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Effects of carbon and chromium on the solidification structure and properties of ferrite–austenite duplex heat-resistant alloy

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Abstract

In order to design a new kind of low-cost high-temperature ferrite–austenite duplex alloy, the effects of carbon and chromium on the alloy solidification structure and properties have been investigated with orthogonal experiments. The addition of carbon promotes strongly the formation of austenite and that of carbides in the alloy solidification structure and refines the alloy grains. With the increase of carbon content, the alloy high temperature strength and oxidation resistance at 1250°C improves at first, but then begins to deteriorate greatly when the carbon content exceeds 0.15%. The addition of chromium facilitates the formation of ferrite in the alloy solidification structure. As the chromium content increases, the alloy rupture strength at 1250°C initially is enhanced, but then reduces rapidly, while the alloy oxidation resistance improves continuously. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Heat-resistance; Duplex alloy; Carbon; Chromium

1. Introduction

Ferro superalloy might be classified into three types in accordance with its matrix structure: ferritic (α) alloy; austenitic (γ) alloy; or ferrite–austenite ($\alpha + \gamma$) alloy. In general, ferritic ferro superalloy might be characterized by its excellent oxidation resistance, while austenitic ferro superalloy is characterized by its good toughness and strength. The service temperature of the former is much higher than that of the latter. Fe–Cr–Al alloy, one of the most important ferritic ferro superalloys, is used widely as an electric heating alloy, as a structure material of heat-treatment furnaces, and for nuclear industry equipment etc. [1–3]. Fe–Cr–Ni alloy, Fe–Cr–Ni–N, and Fe–Cr–Mn–N alloy are typical austenitic ferro superalloys, often used to make high temperature structural components [4–7]. The duplex ferro superalloy should have the merits of both the ferritic alloy and the austenitic alloy.

High carbon content usually does not facilitate the oxidation resistance of Fe–Cr–Al alloy, but a certain amount of carbon can refine the solidification structure of Fe–Cr–Al alloy, and fine grains will improve the alloy oxidation resis-

tance [8,9]. 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 [5,10]. The zig-zag nature of the grain boundaries due to carbides precipitating enhances the creep rupture strength of the alloy [11].

Chromium is one of the basic elements in ferro superalloy. High chromium content can improve the alloy oxidation resistance, and a certain amount of chromium content can increase the alloy strength by its solution in the alloy matrix and forming carbides with carbon [12].

In order to design a new kind of low-cost high-temperature ferrite superalloy, which can be made out of low-cost industry raw materials with conventional melting and casting processes, the effects of additions of carbon and chromium to Fe–Cr–Ni–Al duplex superalloy on its solidification structure and properties will be investigated.

2. Experimental details

The alloy was made out of low-cost raw materials, such as scrap steel, ordinary low carbon Cr–Fe alloy etc., with a middle frequency induction furnace in a foundry shop. Totally, twenty-five groups of samples were cast in ordinary graphite moulds. The alloy chemical composition was

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Table 1

Compositions of the experimental alloys and test results (with addition of 1.0 Mo wt%; Fe, balance)

Alloy No.	C (wt%)	Cr (wt%)	Ni (wt%)	Al (wt%)	Rupture strength at 25°C (MPa)	Rupture strength at 1250°C (MPa)	Oxidation weight gain (g/m ² /h)
1	0.05	14.5	5.13	1.94	432.7	12.8	3.87
2	0.06	17.4	7.81	2.87	486.8	20.7	1.96
3	0.07	19.9	9.87	4.12	521.4	26.3	2.42
4	0.08	23.4	12.12	5.05	421.3	15.3	0.63
5	0.09	26.6	14.85	5.93	96.4	6.1	0.57
6	0.11	13.9	8.17	3.77	451.5	14.6	4.4
7	0.1	17.1	10.18	4.69	388.6	16.5	0.94
8	0.09	20	11.91	6.02	293.4	18.2	2.02
9	0.11	24.5	15.03	1.88	375.8	21.4	1.74
10	0.11	27.9	5.44	3.13	121	7.9	0.42
11	0.15	13.7	10.33	5.83	433.1	22.3	1.33
12	0.15	16.5	12.6	2.31	457.3	33.6	6.37
13	0.13	21	14.9	3.15	463.1	27.4	0.23
14	0.16	23.1	5.18	3.91	233.8	13.8	0.12
15	0.16	26.9	7.85	5.06	81.4	12.2	0.28
16	0.22	14.3	12.23	3.22	472.6	18.1	2.47
17	0.23	16.9	14.78	3.75	463.3	23.4	5.57
18	0.19	20.1	4.94	4.94	176.7	14.2	3.66
19	0.2	22.5	7.88	5.79	191.1	12.1	1.24
20	0.2	26.5	10.12	1.77	307.6	14.8	1.41
21	0.24	13.4	15.54	5.14	535.8	21.8	4
22	0.24	17.3	5.17	6.04	188.2	14.7	2.18
23	0.26	20.6	8.23	1.93	242	13.5	2.66
24	0.27	22.6	9.87	2.95	234.7	13.4	3.86
25	0.27	26.8	12.11	3.06	216.6	11.7	0.14

