

THE EFFECT OF SILICON ADDITIONS ON THE THERMAL STABILITY AND MORPHOLOGY OF CARBIDES IN A Ni-Mo-Cr SUPERALLOY

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Abstract

The effect of silicon additions on the thermal stability and morphology of carbides has been investigated in a Ni-Mo-Cr superalloy. It is found that granular M_6C carbides form at the grain boundaries in the standard heat. The size and morphology of M_6C carbides remain unchanged in the aging treatment at 700-800 °C up to 1000 h. While in the non-silicon heat, the intergranular carbides are examined as M_2C type carbides by TEM at the initial stage of the aging treatment. With the aging time increasing, the fine granular M_2C carbides transform into coarse planar M_6C carbides. It can be concluded that silicon additions can lead to the more stable intergranular carbides in the Ni-Mo-Cr superalloy.

Introduction

Hastelloy N is a Ni-Mo-Cr superalloy developed in Oak Ridge National Laboratory for Molten-Salt Reactor Program in the 1970s. This alloy contains 16%-17% molybdenum for strengthening and 7% chromium sufficient to impart moderate oxidation resistance in air but not enough to lead to high corrosion rates in salt. There is additional 0.5%-1% silicon in the air-melted heats of this alloy for deoxidants as compared to the vacuum-melted heats.

It was found that silicon additions play a more important role in the structure and postirradiation properties of Hastelloy N. R. E. Gehlbach and H. E. McCoy^[1] found that the microstructure of Hastelloy N is characterized by stringers of massive primary M_6C carbides in matrix. The M_6C carbides in air-melted heats are enriched in silicon and are not dissolved at high annealing temperatures but melt and transform to a noncarbide phase. In vacuum-melted heats with low silicon contents, primary M_6C carbides go into solid solution. Enough experiments^[5-9] suggested that helium generation from the (n, α) reaction of boron at grain boundaries causes the irradiation brittleness in Hastelloy N. The massive primary M_6C carbides in air-melted heats can effectively fix boron atoms in the matrix and decrease the quantity of helium forming at grain boundaries to improve the irradiation brittleness.

On the other hand, H. E. McCoy and R. E. Gehlbach^[10] found that the additions of silicon have obvious effects on the morphology of intergranular carbides in Hastelloy N. In the air-melted heats, the fine M_6C carbides precipitate at the grain boundaries and remain stable over an irradiation temperature range of 650-760 °C. These fine precipitates may make it more difficult for cracks to propagate along the grain boundaries and increase the resistance to the intergranular fracture. The vacuum-melted heats form M_2C carbides whose size and morphology depended

markedly upon the irradiation temperature. Irradiation at 760 °C results in coarser-dispersions of the M₂C carbides and inferior postirradiation properties. So, it can be conclude that the carbides distribution (or the content of silicon) is of importance in two respects: (a) it will likely determine the distribution of helium, and (b) it will determine how easily cracks can propagate.

However, the content of silicon is not the only variable in these studies mentioned above. The potential effect of different melting methods on the carbides distribution should not be neglected. In this paper, one standard vacuum-melted heat with 0.5% silicon and one non-silicon vacuum-melted heat are used to investigate the effect of silicon additions to the stability and morphology of carbides in Ni-Mo-Cr superalloy.

Experimental procedure

As shown in Table I, the Nominal chemical composition (wt. %) of the two heats is identical to that of the standard Hastelloy N. The process for fabrication of the wrought alloy is as follows. The cast materials were prepared by vacuum induction melting (VIM). And then the ingots were hot forged into 20mm-in-diameter bars. All samples were cut from the bars and then annealed in heat treating furnace at 1177 °C for 0.5h, followed by water quenched (WQ). Subsequently, the samples were exposed at 700, 750 and 800 °C for 1-1000 h, respectively.

Table I: Nominal Chemical Composition of Ni-Mo-Cr Alloy.

Alloy Heat	Ni	Mo	Cr	Fe	Mn	Si	C
Standard heat	72	17	7	4	0.5	0.5	0.05
non-silicon heat						0	

Metallographic samples were prepared using standard metallographic mechanical grinding and polishing techniques and etched with the mixed solution (3g CuSO₄+10ml H₂SO₄+40ml HCl+50ml Water) to reveal the microstructure. The microstructures were examined by optical microscope (OM) and scanning electron microscope (SEM, LEO 1530VP) with energy dispersive spectrometer (EDS) analysis. Furthermore, transmission electron microscopy (TEM, tecnai G2 F20 S-TWIN) was used for phase identification. TEM samples were prepared by electrochemical polishing at a solution of 5% perchloric acid and 95% alcohol at about 243 K.

