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The influence of carbon addition on carbide characteristics and mechanical properties of CM-681LC superalloy using fine-grain process

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ABSTRACT

This study investigates how carbon addition affects the carbide characteristics and mechanical properties of CM-681LC nickel-base superalloy with grain size of 80 μm prepared using the fine-grain process. Experimental results indicate that carbon addition from 0.11 wt% to 0.15 wt% greatly increases the amount of carbides, but the shape and size of carbides are similar due to the short solidification time of the fine-grain process, which limits the growth of carbides. The increase of carbides by proper carbon addition effectively improves the tensile strength by about 5% and the tensile elongation by over 30% at room and moderate temperatures (21–760 °C). The fracture analyses reveal that the carbon addition in fine-grain CM-681LC superalloy can changes the fracture modes from typical intergranular fracture modes to transgranular and intergranular mixed modes. The better carbon content of CM-681LC superalloy applied in the fine-grain process is 0.15 wt%, which has better mechanical properties.

1. Introduction

The CM-681LC superalloy, a nickel-base superalloy developed by Cannon-Muskegon (CM) Corporation in the United States of America, exhibits outstanding mechanical properties under high temperature conditions. The CM-681LC superalloy has a nominal 0.11 wt% carbon content, which is added to precipitate carbides providing the strengthening effect. This alloy can be applied for casting of polycrystalline and directionally solidified (DS) crystalline [1].

The fine-grain process (FGP) developed by Howmet Corporation uses a controlled low temperature gradient to limit the growth of grains [2]. Fine-grain castings have advantages such as refined carbides and precipitates, enhanced strength and elongation, and improved mechanical properties [3]. Thus, fine-grain processes are beneficial for the strength and fatigue life of castings working at moderate temperatures (427–760 °C).

Carbides play important and complex roles in nickel-base superalloys, and their effects on mechanical properties are not clearly understood yet. The literatures [4,5] point out that carbon can be a grain boundary (GB) strengthening element and mainly affects the amount, size, and shape of carbides. In general, discrete carbides precipitated at GBs can inhibit GB sliding to improve the strength of superalloys at elevated temperatures. Conversely, the coarse or script-like MC primary carbides that exist within grain interior or at GB are regarded as the factor leading to low ductility during tensile tests. Because of the extremely brittle property of MC carbides, they may act as crack initiation sites and propagation paths. Therefore, adding the proper proportion of carbon with the carbide precipitation in the appropriate amount, size, and shape is likely to improve the mechanical properties of alloys [6–10].

Though CM-681LC superalloy with 0.11 wt% carbon can be used in polycrystalline and DS crystalline processes, the optimum carbon content for better properties of the fine-grain process is not known. However, it is known that the GBs of fine-grain castings represent a greater amount than that of traditional or columnar grain castings. Further, carbon mainly affects the amount, size, and shape of carbides as well as strengthens GB by carbide precipitation. Therefore, the mechanical properties of fine-grain CM-681LC superalloy sees improvement by increasing carbon content properly to improve the GB strength and carbide characteristics. The main aim of this investigation is to study the effects of carbon addition on carbide characteristics of CM-681LC superalloys prepared by fine-grain process. This work also discusses the effects of carbide characteristics on the mechanical properties and fracture modes at various temperatures of the fine-grain CM-681LC superalloy.

2. Material and methods

The experiments in this study used CM-681LC nickel-base superalloy ingots as the material. Equiaxed fine-grain test bars with 0.11 wt% and 0.15 wt% carbon content were cast using the fine-grain process, which has a controlled low temperature gradient. The pouring and mold temperatures were 1380 °C and 1100 °C, respectively.

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Table 1
Chemical compositions of 11C and 15C (unit in wt %).

Alloys	Cr	Co	Mo	W	Re	Ta	Al	Ti	Hf	C	B	Zr	Ni
11C	5.5	9.3	0.51	8.4	2.9	6.1	5.71	0.16	1.49	0.11	0.19	0.12	Bal.
15C	5.3	9.3	0.50	8.4	2.8	5.8	5.52	0.12	1.45	0.15	0.19	0.12	Bal.

Table 2
Chemical compositions of carbides in 11C and 15C measured by EDS (unit in wt %).

		C	Ni	Cr	Hf	Ta
11C	Script-like carbides within the grain interior	6.7	2.2	1.3	31.4	58.3
	Blocky carbides within the grain interior	6.3	2.5	1.2	32.1	57.8
	Blocky carbides at GBs	6.5	4.3	2.5	35.8	50.9
	Particle-like carbides at GBs	3.8	18.5	57.3	13.0	7.3
15C	Script-like carbides within the grain interior	6.0	2.1	1.6	34.9	55.4
	Blocky carbides within the grain interior	6.8	2.5	0.9	29.7	60.1
	Blocky carbides at GBs	5.9	5.6	2.0	28.3	58.1
	Particle-like carbides at GBs	3.5	20.2	54.9	15.1	6.3