designed with the orthogonal experiment method, in which both the carbon content and chromium content were classified into five quantity grades, 0.05, 0.10, 0.15, 0.20, 0.25 wt%; and 14, 17, 20, 23, 27 wt%; respectively.

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 at 1250°C in air, of which the dimensions were $\Phi 15 \times 30$ mm, was determined with the weight-gain method, in which the period of cyclic oxidation was 100 h, totally five periods being applied. The rupture strength of the specimens at 1250°C in air, of which the dimensions were $\Phi 16 \times 300$ mm, was tested with a Gleeble 1500 tester. The test parameters are the following: heating velocity 5°C/s; holding time at 1250°C for 5 min before drawing; and 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 for twenty-five groups of samples corresponding to the main actual chemical compositions are given in Table 1. In this orthogonal experiment, the average chemical compositions and results corresponding to every carbon content grade, which has five groups of samples, are given in Table 2, whilst those to every chromium content are given in Table 3.

3.1. Effects of carbon on solidification structure and properties of duplex alloy

The effect of the carbon content on the alloy solidification structure could be seen clearly through comparisons among Fig. 1, Fig. 2, and Fig. 3. As the carbon content increases, the amount of carbides in the solidification

Table 2

The average chemical compositions and results corresponding to every carbon content grade

C (wt%)	Cr (wt%)	Ni (wt%)	Al (wt%)	Rupture strength at 25°C (MPa)	Rupture strength at 1250°C (MPa)	Oxidation weight gain (g/m ² /h)
0.072	20.34	9.96	3.98	391.7	16.24	1.89
0.104	20.68	10.2	3.9	326.1	15.92	1.9
0.154	20.22	10.2	4.05	333.7	21.86	1.67
0.208	20.07	9.99	3.89	322.3	16.52	2.77
0.255	20.11	10.2	3.82	283.5	15.02	2.67

Table 3

The average chemical compositions and results corresponding to every chromium content grade

Cr (wt%)	C (wt%)	Ni (wt%)	Al (wt%)	Rupture strength at 25°C (MPa)	Rupture strength at 1250°C (MPa)	Oxidation weight gain (g/m ² /h)
13.9	0.16	10.3	3.98	465.1	17.92	3.21
17	0.16	10.1	3.93	396.8	21.78	3.4
20.3	0.15	9.97	4.03	339.3	19.9	2.2
23.2	0.17	10.0	3.92	291.3	1.52	1.52
26.9	0.17	10.1	3.79	164.6	10.54	0.56

structure increases by a great deal, and the morphology of the carbides also varies. When the carbon content is about 0.10 wt%, the shape of carbides is that of small pellets (Fig. 1). When the carbon content reach about 0.15 wt%, fine chains of carbides appear (Fig. 2). With higher carbon content, the carbides make up a coarse skeleton (Fig. 3). Moreover, the alloy grain becomes finer, and the grain boundary wider and more zig-zag with the increase of the

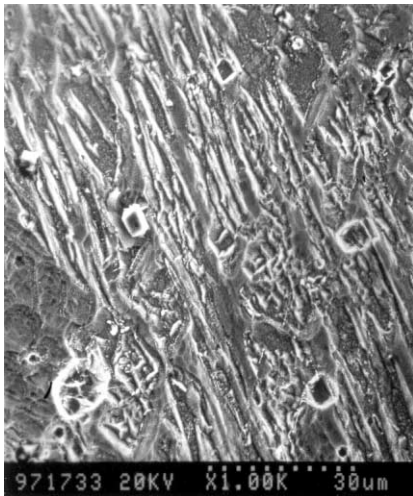


Fig. 1. Granular carbides in no.6 alloy with 0.10 wt% carbon content.