Results and discussion

Microstructure of Solution-Treated Ni-Mo-Cr Superalloy

The microstructure observations of Ni-Mo-Cr superalloy solution-treated at 1177 °C for 0.5 h are shown in Fig. 1. It can be seen that the microstructure consists of equiaxed grains. As shown in Fig. 1a, there are many stringers of primary M₆C carbides along the longitudinal direction in the standard heat. While the stringers in the non-silicon heat almost decompose into the matrix and only a small quantity of M₆C carbides particles randomly disperse inside the grains or at the grain boundaries. Because the contents of carbon in the two heats are both 0.05%, it can be inferred that there are more carbon atoms solubilize in the matrix of the non-silicon heat than that of the standard heat.

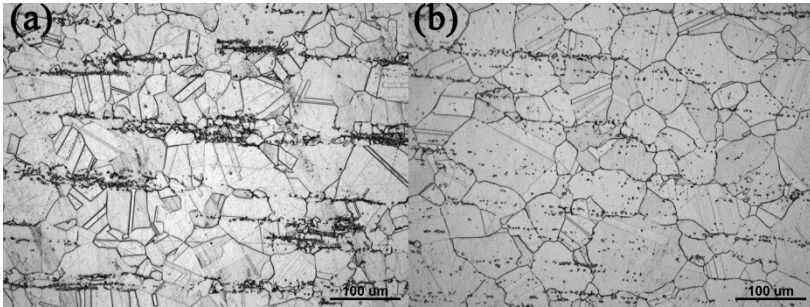


Figure 1. Microstructures of Ni-Mo-Cr superalloy in (a) the standard heat and (b) the non-silicon heat.

The Precipitation Behavior of M_6C Carbides in Standard Heats

Fig. 2 shows the progressive morphological changes of intergranular precipitates under the aging treatment at 750 °C with increasing aging time. The selected area electron diffraction pattern in Fig. 3 indicates that the intergranular precipitates are M_6C carbides, and the EDS analyses in Fig. 3(c) show that the M_6C carbides contain Ni and Mo as the main metal atoms. As shown in Fig. 2(a), the grain boundaries without any carbides are observed after the solution treatment. And as aging time increases to 100 h, it is observed that the granular M_6C carbides form at grain boundaries. The size of M_6C carbides is 200 nm. The morphology and size of the granular M_6C carbides remain unchanged during aging treatment up to 1000 h as shown in Fig. 2(c) and (d). Also, the density of granular M_6C carbides is unchanged during the whole process. The evolution process of intergranular M_6C carbides at 700 and 800 °C are consistent with that described at 750 °C.

The Precipitation and Decomposition Behavior of Carbides in Non-silicon Heats

The microstructure observations of the non-silicon heat exposed at 700-800 °C for 1-500 h are shown in Fig. 4. It can be found that granular precipitates form densely at almost all grain boundaries at the initial stage of aging treatment as shown in Fig. 4(a), (d) and (c). These fine granular precipitates are identified as M_2C carbides and consist mostly of Mo, Cr and C atoms as shown in Fig. 5. The size of granular M_2C carbides is 100 nm. When specimens are exposed for a longer time, the fine granular M_2C carbides dissolve from a portion of grain boundaries and then the planar precipitates form as shown in Fig. (b), (e) and (h). The planar precipitates are identified as M_6C carbides by the diffraction pattern in Fig. 6. It can be observed that the fine granular M_2C carbides are replaced completely by coarse planar M_6C carbides at grain boundaries at the final stage of aging treatment as shown in Fig. 4(c), (f) and (i).