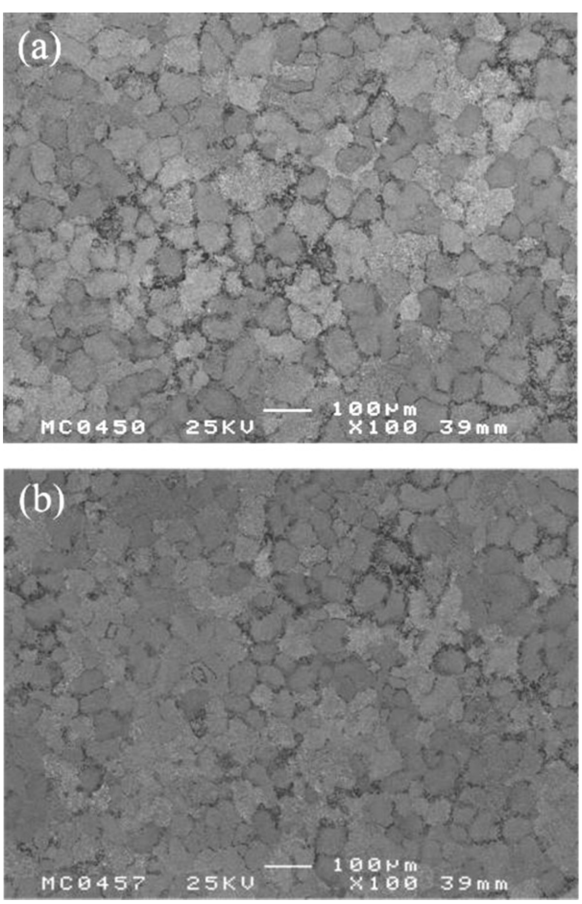

Fig. 1. SEM images showing the grain sizes of (a) 11C and (b) 15C after HIP and heat treatment.

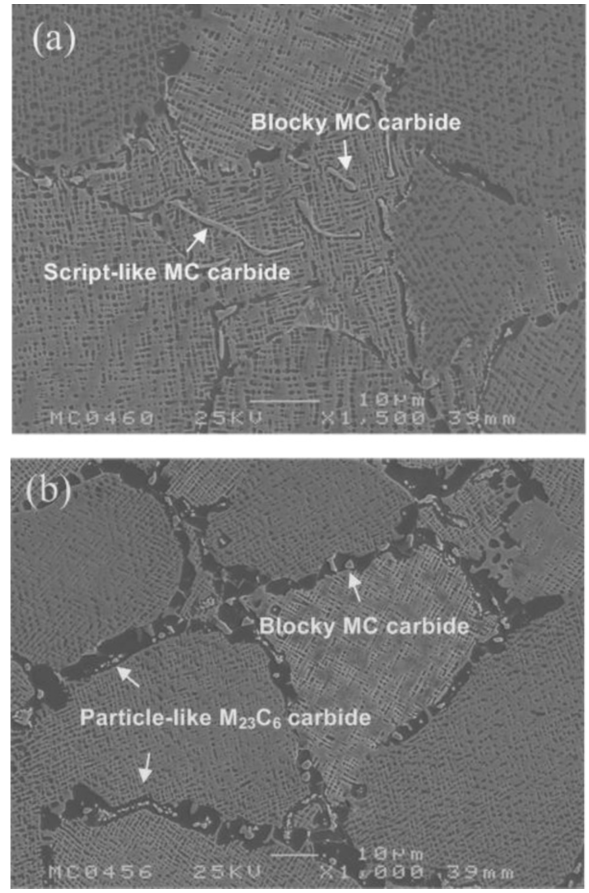

Fig. 2. SEM images showing the carbide morphology (a) within grain interior and (b) at GBs in 11C.

The compositions of the test bars were analyzed using spark emission spectroscopy and carbon-sulphur analyzer. All test bars were treated with hot isostropic pressing (HIP) to reduce micropore caused by rapid solidification shrinkage for fine-grain process. HIP was performed at 1185 °C under an Ar gas pressure of 172.25 MPa for 5 h. Test bars were then subjected to solid solution treatment in a vacuum at 1185 °C for 4 h, followed by cooling in an Ar atmosphere to room temperature. An aging treatment was then performed at 1038 °C for 2 h in a vacuum, before cooling to room temperature in an atmosphere of gaseous Ar. The test bars were secondarily aged at 871 °C for 20 h in a vacuum and then cooled to room temperature in a furnace. The grain sizes were observed with secondary electron imaging (SEI) using scanning electron microscopy (SEM), and the intercept method was applied to determine grain sizes. The microstructures were characterized by SEM and transmission election microscopy (TEM). SEM specimens were prepared using standard mechanical polishing procedures and etched in 30 ml lactic acid + 10 ml HNO_3 + 5 ml HCl solution. Twin jet electrolytic etching was employed in 90% CH_3COOH + 10% $HClO_4$ solution to prepare TEM specimens. Microanalysis of the specimens was performed with X-ray energy dispersive spectroscopy (EDS) in SEM. In addition, the average length, aspect ratio (the ratio of long axis and short axis), and area fraction of total carbides were analyzed with a metallurgical analyzer. One hundred fields from the samples were taken by a 200 times optical microscope to measure the mean value. The GB carbide characteristics were determined and identified from at least 10 different GBs possessing more than 100 carbides. Quantitative statistical analyses were applied to differentiate MC carbide (1–5 μm) and $M_{23}C_6$ carbide (0.2–0.8 μm) at GBs. The tensile tests were performed using an Instron 1125 universal test machine at 21, 427, 760 and 982 °C. The gauge size of all test bars was 6.3 mm in diameter and 26 mm in length. The fracture morphology was observed using SEM.

Table 3
Characteristics analysis results of the total carbides in 11C and 15C.