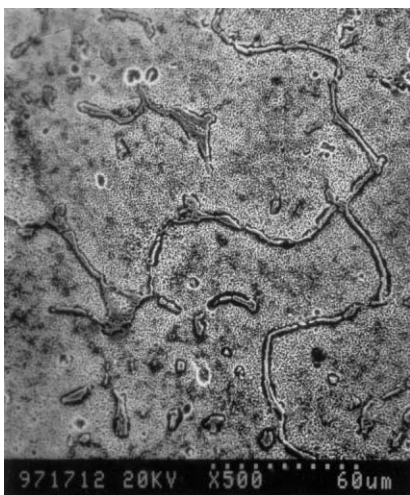


Fig. 2. Carbides chain in no.12 alloy with 0.15 wt% carbon content.

carbon content (Fig. 3). The effect of the carbon content on the alloy mechanical properties is shown in Figs. 4 and 5. When the carbon content increases from 0.05 to 0.25 wt%, the alloy rupture strength at 25°C keeps decreasing slightly (Fig. 4), while the alloy at 1250°C improves significantly at first, and then begins to fall acutely when carbon content exceeds 0.15 wt% (Fig. 5). $M_{23}C_6$ carbide is the main type of carbide in the tested alloys in which the minimum Cr/C ratio is greater than 40.0, and the chemical composition of $M_{23}C_6$ is (Cr, Fe, Mo)₂₃C₆ [12] (Fig. 6). Carbides incline to precipitate at grain boundaries or phase boundaries, of which the energy potential is higher than that of the matrix. $M_{23}C_6$ carbide has a complex fcc structure, and has some special

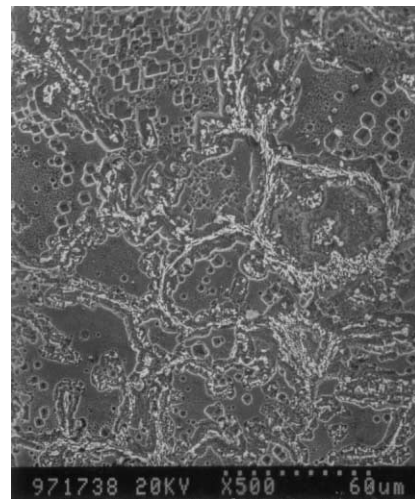


Fig. 3. Carbides skeleton in no.20 alloy with 0.20 wt% carbon content.

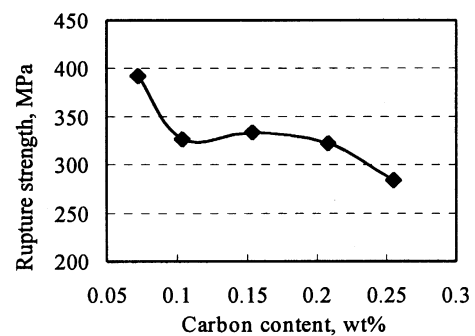


Fig. 4. The alloy rupture strength at 25°C as a function of carbon content.

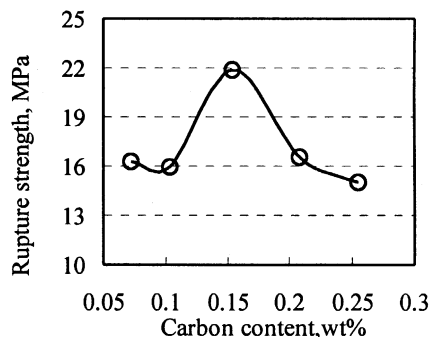


Fig. 5. The alloy rupture strength at 1250°C as a function of carbon content.

crystal orientations with austenite, such as $(100)_{M_{23}C_6} // (100)_\gamma$ and $(001)_{M_{23}C_6} // (001)_\gamma$ [13]. Austenite has also an fcc structure. Otherwise, ferrite has a bcc structure, and there is no special crystal orientation between ferrite and $M_{23}C_6$ carbides. Thus austenite may bind with $M_{23}C_6$ carbides more firmly than ferrite. The phase interface between ferrite and austenite has a higher energy potential than the matrix, and most probably is the micro-crack source in the rupture test at room temperature. As the binding between carbides and austenite is rather different to that between carbides and ferrite, when carbon content rises, increasingly more carbide appears at the interfaces between ferrite and austenite, so that the phase interface weakens. Thus when the carbon content increases from 0.05 to 0.25 wt%, the alloy rupture strength at room temperature keeps decreasing slightly.