From Fig. 4, it can also be found that the sequential evolution of the morphology of grain boundaries with the aging time increasing. At the initial stage of aging, the grain boundaries keep smooth with the M_2C carbides on them. When M_6C carbides form at a longer aging time, the grain boundaries become serrated. It has been reported that the morphology of grain boundaries

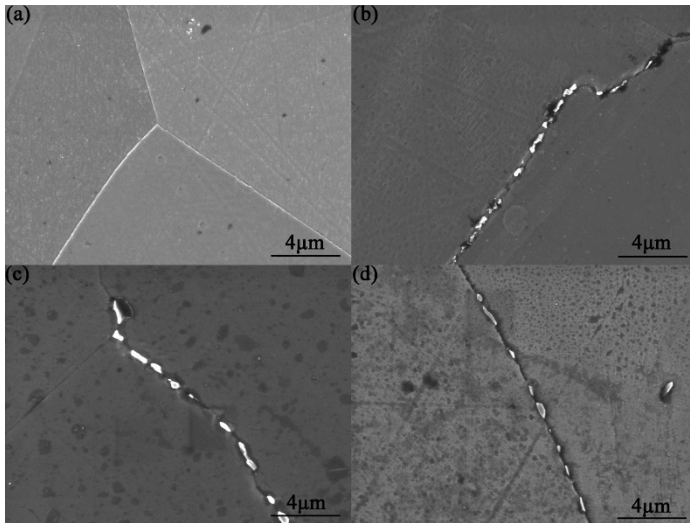


Figure 2. the morphology of intergranular precipitates in the standard heat after: (a) solution treatment, (b) aging at 750°C for 100 h, (c) aging at 750°C for 500 h, and (d) aging at 750°C for 1000 h.

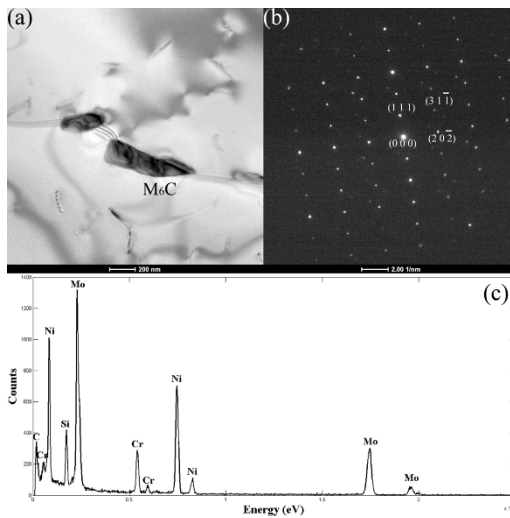


Figure 3. TEM analysis of grain boundaries M_6C carbides in the standard heat at 750°C for 100 h: (a) microstructure observation and (b) corresponding diffraction pattern and (c) the EDS analyses.

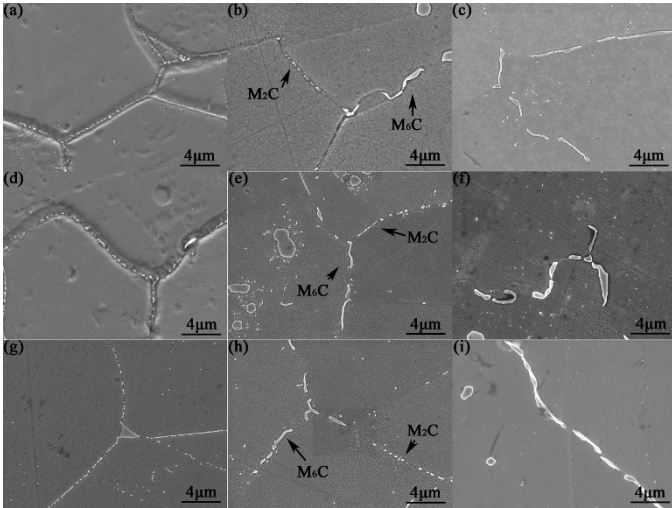


Figure 3. the morphology of intergranular precipitates in the non-silicon heat after (a) aging at 700°C for 100 h, (b) aging at 700°C for 200 h, (c) aging at 700°C for 500 h, (d) aging at 750°C for 100 h, (e) aging at 750°C for 140 h, (f) aging at 750°C for 200 h, (g) aging at 800°C for 1 h, (h) aging at 800°C for 20 h, and (i) aging at 800°C for 100 h.