Area fraction (%)		Average length (μm)		Aspect ratio	
11C	15C	11C	15C	11C	15C
0.91	1.57	12.84	13.82	1.85	1.91

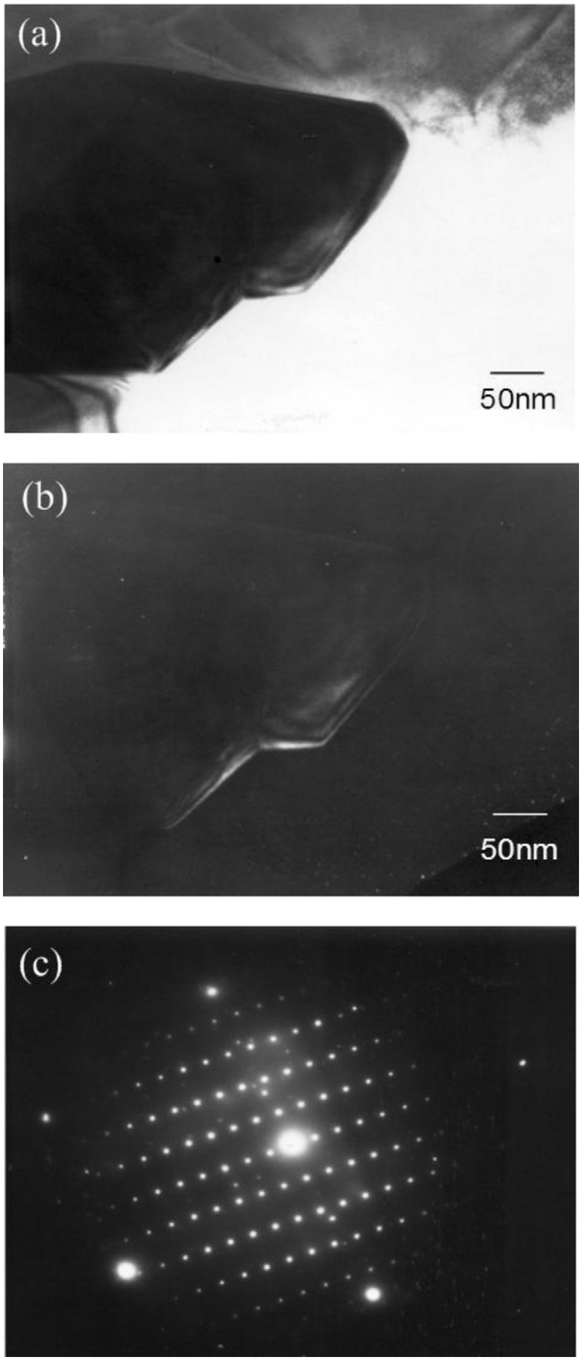

Fig. 3. (a) Bright-field image of a $Cr_{23}C_6$ ($M_{23}C_6$) carbide, (b) dark-field image of the carbide, and (c) selected-area diffraction pattern corresponding (a).

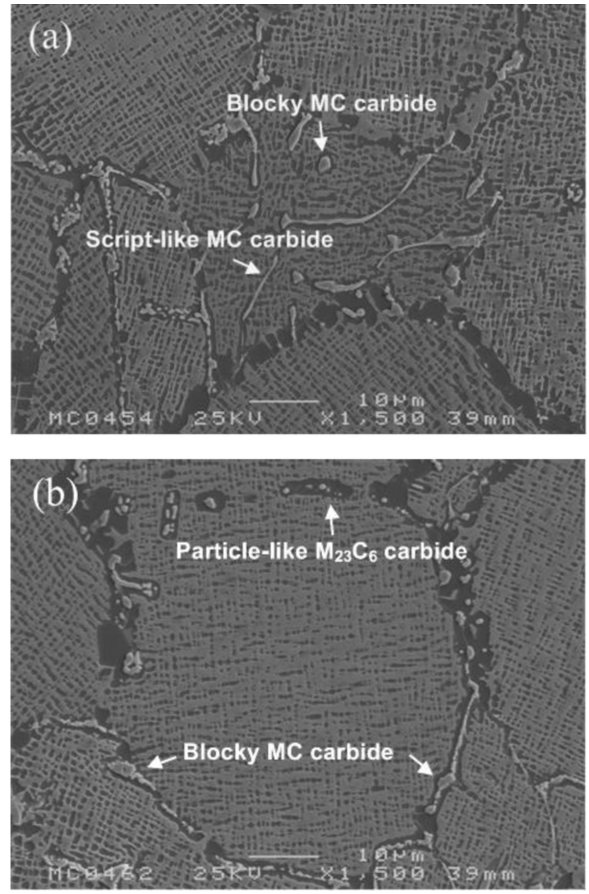

Fig. 4. SEM images showing the carbide morphology (a) within grain interior and (b) at GBs in 15C.

3. Results and discussion

3.1. Compositions and grain sizes

The main alloy compositions of fine-grain test bars with different carbon content were analyzed with spark emission spectroscopy, while the carbon content was analyzed using a carbon–sulphur analyzer. Table 1 shows the results and the carbon weight percentage is 0.11% and 0.15%, respectively (indicated as 11C and 15C in this study).