In the rupture test at 1250°C, the grain boundaries may most probably have become weaker than the matrix and the phase interfaces, and become the key factor affecting the alloy strength. When the carbon content increases from 0.05–0.15 wt%, the solution of carbon promotes the formation and stabilization of the austenite; and an adequate amount of fine carbides precipitates on the grain boundaries, and the grain boundaries become zig-zag (Fig. 2), which increases the resistance to the slip of dislocations [11]. Thus the strength of the grain boundaries becomes

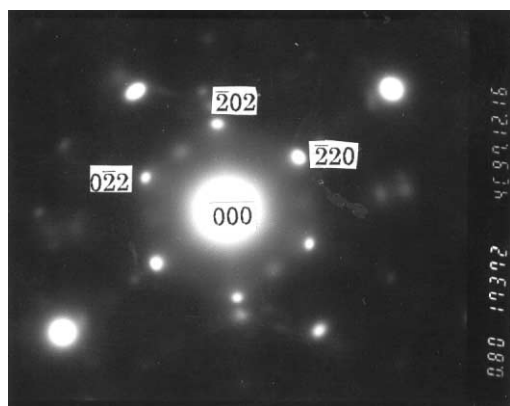


Fig. 6. Electron diffraction patterns of $Cr_{23}C_6$ in no.14 alloy, $[111]$ axis of zone.

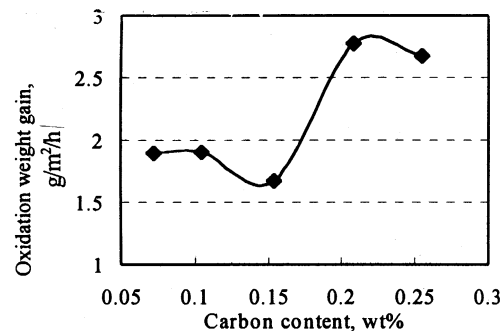


Fig. 7. The alloy oxidation weight gain at 1250°C as a function of carbon content.

improved. However, too much carbon results in the carbides coarsening, and a great amount of carbide precipitates along the grain boundaries (Fig. 3), which can cause a large stress concentration, and micro-crevices, hence, the grain boundaries become much weakened. Therefore, the alloy strength at 1250°C improves significantly at first, but then begins to fall acutely with the increase of carbon content. Fig. 7 shows the effect of the carbon content on the alloy oxidation resistance. With an increase of the carbon content, the alloy oxidation weight-gain rate at 1250°C reduces a little at first, until the carbon content reaches about 0.15 wt%, when it then increases intensely, i.e. the alloy oxidation resistance improves initially, but then deteriorates substantially. When the carbon content increases from 0.05 to 0.15 wt%, the alloy grains become refined 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, thereby the alloy oxidation resistance improves. However, too much carbon would result in the formation of a great amount of carbides, which decrease the chromium activity, and carbon oxidation would compete with chromium oxidation. Moreover, the precipitation of a large amount of carbides along the grain boundaries or phase interfaces might result in cavitations or even crevices, which facilitates the ingress of oxidant, so that internal oxidation would occur. The gathering and escape of CO or CO_2 as a result of internal oxidation weaken the compactness and adherence to the

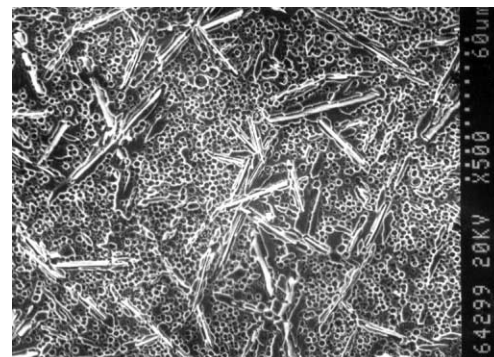


Fig. 8. Needle-shaped structure of σ phase in no.5 alloy.

