Effects of carbon and titanium on the solidification structure and properties of ferrite heat-resistant alloy

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Abstract

In order to design a low-cost high temperature ferrite alloy, the effects of carbon, and titanium on its solidification structure and properties have been studied. When the carbon content is increased from 0.07 to 0.35 wt\%, the alloy grains become finer, and the grain boundaries become wider and more zigzag. The alloy oxidation weight-gain rate at 1300°C keeps increasing clearly, however, that at 1350°C decreases at first then increases. When the carbon content is above 0.15 wt\% the alloy strength at 1300°C decreases acutely. When the titanium content increased from 0.30 to 0.60 wt\%, the alloy grains became fine, and both the alloy strength and oxidation resistance improved remarkably.

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1. Introduction

Fe–Cr–Al alloy is well known by its excellent oxidation resistance and sulphurization resistance at high temperature, and is therefore used widely for electric heating alloy, structure materials of heat-treatment furnaces, nuclear industry equipment, etc. [1–4]. It is generally made out of high pure raw materials, which are melted and cast in vacuum or protective atmosphere. As the VOD and AOD processes have spread in Europe and America, etc., the making and using of super high temperature of Fe–Cr–Al alloy have become more popular.

Usually high carbon content does not facilitate the oxidation resistance of Fe–Cr–Al alloy, so the carbon content if often limited to rather small quantities, such as below 0.05 wt\%. The VOD or AOD process makes this easier. It is very hard to reduce the carbon content of Fe–Cr–Al alloy to 0.05 wt\% or less, if the alloy is made with the conventional melting and casting process, and out of low cost industry raw materials, such as scrap steel, ordinary low carbon Cr–Fe alloy etc. Furthermore, a low carbon content decreases the alloy castability substantially, makes it difficult to cast complex structure components, and results in the grain coarsening of the alloy during long service. On the other hand, a certain amount of carbon can refine the solidification structure of Fe–Cr–Al alloy, and fine grains will improve the alloy oxidation resistance [5,6]. Moreover, a certain amount of carbon can increase the strength of high temperature alloy through the combined effects of precipitation strengthening by fine intra-granular and inter-granular carbides, and strengthening by the solution of carbon in solid [7,8]. The zigzag nature of the grain boundaries due to carbides' precipitating enhances the creep rupture strength of the alloy [9].

The addition of titanium to the high-temperature alloy together with carbon refines its solidification structure notably, and improves its strength, and inhibit grains from coarsening in long service at high temperature [10].

In order to design a new kind of low-cost high temperature ferrite alloy, which could be made out of low cost industry raw materials with conventional melting and casting processes, effects of additions of carbon, and titanium of Fe–Cr–Al alloy on its solidification structure and property are studied. The alloy will be used as an electric heating alloy and as a structural material.

2. Experimental details

The alloy was made out of conventional industrial materials with a mid-frequency induction furnace in a foundry shop. Totally, eleven groups of samples were been cast in ordinary
gramite moulds. The first five groups were for investigating the carbon effect, in which the carbon content was classified in to five quantity grades, 0.5, 1.0, 1.5, 2.5, 3.5 wt%. The action of the titanium content showed in the last six groups.

The size of the cast rods is $\Phi 30 \times 300$ mm. All of the specimens were machined from cast rods. The oxidation resistance of the specimens both at 1300 and 1350°C in air, of which the dimensions of the samples were $\Phi 15 \times 30$ mm, were determined with the weight-gain method, in which the period of cyclic oxidation was 100 h, where totally six periods were applied. The rupture strength of the specimens at 1300°C in air, of which the specimen dimensions were $\Phi 16 \times 30$ mm, was tested with a Gleeble 1500 tester. The parameters were as follows: heating velocity 5°C/s; holding time at 1300°C 5 min before drawing, drawing rate 5 mm/s. The rupture strength at room temperature was tested with a 600 kN universal mechanical tester.

### 3. Results and analyses

The results of eleven groups of samples corresponding to the actual chemical compositions are given Tables 1 and 2.