The grain sizes obtained by traditional investment casting process (using a superheating temperature of about 150 °C) are 3–5 mm, and their morphology tends to be columnar. The grain sizes of 11C and 15C obtained by the fine-grain process in this study are both 80 μm (Fig. 1(a) and (b)), and the structures are both equiaxed, different to the grain sizes and structures of traditional casting process. It suggests that the carbon content has a negligible effect on grain size and grain shape of fine-grain castings.

3.2. Carbide characteristics

Fig. 2(a) presents the carbide morphology in 11C. The carbides with script-like and blocky morphology within grain interior are rich in Ta and Hf, shown in Table 2. On the basis of the US patent for CM-681LC superalloy [1], these carbides can be confirmed as MC carbides. Fig. 2(b) shows the morphology of GB carbides in 11C, revealing blocky and discontinuous particle-like carbides precipitated at GBs. The EDS analysis results show that blocky carbides at GBs in 11C are rich in Ta and Hf (Table 2), so confirming that these are MC carbides. The particle-like carbides at GBs are rich in Cr (shown in Table 2), indicating that they are $M_{23}C_6$ carbides. This identification was confirmed by TEM. Fig. 3 presents bright-field and dark-field images of an $M_{23}C_6$ carbide and its selected-area diffraction pattern.

Fig. 4(a) shows the carbide morphology in 15C. The EDS analyses shown in Table 2 show that the script-like carbides within grain interior are rich in Ta and Hf, and are MC ((Ta, Hf)C) carbides. The blocky carbides within grain interior are enriched with Ta and Hf (Table 2), and are also MC ((Ta, Hf)C) carbides. Fig. 4(b) shows the morphology of GB carbides in 15C. The microstructure observations display that the morphology of GB carbides in 15C is similar to 11C, including blocky and discontinuous particle-like carbides. The EDS analysis results in Table 2 show that the blocky carbides are rich in

Table 4
Statistical results of the GB carbide characteristics in 11C and 15C.

Alloys	Particle size of MC carbides at GBs (μm)	Aspect ratio of MC carbides at GBs	Linear density of MC carbide at GBs (no./mm)	Linear density of M23C6 carbide at GBs (no./mm)
11C	3.3	1.35	46	432
15C	3.9	1.52	71	664

Table 5
Tensile test results of 11C and 15C at various temperatures.

Test temp. (°C)	U.T.S. (MPa)		Y.S. (MPa)		Elongation (*E* %)	
	11C	15C	11C	15C	11C	15C
21	1085	1170	936	989	4.7	8.5
427	1156	1221	967	1012	6.9	9.1
760	1003	1065	945	997	4.3	6.6
982	657	671	505	513	4.1	5.0

Ta and Hf, and the particle-like carbides are rich in Cr. These results show that the main carbides at GBs in both 11C and 15C are blocky (Ta, Hf)-rich MC carbides and particle-like Cr-rich $M_{23}C_6$ carbides.

Carbon plays the role of a GB strengthening element in Ni-base superalloys. Carbons can form various carbides with carbide forming elements within grains and at GBs. The carbides effectively obstruct the movement of dislocations and inhibit the GB sliding, then providing the strengthening effect to improve the mechanical properties of superalloys [4].

The main carbides of CM-681LC superalloy are MC carbides precipitated during solidification. The MC carbide in superalloy has a tendency to decompose into $M_{23}C_6$ or M_6C with heat treatment or thermal exposure [10–13]. Generally, the $M_{23}C_6$ carbides are rich in Cr and the M_6C carbides are rich in Mo or W [10–12]. The EDS and TEM analysis results indicate that MC carbides in CM-681LC superalloy were transformed to discontinuous particle-like $M_{23}C_6$ carbides at the GBs after HIP and heat treatment. Hence, the main carbides in 11C and 15C are script-like or blocky (Ta, Hf)-rich MC phase and particle-like Cr-rich $M_{23}C_6$ phase.

Table 3 presents statistical results for the area fraction, average length, and aspect ratio of total carbides (including within grain interior and at GBs) in 11C and 15C. These results show that the carbon content increases from 0.11 to 0.15 wt%, and the total area fraction of carbides increases greatly from 0.91 to 1.57%. Additionally, the average carbide length increases from 12.84 to 13.82 μm, while the aspect ratio increases from 1.85 to 1.96.

In order to investigate the effect of carbon addition on the characteristics of GB carbides, examination of GB carbide characteristics was made. Table 4 shows the statistical results for the characteristics of GB carbides in 11C and 15C. It demonstrates that the linear density of MC and $M_{23}C_6$ carbides at GBs increase greatly by carbon addition. The particles size of MC carbides at GBs slightly increases from 3.3 μm to 3.9 μm, and the aspect ratio of MC carbides at GBs slightly increases from 1.35 to 1.52.

