EFFECT OF SILICON ON GRAIN BOUNDARY CARBIDE PRECIPITATION AND PROPERTIES OF A COBALT-FREE WROUGHT NICKEL-BASE SUPERALLOY

Y.S.Wang X.M.Guan H.Q.Ye
J.Bi A.S.Xu*
Institute of Metal Research
Academia Sinica, Shenyang
The People's Republic of China

The tensile strength, ductility or impact value of a wrought nickel-base superalloy Ni-15Cr-6W-3Mo-2Al-2Ti depends markedly upon the silicon content of the alloy. On plotting these mechanical properties vs silicon content which ranges from 0.1 to 0.89%, saddled curves shown by the existence of minima at 0.4-0.6%Si occur, which are caused by the variation of mechanical properties with the type, amount and morphology of carbides as well as with the sequence of carbide precipitation in the alloy as influenced by the silicon content. Present work indicates that silicon plays an important role in the formation of M_6C.

* An Engineer of BenXi Steel Works.

INTRODUCTION

Due to the purity of raw material and smelting process, it is unavoidable that there is some silicon in superalloys. It is usually less than 0.2% for high quality superalloys produced by vacuum melting processes (1). The content of silicon should be restricted, because it has a strong tendency of segregation during solidification, and it is also an element, strongly promoting the formation of TCP phases, such as sigma, Laves and G. Therefore, excess silicon lowers the hot workability, and decreases the room temperature ductility and rupture strength (2,3).

Influence of silicon on grain boundary carbide precipitation, including type, morphology and amount, has been investigated. The saddle shaped curves of room temperature tensile strength, ductility and impact value with silicon content have been explained by the morphology and the relative amounts of $M_{23}C_6$ and M_6C which are controlled by silicon content in the alloys.

MATERIALS AND EXPERIMENTAL RESULTS

Experimental alloys were prepared by three melting processes (VIM+ESR, AIM+ESR, EAM+ESR). The chemical compositions of alloys with various silicon contents are listed in Table 1.

Heat treatment was as follows: 1180°C/2 hours, A.C. + 1050°C/4 hours, A.C. + 800°C/16 hours, A.C.. Samples were prepared from either 22mm diameter rolled bars or stamp formed blades. Standard tensile specimens of gauge diameter 5mm and gauge length 25mm and standard U-notched impact specimens were cut from rolled bars and unnotched impact specimens (5x10x55mm) were longitudinally taken from blades. Besides, unnotched impact specimens (5x5x40mm) and tensile specimens (gauge diameter 3mm and gauge length 15mm) were machined from blades.

Influence of Silicon on Mechanical Properties

The effect of silicon on room temperature tensile properties and impact values is shown in Fig.1

Table 1. Chemical Composition of Experimental Alloys (wt%)*

Heat No.	Process	C	Si	Cr	W	Mo	Al	Ti
N-1	VIM+ESR	0.07	0.10	15.02	5.83	3.71	2.03	2.11
N-2	AIM+ESR	0.07	0.20	14.94	6.11	3.40	2.00	2.17
N-3	"	0.05	0.30	15.27	6.08	3.10	2.15	2.10
N-4	"	0.05	0.37	14.92	6.03	3.02	2.08	2.08
N-5	"	0.06	0.40	14.20	6.05	3.13	2.22	2.05
N-6	"	0.05	0.44	15.51	6.15	3.12	2.00	2.02
N-7	"	0.06	0.48	15.50	6.15	3.10	2.06	2.03
N-8	"	0.05	0.54	15.06	6.17	3.08	1.98	2.14
N-9	"	0.06	0.61	15.00	6.07	3.12	2.05	2.07
N-10	"	0.05	0.77	14.45	5.93	3.20	2.01	2.03
N-11	"	0.06	0.89	15.11	6.06	3.06	2.04	2.02
N-12	EAM+ESR	0.05	0.38	14.66	5.91	3.43	2.12	2.18
N-13	"	0.07	0.42	14.63	6.05	3.40	2.11	2.20
N-14	"	0.04	0.49	14.55	5.82	3.34	1.91	2.30
N-15	"	0.06	0.53	14.58	5.87	3.34	1.93	2.17
N-16	"	0.07	0.57	14.61	6.08	3.36	2.15	2.15

