Effects of Ce Addition on the Microstructure and Mechanical Properties of Accident-Tolerance Fe-Cr-Al Fuel Cladding Materials

Naimeng Liu, ZhongWu Zhang, Yang Zhang, Ye Cui, Dan Chen, Yu Zhao, SongSong Xu and Hao Guo

Abstract Fe-Cr-Al alloys are promising materials for accident-tolerance fuel cladding applications due to their excellent performance of oxidation and corrosion resistance under elevated temperature. In this study, effects of the addition of a small neutron absorption cross section rare-earth element Cerium (Ce) on the microstructure and mechanical properties of Fe-Cr-Al alloys with 0–0.1 wt% Ce have been investigated. As Ce content increased, the grains became size-refining obviously and number of precipitates increased. The results of EDS showed that the precipitates were mainly consisted of intermetallic compounds. Notably, the ultimate tensile strength and elongation reached the optimized values when the content of Ce was 0.02 wt%. However, the tensile properties decreased when Ce content was above 0.05 wt%, which may be due to the excess of intermetallic compounds.

Keywords Fe-Cr-Al alloys · Cerium · Grain refinements · Incoherency
Mechanical properties

Introduction

FeCrAl ferritic alloys are highly considered as optional accident-tolerance fuel cladding materials due to their more outstanding oxidation and corrosion resisting ability exhibited under elevated temperatures compared to Zr-based alloys, which may even cause hydrogen gas generation under the condition of losing coolant accidents [1, 2]. Currently, the investigation focused on FeCrAl alloy is usually based on developing the composition to optimize the mechanical properties as well as maintaining adequate oxidation and corrosion resisting performance [1, 3–7].

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The rare earth element Cerium (Ce) is one of those alternative choices for improving the compositions of FeCrAl alloys when considering the contribution of addition of elements on both grain-refinement and neutron absorption cross sections [8, 9]. Applications of Cerium in recent years are basically on stainless steels as well as twinning induced plasticity (TWIP) steels [10, 11]. The results showed that Cerium played a role of refining the size of grains by means of formatting the globular inclusions, which act as nucleation sites or obstacles against the grain growth. However, the interactions between intermetallic inclusions and size refinement on grains and the effects of them on mechanical properties on room temperature have not been fully investigated.

It is the purpose of this work to enlighten the internal laws and the effects of various contents of Cerium addition (0–0.1 wt%) on the grain sizes, the distribution of inclusions and tensile properties at room temperature. The relationships between those compositions designed and the performance shown on both microstructure and mechanical properties are also discussed.

Experimental Methods

Four FeCrAl-RE alloys containing 0, 0.02, 0.05 and 0.1 wt% Ce (denoted as 0 Ce, 0.02 Ce, 0.05 Ce and 0.1 Ce, respectively) were cast in an arc-melting furnace in the atmosphere of Argon, and their compositions are showed in Table 1. The as-cast ingots were hot rolled at 950 °C with a total reduction of 70%. After hot rolling, four specimens were cold-rolled with a total reduction of 10%. The as-rolled alloys were then annealed at 550 °C for 0.5 h.

The grain size, shape and the distribution of precipitation of all alloys produced in this work were properly etched, observed and measured on a Carl Zeiss optical microscopy (OM). The distribution of elements corresponded to the microstructure were undertaken by an Oxford scanning electron microscopy (SEM) equipped with energy spectrum analysis (EDS). Tensile tests were carried out with the loading axis parallel to the rolling direction. Tensile testing specimens were shaped according to ASTM standards shown in Fig. 1, and were tested at room temperature (25 °C) with a tensile test machine.

Table 1 Nominal compositions of FeCrAl-RE alloys produced in this work (wt%)

Designation	Fe	Cr	Al	Y	Ce	C
0-Ce	Bal.	12	4.4	0.2	0	≤ 0.02
0.02-Ce	Bal.	12	4.4	0.2	0.02	≤ 0.02
0.05-Ce	Bal.	12	4.4	0.2	0.05	≤ 0.02
0.1-Ce	Bal.	12	4.4	0.2	0.1	≤ 0.02

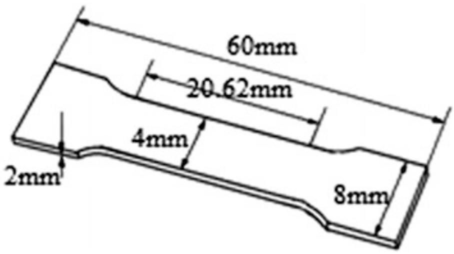

Fig. 1 Tensile testing specimens processed according to GB/T228.1-2010 standards

Results and Discussion

Microstructure

Microstructure of Hot-Rolled Specimens

Figure 2 exhibits microstructures of 950 °C hot- rolled specimens with various content of Ce. The as-rolled specimen showed a mainly coarse columnar grain structure surrounded by some small-sized equiaxed grains, and some of the inclusions are observed. Statistic analysis is performed for the results of average diameters of the grains, showing those specimens get their grains refined comparing to the Fe-12Cr-4.4Al-0.2Y one (Fig. 2a), as shown in Table 2. The distribution of the inclusions is also corresponded with the different content of Ce, as the inclusions dispersed when Ce is doped less than 0.02 wt%, and have a trend of

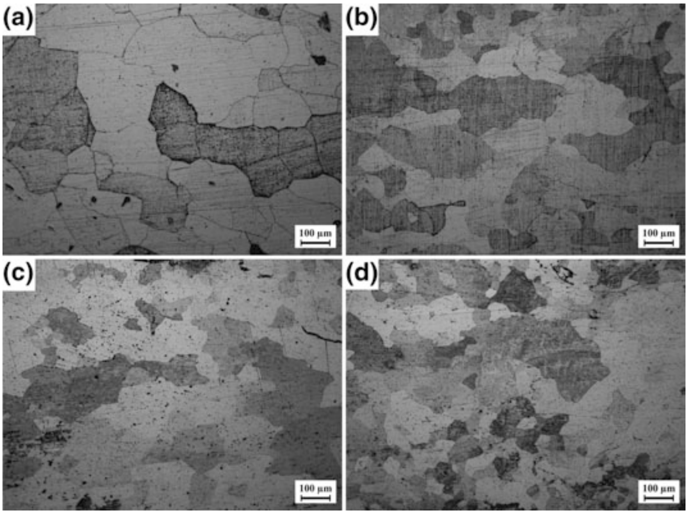

Fig. 2 Microstructures of 950 °C hot- rolled **a** 0-Ce, **b** 0.02-Ce, **c** 0.05-Ce and **d** 0.1-Ce specimens

Table 2 Values of average grain sizes on various hot-rolled specimens

Designation	0-Ce	0.02-Ce	0.05-Ce	0.1-Ce
Average grain size (μm)	161 ± 0.5	121 ± 0.5	116 ± 0.5	106 ± 0.5

centralizing on grain boundaries when Ce is doped more than 0.05 wt%. Almost no inclusions are exhibited in Fe-12Cr-4.4Al-0.2Y specimens.

Microstructure of Cold-Rolled and Annealed Specimens

The microstructures of all four specimens after cold-rolling and annealing at 550 °C for 0.5 h are shown in Fig. 3. As the statistic results shown in Table 3, the average grain size becomes smaller than hot-rolled specimens, because the cold rolling procedure came after hot rolling, making it a larger reduction in total. These results also show a similar trend on grain sizes corresponded to the content of Ce as the results on hot-rolled specimens have shown. The inclusions distribute in the matrix, and appear near grain boundaries when Ce content is more than 0.02 wt%. The size of inclusions is less than 2 μm.