In this study, the added carbon reacts with carbide forming elements to form more MC carbides during solidification and more $M_{23}C_6$ carbides re-precipitate at GBs during aging [10–13]. According to the statistical analyses results, the total area fraction of

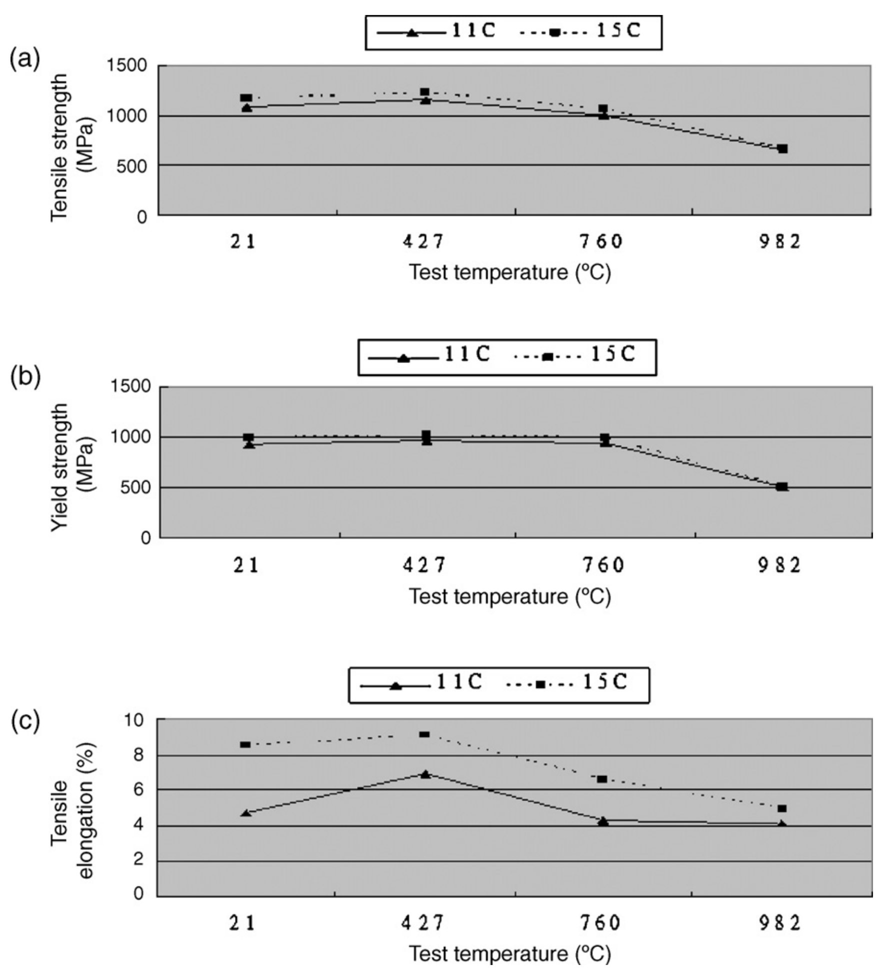

Fig. 5. Comparison of the mechanical properties of 11C and 15C at various testing temperatures.

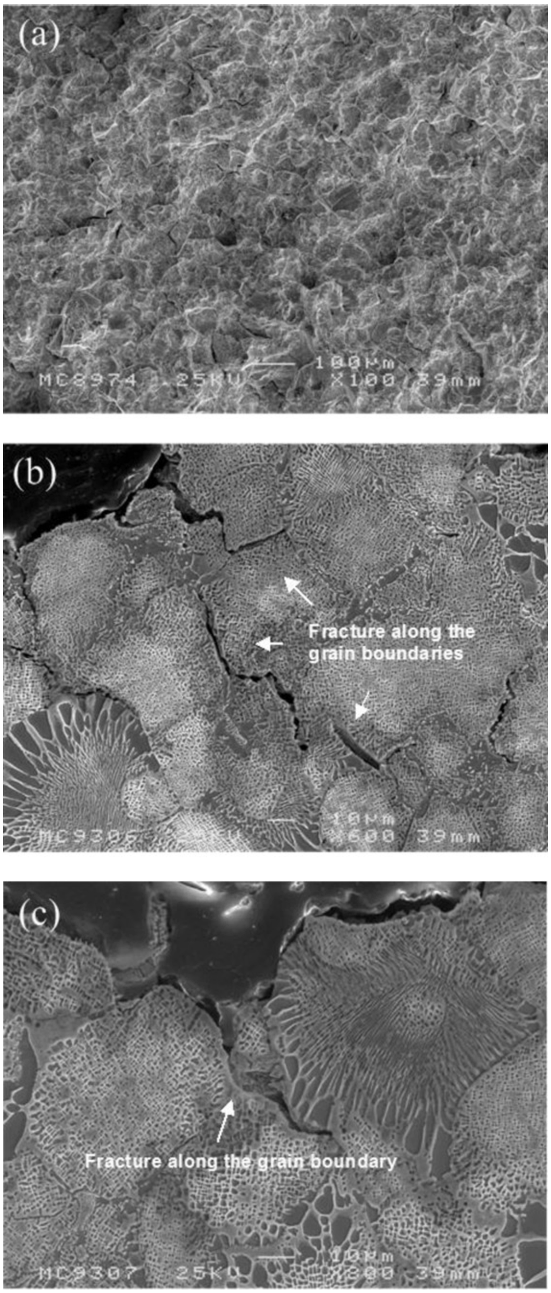

Fig. 6. SEM images of 11C following room-temperature tensile test, showing (a) fracture surface, (b and c) cracks along GBs.