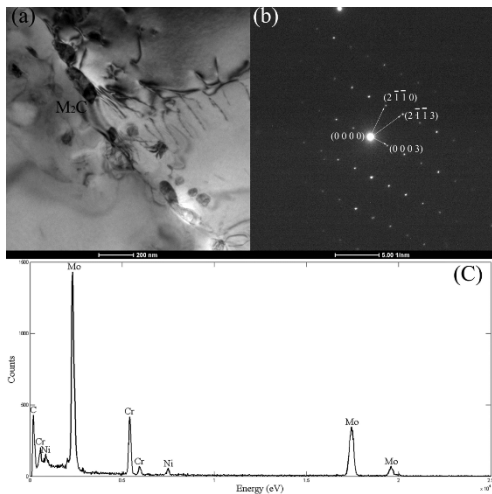


Figure 5. TEM analysis of intergranular M_2C carbides in the non-silicon heat at 750°C for 100 h: (a) microstructure observation and (b) corresponding diffraction pattern and (c) the EDS analyses.

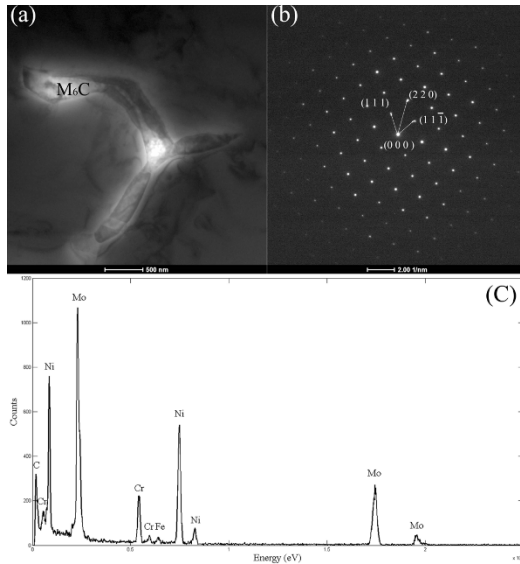
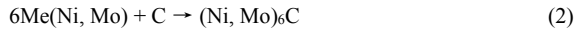
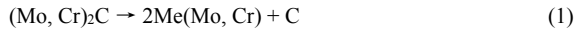


Figure 6. TEM analysis of intergranular M_6C carbides in the non-silicon heat at 750 °C for 100 h: (a) microstructure observation and (b) corresponding diffraction pattern and (c) the EDS analyses

is related closely to the morphology of the intergranular carbides in other alloys^[11-12]. The planar carbides grow from one grain into the adjacent grain and push the local boundary segment to cause serrations. The same process occur in this alloy during the growth of intergranular M_6C carbides.

It can be found that the precipitation of M_2C carbides only occur at the grain boundaries in the non-silicon heat at the initial stage of the aging treatment. This fact probably results from the enrichment of carbon atoms at the grain boundaries in the non-silicon heat. The massive primary M_6C carbides dissolve during the solution treatment. Subsequently, carbon atoms from M_6C carbides are released into the matrix and increase the supersaturation degree of carbon atoms in the matrix, especially at grain boundaries. Research indicates that carbon atoms segregate to dislocations, stacking faults and grain boundaries^[13]. Therefore, the nucleation and subsequent growth of M_2C carbides are promoted by carbon segregation at the grain boundaries. In contrast, the primary M_6C carbides in the standard heat remain stable, and there are not enough carbon atoms for the precipitation of M_2C carbides.

While the M_2C carbides are metastable and decomposes with the aging time increasing at 700- 800 °C, and then the planar M_6C carbides form at grain boundaries. It never be found that the second M_6C carbides are close to M_2C carbides at the same grain boundary segments. This fact indicates that the M_2C carbides do not transform into M_6C carbides directly. The decomposition of M_2C carbides and the precipitation of second M_6C carbides are two independent and successive events as shown in the following expressions:



The instability of M_2C carbide probably results from the high content of Cr as shown in Fig. 5(c). A first-principles study ^[14] on the structural of Mo_2C has proved that the formation enthalpies of Hexa- Mo_2C and Hexa- MoCrC are -0.34 and -0.25 eV per unit cell, which indicates that the Hexa- MoCrC system is relatively instable. As shown in Fig. 4, the critical time for the decomposition of granular M_2C carbides at 700, 750 and 800°C are 500, 200 and 100 h, respectively. The M_2C carbides are more instable at a higher aging temperature. This implies the decomposition process is diffusion controlled. The atoms dissolved from the M_2C carbides diffuse more rapidly at grain boundaries at the higher aging temperature. And then the decomposition process can finish within a shorter time.