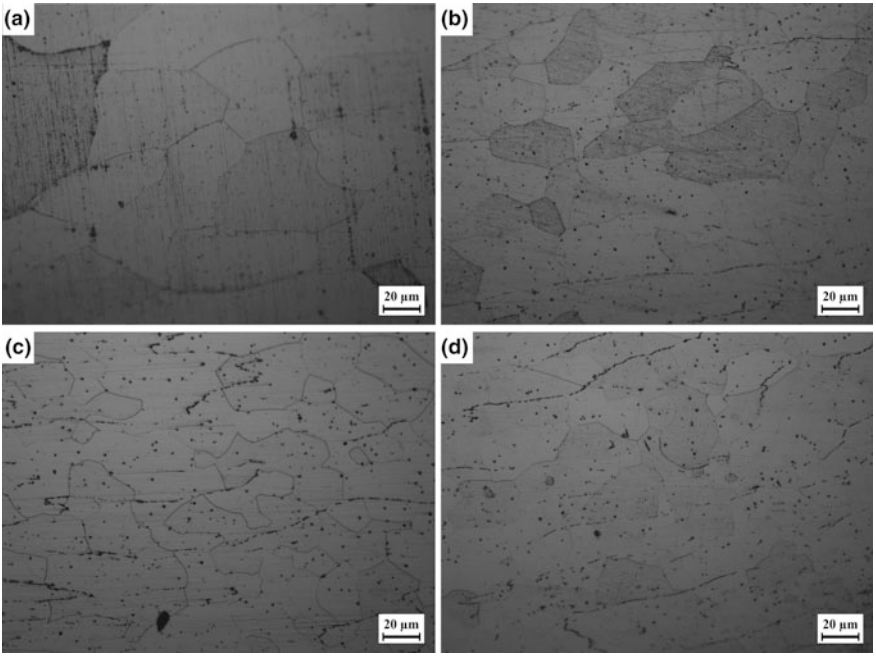

Fig. 3 Microstructures of cold-rolled and annealed **a** 0-Ce, **b** 0.02-Ce, **c** 0.05-Ce and **d** 0.1-Ce specimens

Table 3 Values of average grain sizes on various cold-rolled and annealed specimens

Designation	0-Ce	0.02-Ce	0.05-Ce	0.1-Ce
Average grain size (μm)	94 ± 2.3	81 ± 2.3	76 ± 2.3	71 ± 2.3

Mechanical Properties

Tensile Test Results of Hot-Rolled Specimens

Figure 4 and Table 4 show the results of tensile tests at room temperature on all specimens after 950 °C hot-rolling with various Cerium contents. Each of the samples shown represents the average of three samples. Composition dependence can be illustrated from the engineering stress-strain curves, as total elongation values increase when the content of Ce is between 0.02 and 0.05 weight percent, and reduce immediately when adding 0.1 wt% of Ce. For the magnitude of yield strength (YS) and ultimate tensile strength (UTS) shown in Table, no distinct dependence can be observed as their differences are less than 30 MPa.

Fig. 4 Engineering stress-strain curves of various hot-rolled specimens tested at room temperature

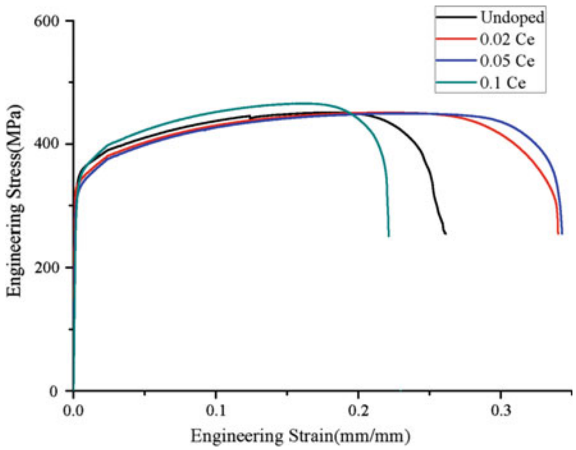

Table 4 Values of tensile properties of various hot-rolled specimens tested at room temperature

Designation	0-Ce	0.02-Ce	0.05-Ce	0.1-Ce
Yield strength (MPa)	350.85	335.23	321.80	348.15
Ultimate tensile strength (MPa)	451.06	450.96	449.47	465.72
Elongation (%)	26.8	36.2	31.9	21.8

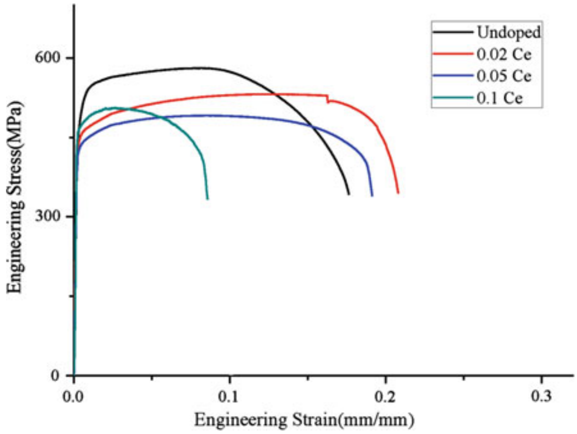

Fig. 5 Engineering stress-strain curves of various cold-rolled and annealed specimens tested at room temperature