#### 3.1. Effects of carbon on the solidification structure and properties of the ferrite alloy

Figs. 1–3 show the effect of the carbon content on the alloy solidification structure. When carbon content is low, for instance, 0.07 wt%, the amount of precipitation at the

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**Table 1**

Chemical compositions of alloy in group I and their test data (note: (1) with addition of 0.5 wt% Re, (2) Cr, 21–25 wt%, and (3) Fe, balance)

| Alloy no. | C (wt%) | Al (wt%) | Ti (wt%) | Rupture strength at 25°C (MPa) | Rupture strength at 1300°C (MPa) | Oxidation weight gain at 1300°C (g/m²/h) | Oxidation weight gain at 1300°C (g/m²/h) |
|-----------|---------|----------|----------|-----------------------------|----------------------------------|-----------------------------------------|-----------------------------------------|
| 1-1       | 0.07    | 4.06     | 0.65     | 196.7                       | 18.5                             | 0.23                                    | 0.88                                    |
| 1-2       | 0.1     | 5.4      | 0.51     | 231.3                       | 19.52                            | 0.24                                    | 0.75                                    |
| 1-3       | 0.15    | 4.73     | 0.44     | 276.4                       | 18.66                            | 0.29                                    | 0.62                                    |
| 1-4       | 0.26    | 4.75     | 0.4      | 228.5                       | 6                                | 0.25                                    | 0.76                                    |
| 1-5       | 0.35    | 4.1      | 0.54     | 179.3                       | 2                                | 0.55                                    | 1.2                                     |

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**Table 2**

Chemical compositions of alloy in group II and their test data (note: (1) with addition of 0.5 wt% Re, (2) Cr, 21–25 wt%, (3) Fe, balance, and (4) *, the alloy is too brittle to get tensile specimens)

| Alloy no. | Ti (wt%) | Al (wt%) | C (wt%) | Rupture strength at 25°C (MPa) | Rupture strength at 1300°C (MPa) | Oxidation weight gain at 1300°C (g/m²/h) | Oxidation weight gain at 1300°C (g/m²/h) |
|-----------|----------|----------|---------|-----------------------------|----------------------------------|-----------------------------------------|-----------------------------------------|
| 2-1       | 0.086    | 4.23     | 0.075   | *                           | *                                | 3.29                                    | 5.0                                     |
| 2-2       | 0.31     | 4.21     | 0.146   | 318                         | 18                               | 0.32                                    | 0.38                                    |
| 2-3       | 0.38     | 4.12     | 0.172   | 212                         | 20.3                             | 0.12                                    | 0.39                                    |
| 2-4       | 0.6      | 3.67     | 0.088   | 278                         | 19.2                             | 0.12                                    | 0.2                                     |
| 2-5       | 1.2      | 4.17     | 0.127   | 12.7                        | *                                | 0.36                                    | 1.25                                    |
| 2-6       | 1.77     | 4.32     | 0.117   | *                           | *                                | 0.58                                    | 1.78                                    |
grain boundaries is very small, and the grain boundaries are nearly straight, the size of a single grain being rather large (Fig. 1). When the carbon content is increased to 0.25 wt%, many carbides appear at the grain boundaries, the size of the alloy grains being about equal to one third or one fourth of that of the former, with the grain boundaries becoming wider and zigzag (Fig. 2). With more carbon, the alloy grains become much finer (Fig. 3).

The effect of the carbon content on the mechanical properties of the alloy can be shown in Figs. 4 and 5. With increase of the carbon content, the alloy rupture strength at room temperature first increases significantly but, then begins to decrease acutely when carbon content exceeds about 0.15 wt% (Fig. 4). However, for the high temperature strength of the alloy at 1300°C, for a carbon content ranging from 0.07 to 0.15 wt% there is very little effect, but when the carbon content is increased to above 0.15 wt%, the high temperature strength of the alloy decreases acutely (Fig. 5).

As the chromium content in each kind of test alloy is very high, the main type of carbides in the alloy is $\text{M}_2\text{C}_6$ [10]. One of the reasons why alloy strength at room temperature improves as the carbon content increases is that the solution of carbon in the solid enhances the alloy grain matrix, whilst another reason is that a small amount of carbides precipitated along the grain boundaries strengthens the grain boundaries. However, because $\text{M}_2\text{C}_6$ carbide has a complex fcc structure, which is rather different to that of ferrite, a bcc structure, there is no special crystal orientation between ferrite and $\text{M}_2\text{C}_6$ [11]. Therefore, as the amount of carbides becomes larger, and the carbides coarsen, a large stress concentration may occur between the carbides and the grain matrix that can result in micro-crevices, and the binding between carbides and the grain matrix weakens remarkably. Thus the alloy rupture strength at room temperature begins to decrease acutely when the carbon content exceeds about 0.15 wt%.