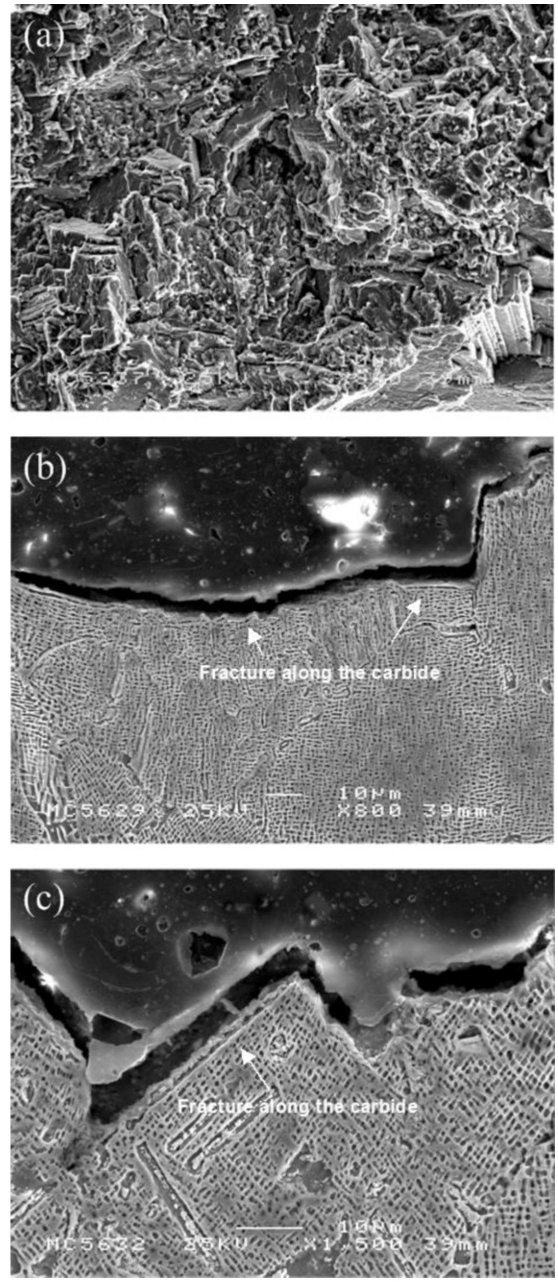

Fig. 7. SEM images of 15C following room-temperature tensile test, showing (a) fracture surface, (b and c) cracks along carbides.

carbides and the linear density of MC and $M_{23}C_6$ carbides at GBs increase greatly by carbon addition. It can be concluded that the principal carbides in 15C are still MC and $M_{23}C_6$ types, but significantly more of them appear than in 11C.

However, the quantitative statistical analysis results reveal that carbon addition in the fine-grain process produces no significant differences in carbide size and shape. The average length and aspect ratio of total carbides in 15C are similar to those in 11C. Further, the particles size and aspect ratio of MC carbides at GBs of 11C and 15C are also similar. It demonstrates that the lower pouring temperature in the fine-grain process reduces the temperature gradient and shortens the solidification time, limiting carbide growth [14].

It summary, carbon addition in the fine-grain process can greatly increase the amount of carbides, but no significant differences appear in the size and shape of the carbides.

3.3. Tensile properties for various temperatures

Table 5 and Fig. 5 show the results of 11C and 15C tensile tested at 21, 427, 760 and 982 °C.

Fig. 5(a) plots the tensile strengths of 11C and 15C for the various test temperatures. The tensile strengths of 11C and 15C at room temperature were 1085 MPa and 1170 MPa, respectively. The increase was 7.8%. At a test temperature of 427 °C, the tensile strength of 11C was 1156 MPa, while that of 15C was higher at 1221 MPa. The strengths of both samples of 11C and 15C decreased rapidly as the test temperature increased over 760 °C, but the tensile strengths of 15C always exceeded those of 11C.

Fig. 5(b) reveals that the variation of yield strengths with temperatures is similar to the variation of tensile strengths. At all test temperatures, the yield strengths of 15C exceeded those of 11C. At room temperature, the yield strength of 11C was 936 MPa, which

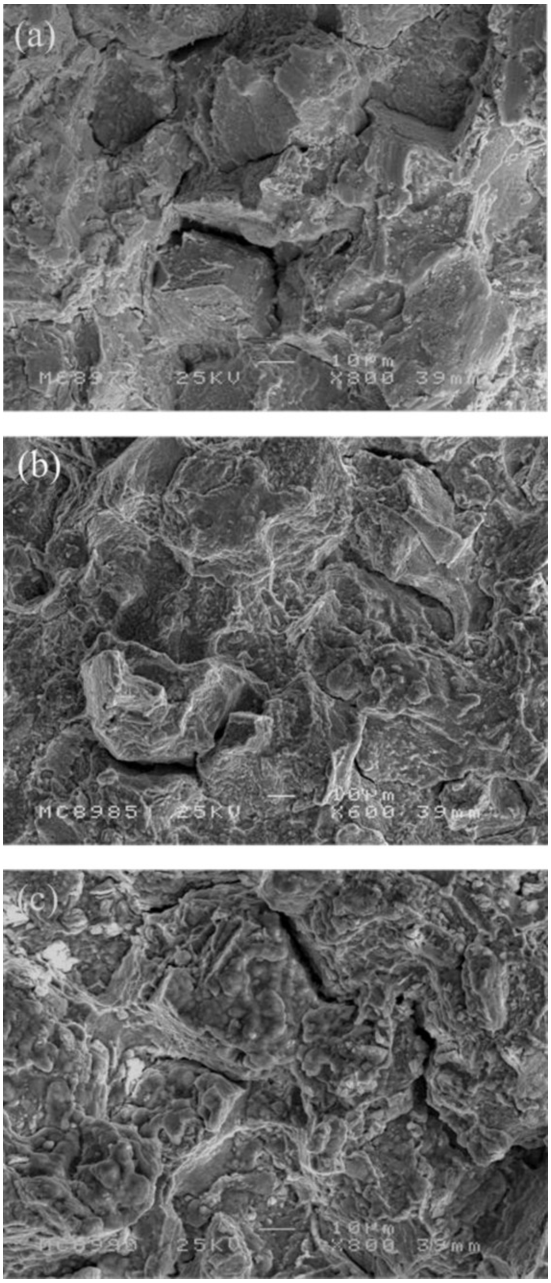

Fig. 8. Fracture surface of 11C following tensile test at (a) 427 °C, (b) 760 °C and (c) 982 °C.