Tensile Test Results of Cold-Rolled and Annealed Specimens

Tensile curves and magnitudes of YS, UTS and total elongation of cold-rolled and annealed specimens are depicted in Fig. 5 and Table 5. When the specimens get cold-rolled, their yield strength and ultimate tensile strength go upward, as their values advanced 40–150 MPa, approximately. An analogous trend as hot-rolled specimens on total elongation values can be shown, as they are on the increase when the content of Ce is between 0.02 and 0.05 weight percent, and decrease immediately when adding 0.1 wt% of Ce. However, it can be appreciated that the ultimate tensile strength values decline continuously as the content of Ce increases. Their largest disparity can be as many as 75.11 MPa. Nevertheless, their strength values go up while elongations reduce as a consequence of work hardening.

Analysis on Distribution of Elements

In addition to pervious research, the present work has also taken a research on the distribution of elements on both the matrix and the inclusions, in order to find their regularities in more detail. Figure 6 and Table 6 shows the SEM image and EDS analysis on the matrix of all specimens with various contents of Cerium. The

Table 5 Values of tensile properties of various cold-rolled and annealed specimens tested at room temperature

Designation	0-Ce	0.02-Ce	0.05-Ce	0.1-Ce
Yield strength (MPa)	532.63	455.86	433.21	459.84
Ultimate tensile strength (MPa)	581.20	531.87	491.53	506.09
Elongation (%)	21.4	21.6	21.3	12.1

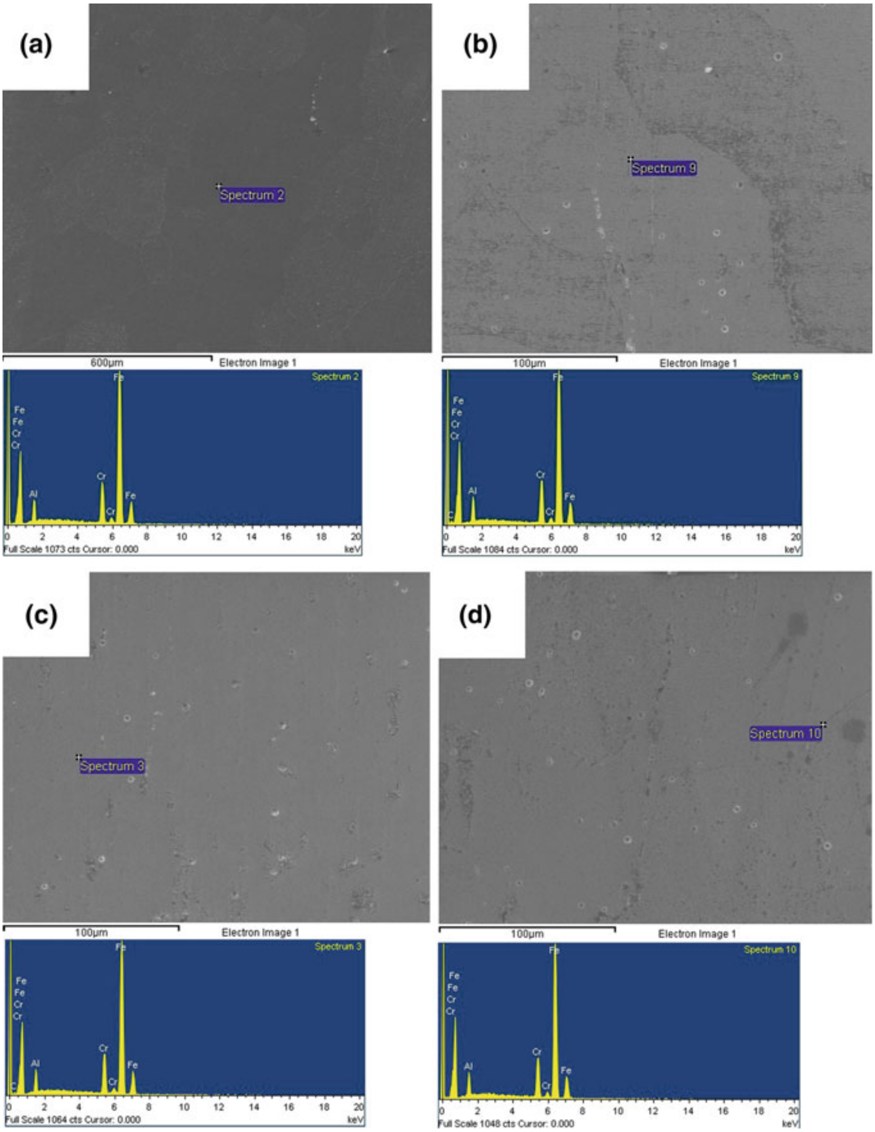

Fig. 6 SEM image and EDS analysis on the matrix of **a** 0-Ce, **b** 0.02-Ce, **c** 0.05-Ce and **d** 0.1-Ce specimens

analysis of energy spectrum shows that there is little component difference between specimens when taking Fe, Cr and Al into consideration, as the original proportion of these elements is equal.

Figure 7 and Table 7 presents the SEM image and EDS analysis on the inclusions of all Ce-doped specimens. It is Fe, Cr and Al constitute the main contents

Table 6 Values of contents in the matrix of all specimens analyzed by EDS (wt%)

Composition	Fe	Cr	Al	C
0-Ce	82.86	12.69	4.46	–
0.02-Ce	78.79	13.03	4.30	Detectable
0.05-Ce	81.50	12.07	4.31	Detectable
0.1-Ce	83.13	12.35	4.52	–