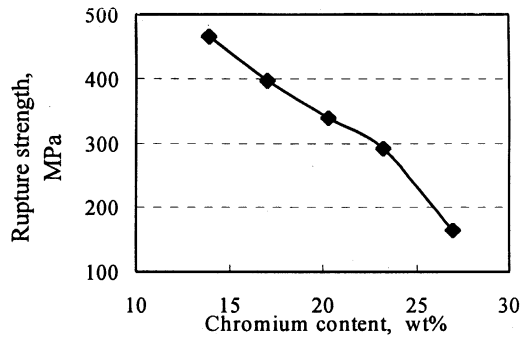


Fig. 9. The alloy rupture strength at 25°C as a function of the chromium content.

alloy matrix of the protective scales. Therefore, the alloy oxidation resistance deteriorates greatly. From the above, it is considered necessary to have 0.15 wt% carbon for both the alloy strength and its oxidation resistance.

3.2. Effects of chromium on solidification structure and properties of duplex alloy

Chromium facilitates the formation of ferrite in the alloy solidification structure, and high chromium content would stimulate the formation of σ phase in the alloy solidification structure, which is generally harmful to the alloy matrix. When chromium content reaches 23 wt%, σ phase appears in the alloy (see the needle-shaped σ phase in Fig. 8). The effect of the chromium content on the alloy mechanical properties is shown in Figs. 9 and 10. As the chromium content increases, the alloy rupture strength at 25°C reduces substantially (Fig. 9). The main reason may be that the chromium content in the tested alloy increases its brittleness temperature to room temperature [12]: the higher the chromium content, the more brittle the alloy. However, the alloy rupture strength at 1250°C becomes slightly enhanced initially, but then reduces rapidly (Fig. 10). The improvement of the alloy strength at high temperature could be attributed to the solution of chromium in the solid, and to a decrease in the formation of σ phase.

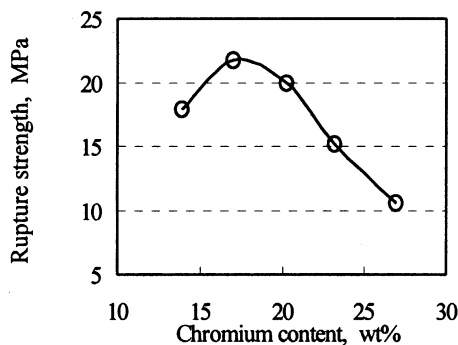


Fig. 10. The alloy rupture strength at 1250°C as a function of the chromium content.

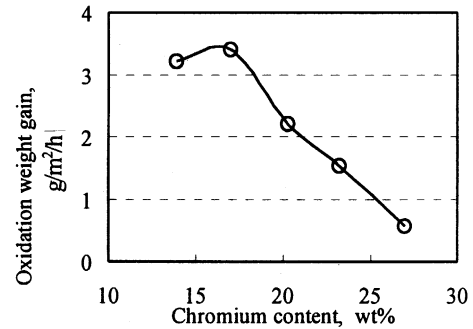


Fig. 11. The alloy oxidation weight gain at 1250°C as a function of the chromium content.

The effect of the chromium content on the alloy oxidation resistance is shown in Fig. 11. In general, the rate of the alloy oxidation weight-gain reduces continuously with the increase of the chromium content, i.e. the oxidation resistance of the alloy continues to improve.

In view of both strength and oxidation resistance, the optimum chromium content should be 20.0 wt%.

4. Conclusions

1. For the test Fe–Cr–Ni–Al duplex alloy, the optimum carbon content is 0.15 wt%, and that of chromium is 20 wt%.
2. With the increase of carbon content, the amount of carbides increases substantially, and the alloy grains become clearly finer. The alloy strength and oxidation resistance at 1250°C improves at first, but then begins to deteriorate greatly when the carbon content exceeds about 0.15%, while the room temperature strength decreases slightly.
3. High chromium content results in the formation of σ phase in the alloy solidification structure. As the chromium content increases, the alloy rupture strength at 1250°C initially is slightly enhanced, but then reduces rapidly, while the alloy oxidation resistance improves continuously, and the room temperature strength also decreases slightly.

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