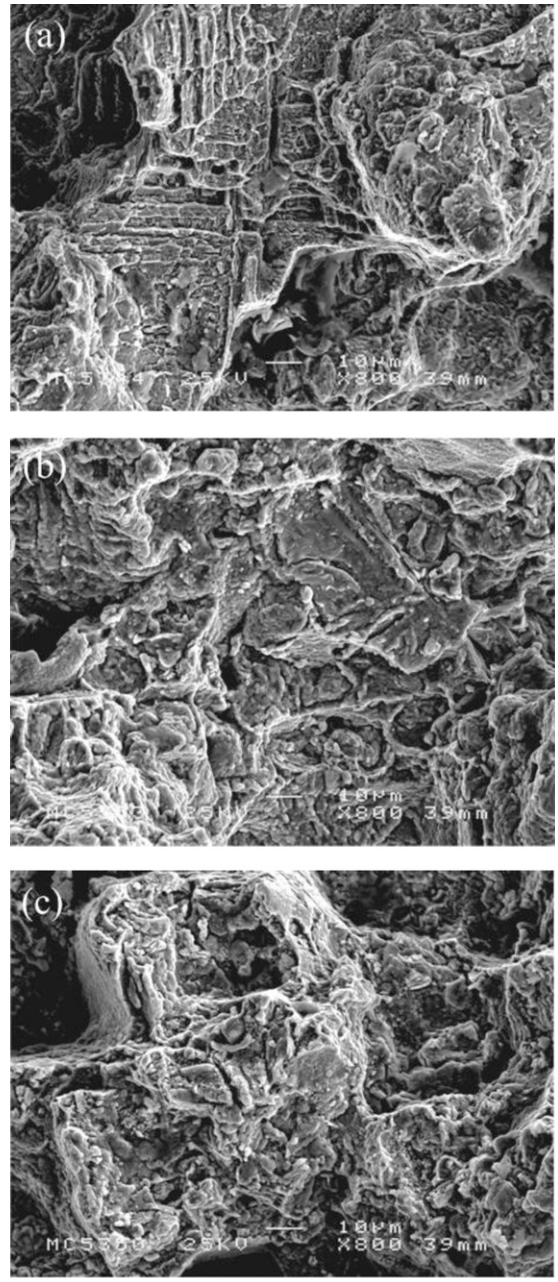

Fig. 9. Fracture surface of 15C following tensile test at (a) 427 °C, (b) 760 °C and (c) 982 °C.

increased to 989 MPa of 15C. In the 760 °C test, the yield strength of 15C was 997 MPa, which was 5.5% higher than that of 11C. At 982 °C, proper addition of carbon content increased the yield strength, but by markedly less than at 760 °C.

Fig. 5(c) presents the relationship between the tensile elongation and the test temperature. The tensile elongation at room temperature of 11C was 4.7%, which increased to 8.5% of 15C. Proper addition of carbon content improved the tensile elongation from 6.9% to 9.1% at 427 °C. At test temperatures of 760 °C and 982 °C, the tensile elongations of 15C also exceeded those of 11C.

The carbides play a very important role in superalloys and the amount, size and shape of carbides have the decisive effect on mechanical properties [4–8]. The present results demonstrate that the total area fraction of carbides and the linear density of MC and $M_{23}C_6$ carbides at GBs increase greatly by carbon addition, which proves that the amount of carbides in 15C are more that those in 11C. The more carbides precipitated within the grain interior could improve the strengthening effect by preventing the movement of dislocations; the more carbides precipitated at GBs could increase the strength of GBs and improve the mechanical properties, since the carbides can postpone the crack extending and avoid the grain boundary sliding [6–8,10,15]. Thus, the tensile strength, yield strength and elongation of 15C could be improved effectively.

Further, the statistical analysis results also reveal that adding the carbon content in fine-grain process produces no significant differences in carbide size and shape. Hence, the extra carbides precipitated by carbon addition in fine-grain process effectively improve the mechanical properties because the carbides are not too elongated, avoiding the crack initiation and propagation along the carbide/matrix interfaces.

However, it is not that the carbon content can be added to infinitude. If the carbon content is too high, there is a negative effect on mechanical properties due to precipitation of scriptlike and elongated carbides, allowing the crack initiation and propagation along carbide/matrix interfaces. Hence, how to get the optimum carbon content to precipitate carbides with proper amount, size, and shape of fine-grain superalloys is an important subject to study.