* Ni bal., V 0.20%, B 0.008%

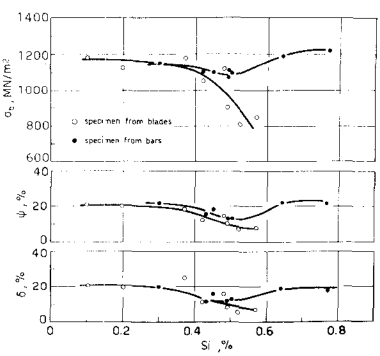


Fig.1. Effect of Si on Tensile Property

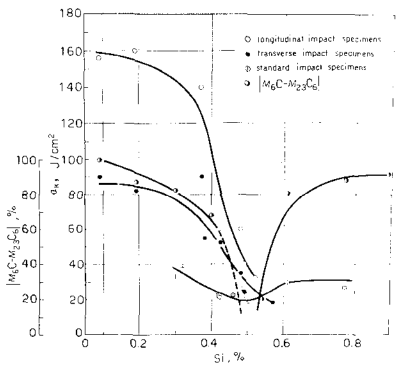


Fig.2. Effect of Si on Impact Property

and 2. It is evident that there is a minimum at 0.5% Si. As silicon content exceeds 0.6%, these properties are restored to those of low silicon content.

Distribution of Alloy Elements

By electron microprobe analysis, the distribution of alloy elements in grains and grain boundaries is shown in Table 2. Obviously, grain boundaries are rich in Cr, Mo and W, whereas poor in Ni, Al and Ti. The distribution of silicon, however, varies with the silicon content in the alloys. As the silicon content is below 0.37%, the amounts in grains and grain boundaries are almost same. At higher silicon contents, the amounts in the grain boundaries are approximately three to four times higher than that in grains. Fig.3 shows the distribution of silicon in grains and grain boundaries vs silicon contents of the alloys. By examining the silicon content on the fracture surface by Auger electron spectroscopy, the intensity of silicon spectrum lines becomes stronger and stronger as the silicon content rises, Fig.4.

Table 2. Distribution of Elements in Grains and Grain Boundaries (wt%)

Heat No.	Location	Cr	Ni	Ti	Al	W	Mo	Si
N-1	in grain	15.27	72.17	2.06	1.97	5.61	3.77	0.00
	in grain boundary	17.80	67.14	1.94	1.75	6.63	4.40	0.00
N-4	in grain	15.56	72.28	1.92	1.75	6.16	2.94	0.17
	in grain boundary	18.08	66.59	2.07	1.47	6.69	3.24	0.19
N-16	in grain	14.96	71.84	2.21	1.55	6.24	3.42	0.34
	in grain boundary	15.77	62.56	2.17	1.08	8.89	5.34	1.06
N-11	in grain	15.74	71.21	1.98	1.84	6.18	2.78	0.45
	in grain boundary	16.25	62.51	1.76	1.22	8.44	5.47	1.40

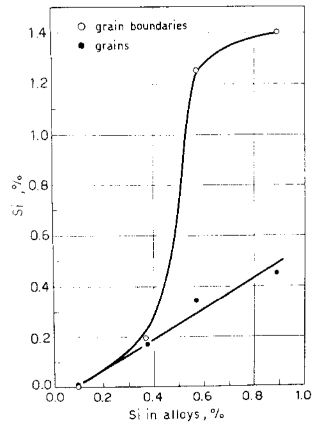


Fig.3. The Relative Distribution of Si in Grains and Grain Boundaries vs Si in Alloys

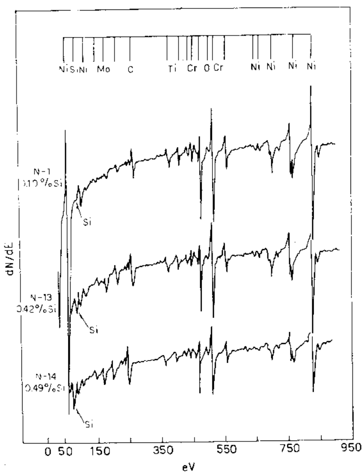
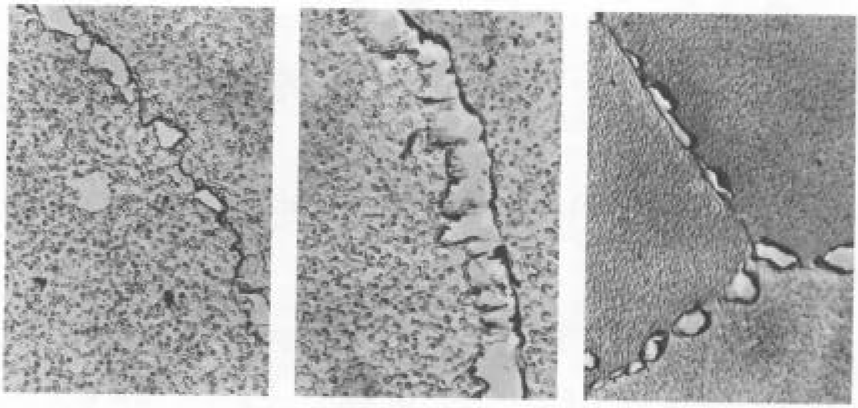