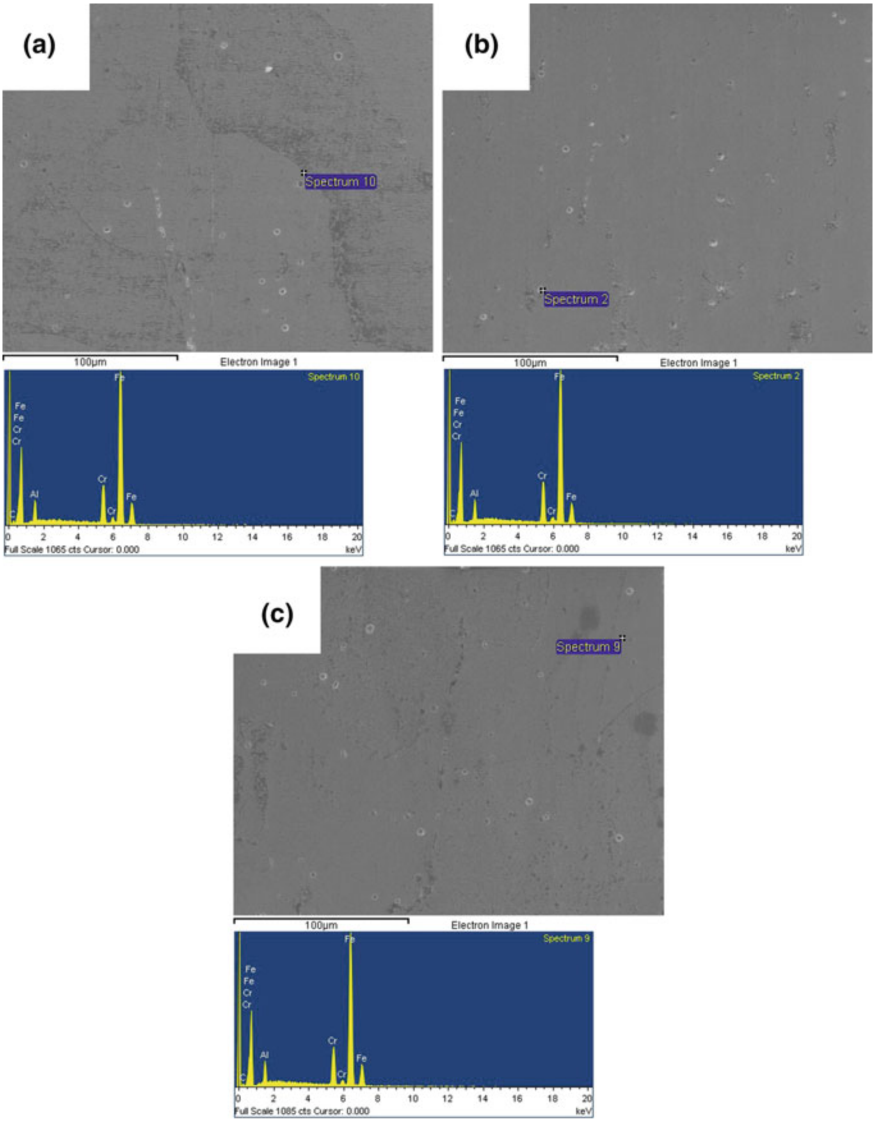

Fig. 7 SEM image and EDS analysis on the inclusions of **a** 0.02-Ce, **b** 0.05-Ce and **c** 0.1-Ce specimens

Table 7 Values of contents in the inclusions of all Ce-doped specimens analyzed by EDS (wt%)

Composition	Fe	Cr	Al	C
0.02-Ce	79.74	12.47	4.09	Detectable
0.05-Ce	79.92	12.37	4.17	Detectable
0.1-Ce	80.92	12.42	4.32	Detectable

and some peaks of C are observed, indicating that there could be some metallic carbides like $M_{23}C_6$, M_7C_3 or M_6C [12, 13], which have the proportion close to the results.

Discussion on Relationships Between Inclusions and Mechanical Performance

As described above, the mechanical properties of the present Fe-12Cr-4.4Al-0.2Y alloys are modified by the increase of inclusions related to the content of Ce, indicating the presence of the optimum range of Ce content. In particular, the inclusions change from uniformly distributed to a trend of segregating to grain boundaries, and their numbers are also boosted as the doping of Ce gets excessive.

The effects of Ce on refining have been investigated by Y. –U. Heo et al. who put the refining effect as a consequence of the dragging force of the Ce-rich compounds against the coalescence of the columnar grains [14]. Similar results on average grain sizes can also be observed as it shown above. According to the formula of Hall-Petch, the grain diameter has an inversely proportional effect on the yield strength of the specimens. The yield strength is improved as the grains get finer. Grain refining has a positive effect on improving the ductility as there are a growing number of grains per unit volume. As a result, the deformation can be dispersed to more grains, making it a homogeneous process preventing stress concentration locally, and retarding the crack initiation eventually. However, as the addition of Ce increases continuously, the size of inclusions are getting larger and the distribution of inclusions changed to a state of segregation, thus degrading the coherency of grain boundaries. Accordingly, their positions can be potential for crack initiation. As a result, the mechanical performance on both strengths and elongations reduced gradually when adding excessive Cerium.

Conclusion

Effects of Ce contents on both the microstructure and mechanical properties of FeCrAl fuel cladding materials were investigated, and the following conclusions were obtained:

(1) The average grain size of Fe-12Cr-4.4Al-0.2Y alloy was remarkably refined as the content of Ce increased. At the same time, intermetallic inclusions gradually occurred, and their distribution changed from dispersing on the matrix to a trend of segregating on grain boundaries when the addition of Ce was more than 0.05 wt%.
(2) As the content of Ce increased, composition dependence can be illustrated on the tensile properties of hot-rolled specimens, as total elongation values increase when the content of Ce is between 0.02 and 0.05 weight percent, and reduce immediately when adding 0.1 wt% of Ce. No distinct dependence can be observed from the magnitude of yield strength and ultimate tensile strength as their differences were within the margin of error. Analogous trend can also be exhibited on the results of cold-rolled and annealed tensile specimens, as the elongations are on the increase when the content of Ce is between 0.02 and 0.05 weight percent, and decrease immediately when adding 0.1 wt% of Ce. However, the margins on both the yield strength and the ultimate tensile strength values declined continuously as the content of Ce increased.
(3) The addition of Ce had effects on both grain refining and inclusion modifications, and the mechanical performance got affected as a consequence. When the doping of Ce was less than 0.02 wt%, the yield strength got improved due to fine-grain strengthening and the ductility was also optimized as the concentration of stress was avoided. However, when the doping of Ce was more than 0.05 wt%, the inclusions were in the state of incoherence with the matrix due to their larger size and segregating distribution, and reduced the tensile properties values eventually.

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