In summary, the carbon addition from 0.11 to 0.15 wt% effectively improves the yield strengths, the tensile strengths and elongations of the fine-grain CM-681LC superalloy mainly by properly increasing the carbides precipitated with proper sizes and shapes. It was proved that the fine-grain CM-681LC superalloy yields better mechanical properties by properly adding carbon content to 0.15 wt%.

3.4. Fracture modes

The fracture surfaces and the longitudinal sections were observed using SEM to investigate the effect of carbon addition on the tensile fracture modes of 11C and 15C.

Fig. 6(a) displays the room-temperature tensile fracture surface of 11C. The main cracks were observed at GBs. The longitudinal sections of a fracture sample (Fig. 6(b) and (c)) also indicate that the cracks of 11C are distributed along GBs. The room-temperature tensile fracture mode of 11C was a typical intergranular fracture mode.

Fig. 7(a) shows the room-temperature tensile fracture surface of 15C and the main cracks are distributed along script-like carbides. Additionally, the longitudinal sections of a fracture sample (Fig. 7(b) and (c)) also indicate that the cracks of 15C are distributed along script-like carbides. The main crack-production sites present near script-like carbides, and the cracks propagate along the extremely brittle carbide/matrix interfaces. Therefore, script-like carbides are the main determinants the fracture of 15C, and the fracture modes are the transgranular and intergranular mixed modes.

The fracture surfaces of tensile tests at 427, 760 and 982 °C were also observed in this study. Figs. 8 and 9 show the fracture surface SEM images of tensile test at 427, 760 and 982 °C of 11C and 15C, respectively. The fracture modes were the same as those at room temperature.

The observations of the fracture surfaces for tensile tests at various temperatures show that the main cracks of 11C were distributed at GBs because the GBs are most weak sites in superalloy. The fracture modes of 11C were typical intergranular fracture modes.

However, the main cracks of 15C are not distributed at GBs due to the strength of GBs improved by extra carbides precipitated. Hence, the main cracks of 15C initiate near script-like carbides and propagate along the carbide/matrix interfaces. The tensile fracture modes of 15C were transgranular and intergranular mixed modes.

It can be concluded that the tensile fracture modes of fine-grain CM-681LC superalloy are changed form typical intergranular fracture modes to transgranular and intergranular mixed modes by adding the carbon content form 0.11 to 0.15 wt%.

4. Conclusions

The influence of carbon addition on carbide characteristics and mechanical properties of fine-grain CM-681LC superalloy can be drawn as follows:

(1) MC carbides and $M_{23}C_6$ carbides exist in both CM-681LC superalloys with 0.11 wt% and 0.15 wt% carbon. The total area fraction of carbides and the linear density of carbides at GBs increase greatly by carbon addition from 0.11 to 0.15 wt %. However, these two alloys exhibit similar carbide shapes and sizes due to the short solidification time in fine-grain process, which limits the growth of carbides.
(2) Proper increase of carbides precipitated with appropriate sizes and shapes by the carbon addition from 0.11 to 0.15 wt% can improve the tensile strength by about 5% and the tensile elongation by over 30% at room and moderate temperatures (21–760 °C) of fine-grain CM-681LC superalloy.
(3) The fracture modes of the fine-grain CM-681LC superalloy are changed from typical intergranular fracture modes to transgranular and intergranular mixed modes by adding the carbon content from 0.11 wt% to 0.15 wt%.
(4) The better carbon content of CM-681LC superalloy applied in the fine-grain process is 0.15 wt%, which has better mechanical properties.

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References

[1] Harris, United States Patent 6,632,299 (2003).
[2] J.M. Lane, Adv. Mater. Process 137 (1990) 107–108.
[3] L. Faxin, Y. Wenming, T. Xin, Y. Aide, C. Wanhua, Mater. Eng. (China) (1990) 7–11 (in Chinese).
[4] A.K. Koul, W. Wallace, Metal. Trans 13A (1982) 673.
[5] Y.H. Kong, Q.Z. Chen, Mater. Sci. Eng. A366 (2004) 135–143.
[6] J.S. Bae, J.H. Lee, S.S. Kim, C.Y. Jo, Scripta Mater. 45 (2001) 503–508.
[7] R. Fernandaz, J.C. lecomte, T.E. Kattamis, Metall. Trans. A9 (1978) 1381–1386.
[8] L. Liu, F. Sommer, H.Z. Fu, Scripta Metall Mater. 30 (1994) 587–591.
[9] J. Chen, J.H. Lee, C.Y. Jo, S.J. Choe, Y.T. Lee, Mater. Sci. Eng. A247 (1998) 113–125.
[10] J. Yang, Q. Zheng, Z. Sun, H. Guan, Z. Hu, Mater. Sci. Eng. A429 (2006) 341–347.
[11] C.T. Sims, N.S. Stoloff, W.C. Hagel, Superalloys II, John Wiley & Sons, New York, 1987, p. 112.
[12] B.G. Choi, I.S. Kim, D.H. Kim, C.Y. Jo, Mater. Sci. Eng. A478 (2008) 329–335.
[13] J. Yang, Q. Zheng, H. Zhang, X. Sun, H. Guan, Z. Hu, Mater. Sci. Eng. A527 (2010) 1016–1021.
[14] E.R. Cutler, A.J. Wasson, G.E. Fuchs, Scripta Mater. 58 (2008) 146–149.
[15] C.T. Sims, N.S. Stoloff, W.C. Hagel, Superalloys II, John Wiley & Sons, New York, 1987, p. 114.