At high temperature, especially above 1300°C, the grain boundaries becomes more important to the alloy strength, and it is very natural that the precipitation of a large amount of carbides along the ferrite grain boundaries is quite harmful to the alloy strength. Thus when the carbon content is above 0.15 wt%, the high temperature strength of the alloy decreases acutely.

The effect of the carbon content on the alloy oxidation resistance at high temperature is shown in Fig. 6. One important and interesting discovery is that the effect of the carbon content increase on the alloy oxidation resistance at
1300°C is quite different from that at 1350°C. Varying the carbon content from 0.07 to 0.25 wt% has little influence on the alloy oxidation weight-gain rate at 1300°C, a higher carbon content increasing the alloy oxidation weight-gain rate noticeably. When the carbon content is increased, the alloy oxidation weight-gain rate at 1350°C decreases at first until the carbon content reaches about 0.15 wt%, when it then increases.

When the carbon content is increased from 0.07 to 0.15 wt%, the alloy grains refine significantly, and fine grains provide more short-cuts for the out-movement of Cr and Al [8,9], which is essential to the formation of continuous and compact protective scales, therefore the alloy oxidation resistance at 1350°C improves. However, such effect is not evident when the alloy is oxidized at 1300°C. On the other hand, too much carbon in the alloy will result in the formation of a great amount of carbides, which decreases the chromium activity, and carbon oxidation will compete with chromium oxidation, or even with aluminum oxidation above 1300°C. Moreover, the precipitation of a large amount of carbides along the grain boundaries might result in cavitations or even crevices, which facilitates the ingress of oxidant, so the internal oxidation would occur. The gathering and escape of CO or CO₂ as a result of internal oxidation weakens the compactness and adherence to the alloy matrix of the protective scales. Therefore, the alloy oxidation resistance deteriorates greatly.

3.2. Effect of titanium on solidification structure and properties of ferrite heat-resistant alloy

The addition of titanium to the ferrite alloy can also refine its solidification structure notably. When the titanium content is below 0.10 wt%, the alloy grains are rather coarse, some of them even being across the whole section (Fig. 7), therefore, the rupture strength is very low: even the sample rod could not be machined into tensile samples (see Table 2). When titanium content increases from 0.30 to 0.60 wt%, the alloy grains become refined and the alloy strength at both room and high temperature improves greatly. However, too high a titanium content would result in a great deal of Laves phase TiFe₂, which increases the brittleness of the alloy, the alloy losing almost all of its strength, and even the sample rod not being able to be machined into tensile samples again (also see Table 2).

Coarse grains of the alloy due to the low titanium content also cause its bad oxidation resistance, where the oxidation weight gain can exceed 3 g/m²/h (Table 2 and Fig. 8). When the addition of titanium is increased from 0.3 to 0.6 wt%, fine grains provide more short-cuts for the out-movement of Cr and Al [8,9], and the alloy oxidation resistance improves remarkably. However, if the titanium content is equal to or greater than 1.2 wt%, titanium oxidation will compete with those of chromium and aluminum, and there will be a lot of TiO₂ in the oxide scale. As the grain structure of TiO₂, which belongs to the isometric system, is quite different to that of Al₂O₃, which belongs to hexagon system (or trigonal system), so a lot of TiO₂ in the oxide scale would result in a large stress, which destroys the compactness and adherence to the matrix of the oxide scale, so that the alloy oxidation resistance deteriorates greatly (see Table 2 and Fig. 8).

4. Conclusions

1. For the test Fe–Cr–Al ferrite alloy, the optimum carbon content is 0.15 wt%, and the optimum titanium content is 0.30–0.60 wt%.
2. With the increase of carbon content, the amount of carbides increases substantially, and the alloy grains become clearly finer; when the carbon content is increased from 0.07 to 0.15 wt% the alloy room temperature strength is improved, but there is little influence on its strength at 1300°C: both of them begin to decrease greatly when carbon content exceeds about 0.15%. The alloy oxidation-resistance at 1350°C improves initially, but then deteriorates as the carbon content is increased, while carbon content ranging 0.07–0.25 wt% hardly affects its oxidation resistance at 1300°C, whilst even greater carbon is harmful.
3. When the addition of titanium is from 0.3–0.6 wt%, the alloy grains become fine, and both the alloy strength and oxidation resistance improve remarkably.

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