QUANTITATIVE CARBON PARTITIONING DIAGRAMS FOR WASPALOY AND THEIR APPLICATION TO CHEMISTRY MODIFICATIONS AND PROCESSING

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Partitioning of carbon between MC, M₂₃C₆ and solid solution was measured for Waspaloy in support of homogenization, chemistry modification, and thermomechanical processing programs. Carbon partitioning diagrams were developed for high, medium, and low carbon ingots. Analysis of wrought samples with selected heat treatments permitted extrapolation of ingot diagrams to wrought structures. Changes in carbon partitioning resulting from lower cobalt and the addition of niobium were determined.

INTRODUCTION

Properties of superalloys are influenced by the distribution and quantity of carbides. They can strengthen, initiate fracture, restrict grain boundary sliding, inhibit grain growth, tie up critical elements and participate in reactions that produce gamma prime denuded zones. The relative amounts of carbides and their distributions are dependent on factors such as chemistry, thermal treatment and microstructure. Therefore, recent programs at Special Metals on homogenization, chemistry modifications, and thermomechanical processing of Waspaloy included a study on carbon partitioning.

MATERIALS AND PROCEDURE

Chemistries of the Waspaloy heats used in this study are given in Table I. