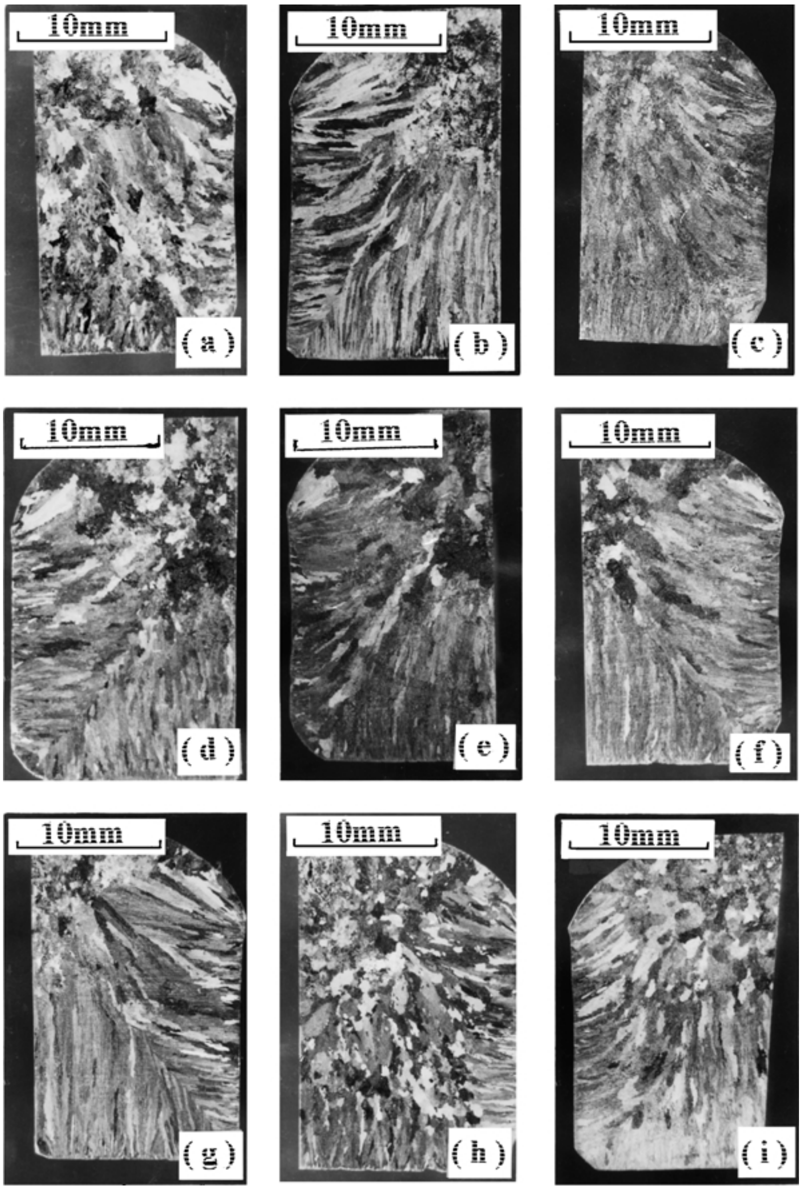

Figure 2 The macrostructures of (a) No RE, (b) 0.05%Ce, (c) 0.3%Ce, (d) 0.05%La, (e) 0.3%La, (f) 0.05%Nd, (g) 0.2%Nd, (h) 0.15%Gd and (i) 0.5%Gd.

with 0.3% Nd (see Fig. 4g), and 2 mm for the alloy with 0.5% Gd (see Fig. 4i).

3.2. Appearances and distributions of oxides and aluminides of the RE elements

Oxides and aluminides of Ce, La, Nd and Gd were observed as the RE elements additions increased. Appearances and distributions of oxides were shown in Fig. 5 when RE addition is 0.1% or 0.15%. Appearances and distributions of Ce and Gd oxides and aluminides were shown in Fig. 6 when Ce and Gd additions are higher. Appearances of co-existences of oxide and aluminide at grain boundary or in grains were present in Fig. 7 when the RE addition is as high as 0.3% or 0.5%.

The oxides and aluminides were verified by analyzing compositions of them. Results of analysis are listed in Table III. From Table III it is known that the spherical phase is oxides of the RE elements and plate-like phase alone boundaries is aluminides of the RE elements. It is deduced that oxides and aluminides of four RE elements are Ce_2O_3 and Ce_2Al_3, LaO_2, La_2O_3, La_2Al_3 and $LaAl_3$, NdO_2, Nd_2O_3 and Nd_2Al_3, and, GdO_2 and $GdAl_2$, respectively.

The characteristics of appearances and distributions of the oxides and the aluminides show that oxides of the RE elements formed in the period of solidification of the liquid owing to their reactions with oxygen atoms, and the aluminides formed as temperature dropped down during heat treatment. The RE elements atoms saturated in grains diffused toward boundaries or oxides in the grain and reacted with aluminum atoms to form aluminides as soon as a certain concentration of the RE atoms was realized. As aluminides formed on the surface of oxides in grains or at boundaries, the appearance of co-existence of aluminide and oxide occur. Fig. 7a and c show the appearance of co-existence at boundaries and Fig. 7b and d show it in grains.

From Figs 5–7 and Table III, it is known that the aluminides of Gd occur in the alloy with 0.5% Gd while the aluminides of Ce, La and Nd occur in the alloys with 0.3% of them. Considering effects of Gd on

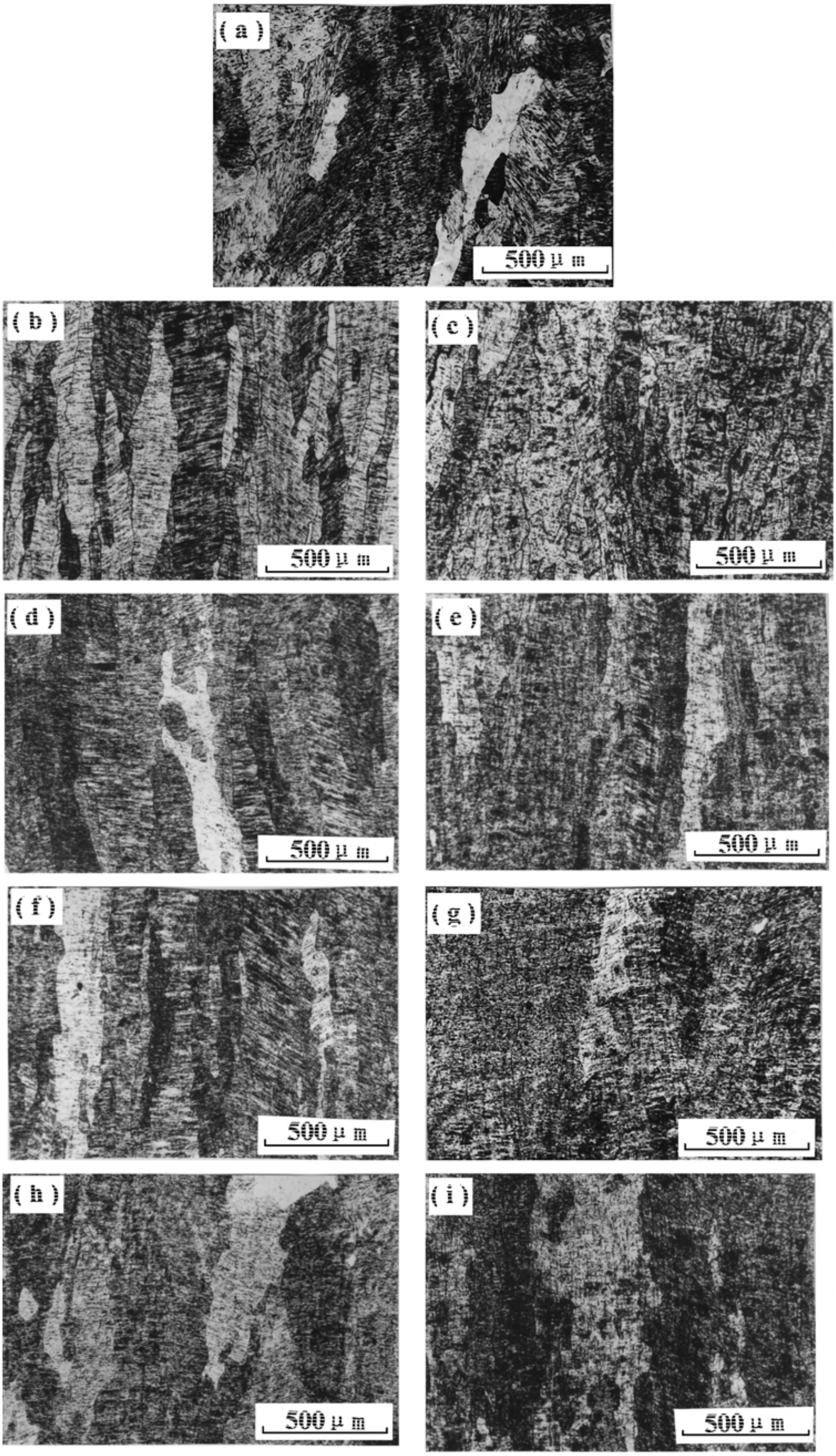

Figure 3 The microstructures of specimens of (a) No RE, (b) 0.05% Ce, (c) 0.3% Ce, (d) 0.05% La, (e) 0.3% La, (f) 0.05% Nd, (g) 0.2% Nd, (h) 0.15% Gd and (i) 0.5% Gd.

the macro- and micro-structures of ingots, (see Figs 2 and 4), Gd has a different behavior of metallurgy from Ce, La and Nd. It is deduced that Gd has a higher solubility in the solution of the alloy than Ce, La and Nd.

3.3. Effects of the RE elements on grain size

The grain sizes were measured for alloys with different additions of the RE elements at the five locations in ingots illustrated in Fig. 1, and the results of

TABLE III Results of compositions analysis of the RE oxides and aluminides (mole fraction, %)

Specimen	Ti	Al	O	Ce	La	Nd	Gd	Phase
Ti-44Al-0.2Ce	1.71	1.24	61.36	35.69	–	–	–	Oxides
Ti-44Al-0.3Ce	–	0.73	58.36	40.91	–	–	–	Oxides
Ti-44Al-0.3Ce	–	62.19	–	37.81	–	–	–	Aluminide
Ti-44Al-0.1La	4.78	0.62	57.62	–	36.98	–	–	Oxide
Ti-44Al-0.3La	–	0.28	56.87	–	42.85	–	–	Oxide
Ti-44Al-0.3La	–	62.13	–	–	37.87	–	–	Aluminide
Ti-44Al-0.3La	–	74.61	–	–	25.39	–	–	Aluminide
Ti-44Al-0.1Nd	6.26	4.53	61.27	–	–	27.94	–	Oxide
Ti-44Al-0.3Nd	–	0.30	63.06	–	–	36.64	–	Oxide
Ti-44Al-0.3Nd	–	63.75	–	–	–	36.25	–	Aluminide
Ti-44Al-0.15Gd	10.26	7.71	60.22	–	–	–	21.80	Oxide
Ti-44Al-0.5Gd	3.86	2.11	61.93	–	–	–	32.10	Oxide
Ti-44Al-0.5Gd	6.14	54.33	7.26	–	–	–	32.27	Aluminide

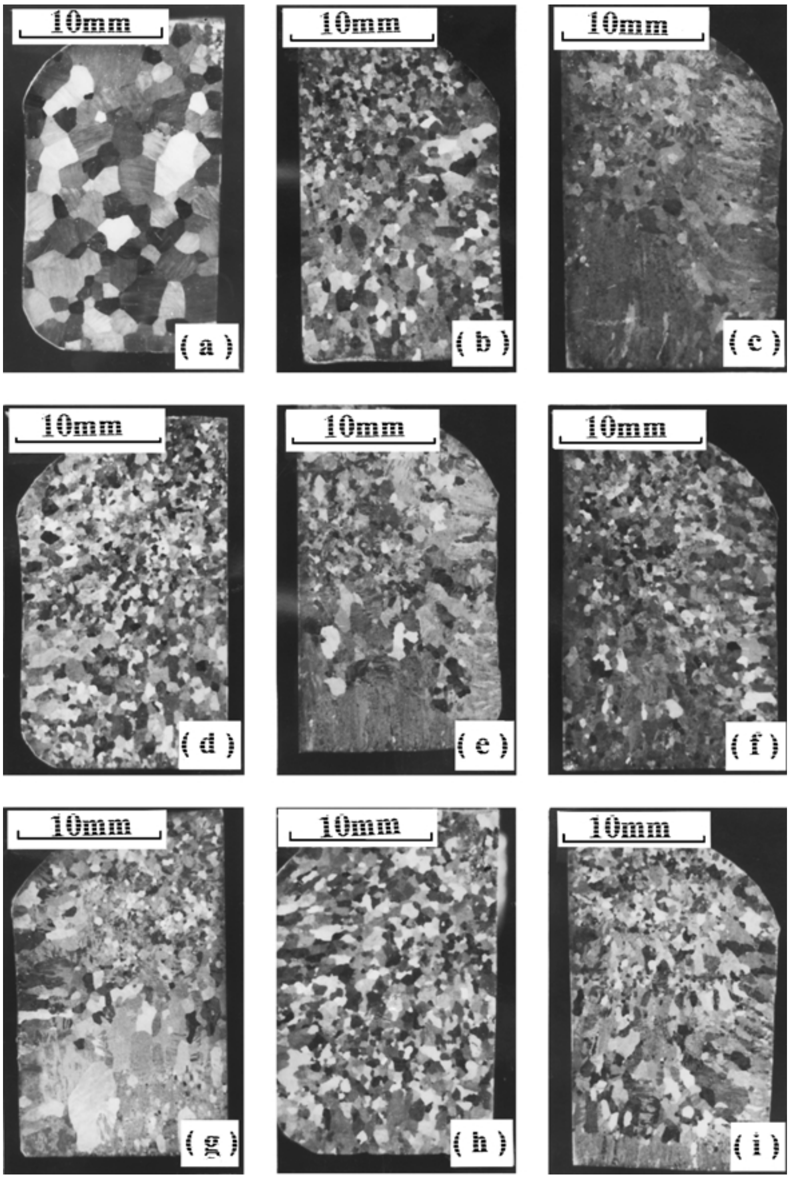

Figure 4 Macrostructures after heat treated of (a) no RE, (b) 0.05%Ce, (c) 0.3%Ce, (d) 0.1%La, (e) 0.3%La, (f) 0.1%Nd, (g) 0.3%Nd, (h) 0.15% Gd, and (i) 0.5%Gd.

average grain sizes are listed in Table IV and shown in Fig. 8.

Three features can be seen from Table IV and Fig. 8. Firstly, there is a proper amount of addition for a particular RE element added, and it is 0.05% for Ce, 0.1% for La and Nd and 0.15% for Gd. Secondly, La and Gd have greater effect of refining grains than Ce and Nd. And thirdly, the alloy is very sensitive to Ce addition and it gets its smallest grain size at 0.05% Ce and the grain size increases quickly as soon as Ce is over 0.05%. On the contrary, the alloy is somewhat obtuse to Gd addition. It gets its smallest grain size at

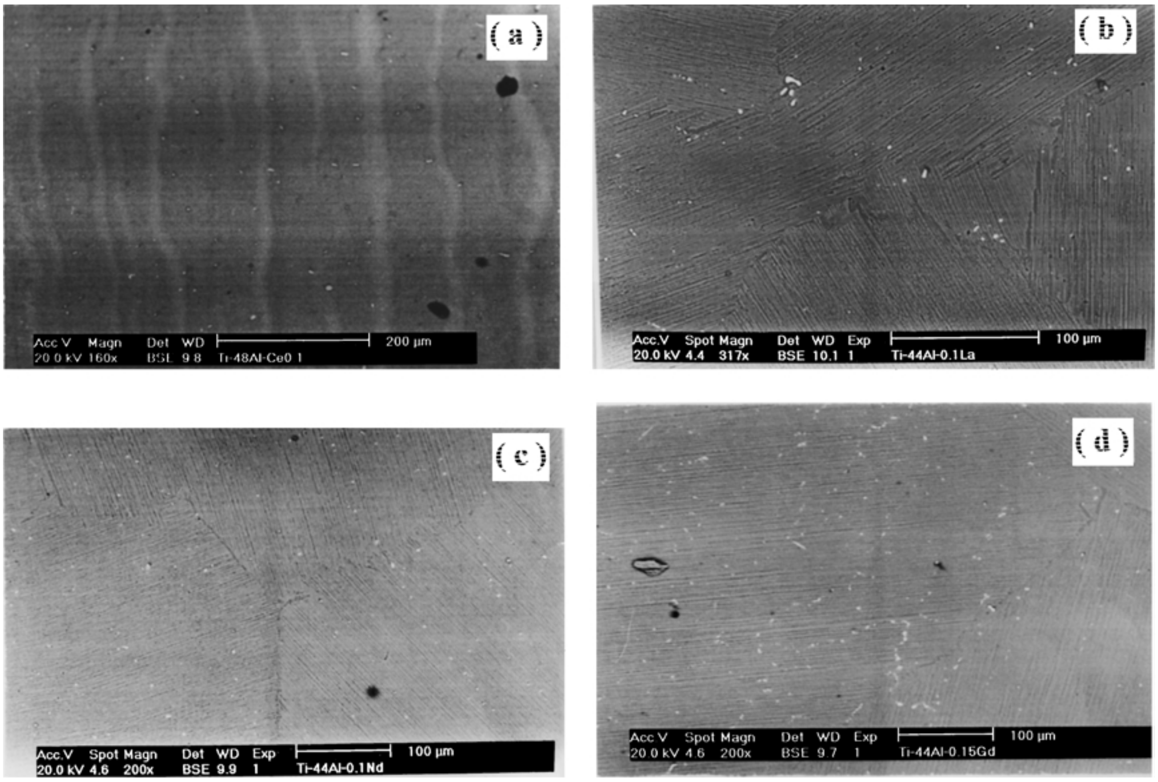

Figure 5 Appearances and distributions of oxide when RE addition is 0.1% or 0.15% (a) 0.1% Ce, (b) 0.1%La, (c) 0.1%Nd, (d) 0.15%Gd.

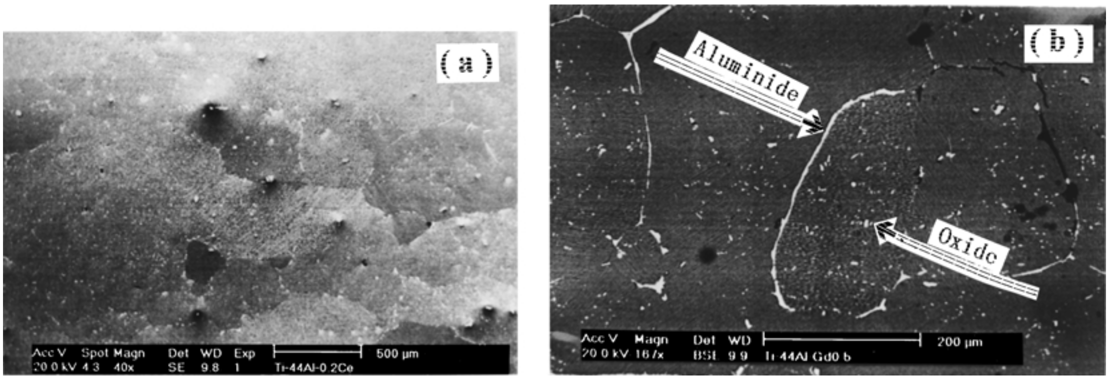

Figure 6 Appearances and distributions of oxides and aluminides of (a) 0.2%Ce, (b) 0.5%Gd.

TABLE IV The average grain sizes (μm) in ingots with different additions of RE elements (%)

RE element additions	0	0.05	0.1	0.15	0.2	0.30	0.50
Alloy with Ce	1424	440	676	–	995	929	–
Alloy with La	1424	397	381	–	479	617	–
Alloy with Nd	1424	478	450	609	625	699	–
Alloy with Gd	1424	–	572	411	444	493	579

0.15% Gd and the grain size increases slowly as Gd increases.

4. Discussion

4.1. Effects of RE elements on solidification behavior of the alloy

It can be known in this investigation that the four RE elements reacted initially with oxygen in the melt of Ti-44Al alloy and then existed as free atoms in the solution to change solidification behavior of the alloy. It has been found that there are some residual columnars at the bottom of ingots after heat treatment and the temperature should be raised for breaking up them. This is an evidence of RE atoms in the lattice of crystal of the alloy.

4.2. Effects of RE elements on heat treatment behavior of the alloy

The facts that the aluminides of RE elements existed in boundaries and co-existed with oxides of RE elements verify that RE atoms in grains migrated toward boundaries and oxides in lattice and combined with aluminum atoms to form aluminides during heat treatment. However, the migration rates of the four RE elements are different from each other. Two aspects of behaviors of RE elements cause this difference, which are, 1), the difference of energies of metallic bounds between Al and Ti atoms and RE elements atoms in the solution, and 2), the difference of solubility of RE elements in the solution of the alloy. It is likely that Ce element has a very strong bound energy, which is verified by

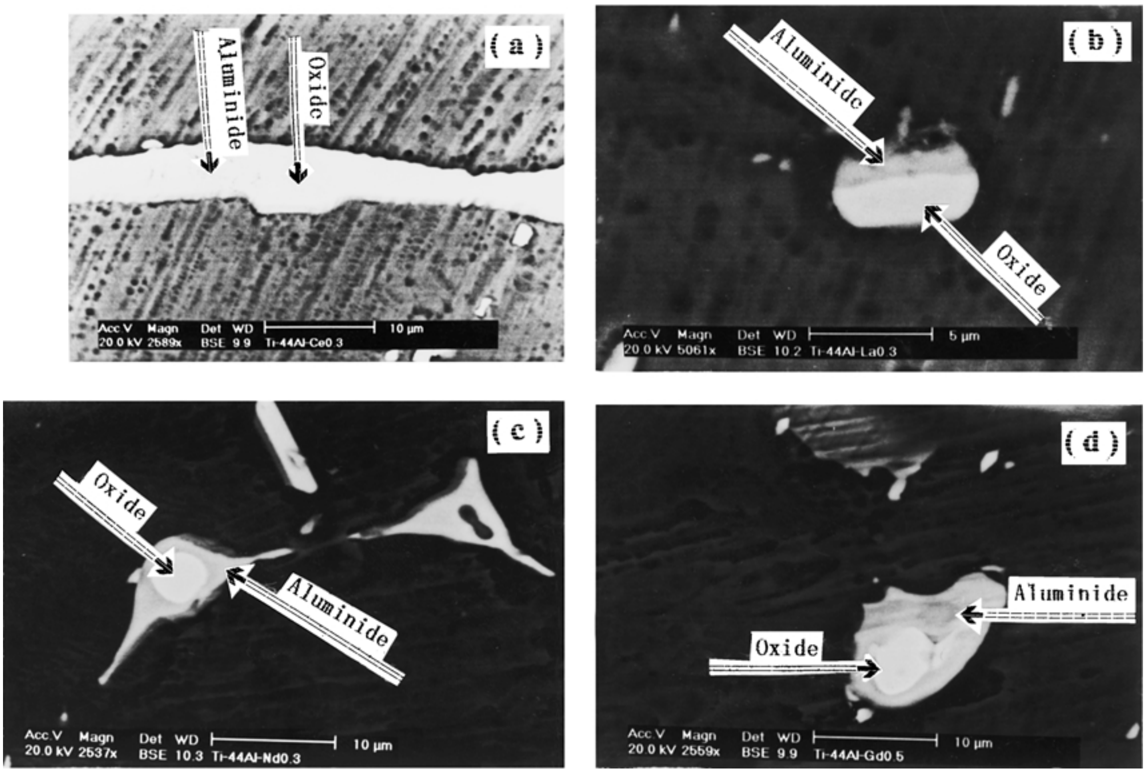

Figure 7 Appearances of coexistences of oxides and aluminides at boundaries (a) 0.3%Ce, (b) 0.3%La, (c) 0.3%Nd, (d) 0.5%Gd.

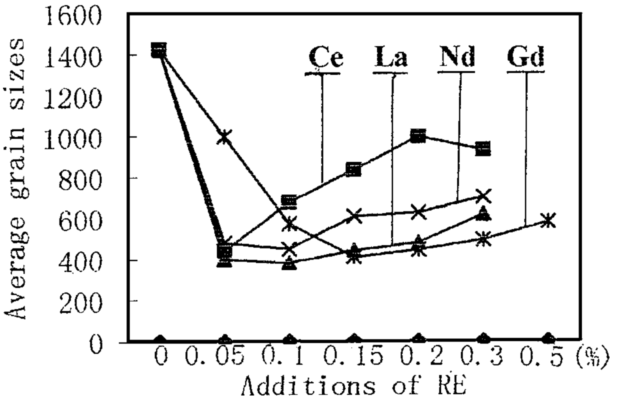

Figure 8 varieties of average grain sizes in the ingots with additions of RE elements.

very strong stability of the columnar colonies during heat treatment, and a minium solubility in the alloy, which is shown by great amount of Ce aluminides at boundaries at very low additions of Ce. Meanwhile Gd element has a weak bound energy and a maximum solubility in the alloy, which are verified by quick dissolving of the columnar colonies during heat treatment and minium amount of Gd aluminides when Gd is smaller than 0.5%.

4.3. Analysis of the differences of effects of four RE element on structures

It is evident that the degrees of effects of Ce and Gd on the structures of the alloy are different. The reason for this difference is their different thermodynamic characteristics. Ce metal, as well as La and Nd, consists of face-centered cubic lattice while Gd metal consists of hexagonal close-packed lattice. Meanwhile the differences of electron arrangements in atoms of RE elements are another reason responsible for the different effects on structures. In the four RE elements, the degree of difference of electron arrangements between Gd and Ce, La and Nd is greater than that between Ce, La and Nd, although there are some small differences between Ce, La and Nd. This is totally corresponding to the different effects of Ce, La, Nd and Gd on structures and grain sizes.

5. Conclusions

1. The four RE elements have obviously changed solidification behavior and promoted the growth of columnar colonies in the as-cast structure in Ti-44Al alloy. Among these elements, Ce has the strongest effect on promoting the growth of columnar colonies and Gd has the weakest one. The sequence of this effect of the four RE elements is Ce, La, Nd and Gd from strong to weak. It is difficult to break up the columnar colonies to get grain colonies during heat treatment when Ce additions are over 0.05%, and it is easier to break the columnar colonies up when Gd additions are less than 0.5%.

2. The four RE elements in the melt initially reacted with oxygen to form oxides that distributed in grains mainly and at boundaries. The RE aluminides occur at boundaries during heat treatment. The aluminides occur as Ce was over 0.1%, La and Nd were over 0.2%, and Gd was 0.5%. Sometimes the aluminides co-existed with oxides at boundaries and in grains.

3. The grains after being heat treated in the alloy were effectively refined by adding proper amount of one of the four RE elements. The average grain sizes were reduced from >1400 μm to 440 μm with an addition of 0.05% Ce, to 381 μm with an addition of 0.1% La,

to 450 μm with an addition of 0.1% Nd, and to 411 μm with an addition of 0.15% Gd. The grain size in the ingot with 0.15at % Gd is finer and more uniform than that with 0.05% Ce, 0.1%La and 0.1% Nd.

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