During the decomposition process, the atoms such as Mo and C are released from M_2C carbide. These atoms contribute to the nucleation, growth and coarsening of second M_6C carbides at grain boundaries. While in the standard heat, the size of granular M_6C carbides at grain boundaries almost remain the same with the aging time increasing. It can be expected that such stable intergranular carbides can result in the better postirradiation performance in the standard heat.

Conclusions

In the standard heat, the size and morphology of intergranular granular M_6C carbides remain unchanged in the aging treatment at 700-800°C up to 1000 hours. In the non-silicon heat, the fine intergranular granular M_2C carbides formed at the initial stage of the aging treatment at 700-800°C. With the aging time increasing, the granular fine M_2C carbides are replaced by coarse planar M_6C carbides at grain boundaries. It can be concluded that silicon addition can lead to stable intergranular carbides in the Ni-Mo-Cr superalloy.

Acknowledgments

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References

1. R. E. Gehlbach and H. E. McCoy, "Phase Instability in Hastelloy N", International Symposium on Structural Stability in Superalloys, ed. Matthew J. Donachie, Jr. (Seven Springs, Pennsylvania: TMS, 1968), 346-366.
2. Y.S. Wang et al., "Effect of Silicon on Grain Boundary Carbide Precipitation and Properties of Cobalt-Free Wrought Nickel-Base Superalloy", the Fourth International Symposium on

Superalloys, ed. John K. Tien, Stanley T. Wlodek, Hugh Morrow III, Maurice Gell, and Gernant E. Maurer (Champion, Pennsylvania: TMS, 1980), 63-72.

3. X. M. Guan, H. Q. Ye, "Intergranular embrittlement caused by the precipitation of M_6C carbide containing silicon", *Journal of Materials Science*, 15 (11) (1980), 2935-2937.
4. F. S. Pan et al., "Carbides in high-speed steels containing silicon", *Metallurgical and Materials Transactions A*, 35 (9) (2004), 2757-2766.
5. W. R. Martin and J. R. Weir, "The Effects of Elevated Temperature Irradiation on the Strength and Ductility of the Nickel-Base Alloy, Hastelloy N" (Report ORNL/TM-1005, Oak Ridge National Laboratory, 1965).
6. W. R. Martin and J. R. Weir, "Effect of Elevated-Temperature Irradiation on Hastelloy N", *Nuclear Applications*, 1 (2) (1965), 160-167.
7. H. E. McCoy and J. R. Weir, "Stress-Rupture Properties of Irradiated and Unirradiated Hastelloy N Tubes", *Nuclear Applications*, 4 (2) (1968), 96-104.
8. H. E. McCoy, "Effects of Irradiation on the Mechanical Properties of Two Vacuum-Melted Heats of Hastelloy N" (Report ORNL/TM-2043, Oak Ridge National Laboratory, 1968).
9. H. E. McCoy, "Variation of the mechanical properties of irradiated Hastelloy N with strain rate", *Journal of Nuclear Materials*, 31 (1) (1969), 67-85.
10. H. E. McCoy and R. E. Gehlbach, "Influence of Irradiation Temperature on the Creep Rupture Properties of Hastelloy N", *Nuclear Technology*, 11 (1) (1971), 45-60.
11. H.U. Hong and S.W. Nam, "Improvement of creep-fatigue life by the modification of carbide characteristics through grain boundary serration in an AISI 304 stainless steel", *Journal of Materials Science*, 38 (7) (2003), 1535-1542.
12. L. Jiang, "The effect of $M_{23}C_6$ carbides on the formation of grain boundary serrations in a wrought Ni-based superalloy", *Materials Science and Engineering: A*, 536 (2012), 37-44.
13. W. H. Jiang et al., "Secondary carbide precipitation in a directionally solidified cobalt-base superalloy", *Metallurgical and Materials Transactions A*, 30 (3) (1999), 513-520.
14. H. L. Liu et al., "A first-principles study on structural and electronic properties of Mo_2C ", *Scripta Materialia*, 60 (11) (2009), 949-952.