Fig.4. Typical Auger Spectrum of Fracture Surface of Different Si Contents in Alloys

Influence of Silicon on Carbide Precipitation

As the silicon content increases from 0.1 to 0.77%, the grain size changes from ASTM 1-4 to 3-6. The type, morphology, composition and amount of carbides on grain boundaries vary with the silicon content. The morphology of carbides on the grain boundaries can be seen in Fig.5, it is in a discontinuous blocky form at less than 0.4%Si, and as the silicon content increases to 0.4-0.6%, it becomes thicker and continuous, and nearly covers the whole grain boundaries. As the silicon content exceeds 0.6%, a granular carbide form is appeared again on the fracture surface as examined by carbon replica technique, Fig.6.



(a) N-1 0.10%Si (b) N-16 0.57%Si (c) N-10 0.77%Si

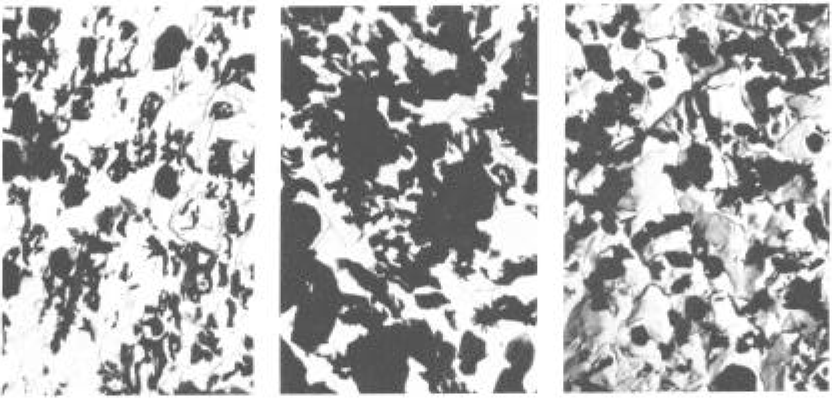
Fig.5. Morphologies of Grain Boundaries

Carbide Types and Their Relative Amounts

The carbides were electrolytically extracted and identified by X-ray analysis. Their relative amounts of $M_{23}C_6$ and M_6C as a function of silicon content were determined by a focusing powder monochromatic technique. The results were shown in Table 3 and Fig.7. Generally speaking, the carbide precipitation can be divided into four stages:

(1) less than 0.1%Si. Only $M_{23}C_6$ exists in the alloy.
(2) 0.1-0.4%Si. M_6C begins to precipitate out with a rate of 3.5% per 0.1% of silicon. In this stage the amount of M_6C is less than 20%.
(3) 0.4-0.6%Si. M_6C increases ten-fold more rapidly at a rate of 35-40% per 0.1%Si.
(4) greater than 0.6%Si. The precipitation of M_6C

slows down again, and that of $M_{23}C_6$ is almost suppressed. The relative amount of M_6C exceeds 90%.



(a) N-1 0.10%Si (b) N-14 0.49%Si (c) N-9 0.61%Si

Fig.6. Morphologies of Carbides on Fracture Surface

Table 3. Relative Amounts of $M_{23}C_6$ and M_6C at Different Si Contents

Si %	$I(M_6C)/I(M_{23}C_6)$	$W(M_6C)/W(M_{23}C_6)$	$M_{23}C_6$ %	M_6C %
0.10	—	--	100	--
0.20	0.13	0.017	93	7
0.30	0.167	0.096	91.2	8.8
0.40	0.284	0.164	85.9	14.1
0.42	1.296	0.76	57.1	42.9
0.49	6.83	3.95	22.2	77.8
0.54	2.625	1.51	39.8	60.2
0.57	8.67	5.0	16.6	83.4
0.61	16.35	9.45	9.6	90.4
0.77	24.83	15.0	6.3	93.7
0.89	37.4	21.6	4.4	95.6

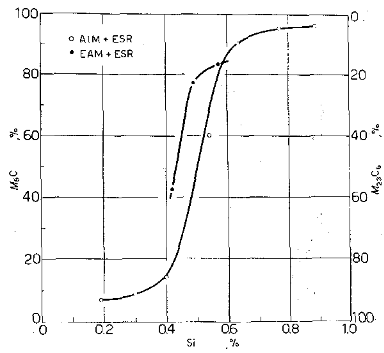


Fig.7. The Relative Amount of $M_{23}C_6$ and M_6C vs Si Content in Alloy

The amount of carbides increases with silicon content. As the silicon content increases from 0.37 to o.89%, the amount of carbides increases from 0.44 to 1.43%, and their composition is shown in Table 4. It should be pointed out that the silicon content in M_6C is 4%, and none in $M_{23}C_6$.

Table 4. Chemical Composition of $M_{23}C_6$ and M_6C (wt%)

Carbide Type	Ti	Si	Mo	W	Cr	Fe	Ni
$M_{23}C_6$	9.55	--	15.90	13.99	28.77	6.80	3.40
M_6C	4.44	4.00	23.16	21.51	11.14	5.20	19.64

DISCUSSION AND CONCLUSION

By the results of microstructure and phase analysis, the minimum properties between 0.4–0.6%Si are mainly due to the change of carbide type, morphology and distribution. If a curve of silicon content in alloys with the absolute value of the difference of M_6C and $M_{23}C_6$ amounts is plotted in Fig.2, it also shows a saddle shaped curve with a minimum at 0.5% Si. It is concluded that the effect of silicon is via the change of the morphology, amount and distribution of the precipitate of the carbides. Silicon accelerates M_6C formation due to the high solubility of silicon in this type of carbide. Between 0.4-0.6% Si, appreciable amount of continuous platelets of M_6C almost covers the whole grain boundary, which weakens the cohesive force between grains, this is the main reason of degradation of the mechanical properties of the alloy. If the silicon content lies outside the above range, M_6C and $M_{23}C_6$ are in a discontinuous granular form which may strengthen the grain boundary.

On account of silicon greatly changes the carbide precipitation process thermodynamically and kinetically, the Sims's relation of formation of M_6C when $Mo+\frac{1}{2}W \geq 6\%$ in nickel-base superalloys is not valid any more, for instance, in the alloy studied. If the silicon content is low (0.1%Si), even if $Mo+\frac{1}{2}W=6.6\%$, no M_6C was found out, and when Si content is higher, M_6C would be come out at $Mo+\frac{1}{2}W=6\%$.

Melting process influences the carbide precipitation. The impurities and gas contents in alloys produced by arc furnace duplex with ESR are higher, which favors the condition of uneven nucleation and growth of M_6C. As a result of that, the ductile-brittle transition curve moves toward low silicon range.

Conclusions can be made as follows:

(1) Silicon has a great influence on room temperature tensile strength, ductility and impact toughness. A minimum at about 0.4-0.6%Si occurs.

(2) Silicon is evenly distributed in grains and grain boundaries of alloys with less than 0.4%Si, and $M_{23}C_6$ will be the main carbide.

(3) As the silicon content exceeds 0.4%, silicon considerably segregates to grain boundaries, nearly 3-4 times greater than in grains. It greatly enhances the M_6C precipitation. At above 0.6%Si, the relative amount of M_6C is greater than 90%.

(4) The reason of the minimum properties of alloys with 0.4-0.6%Si is not the formation of M_6C itself, but is chiefly due to morphology and distribution. The continuous M_6C film weakens the grain boundary and lowers the strength and ductility.

ACKNOWLEDGMENTS

Thanks are due to J. Y. Wang for performing the experiments on electrolytic extraction of carbide phases and to S. Z. Lin and X. Z. Zhang on X-ray analysis.

REFERENCES

(1) W. Betteridge, J. Heslop, "The Nimonic Alloys," Second Edition, London, 1974, p.23.

(2) F. J. Rizzo, J. D. Buzzanell, J. Metals, No.10, 1969, p.24.

(3) M. Sakakikara, S. Sekina, "Superalloys Processing, Proc. of the Second International Conference," 1972.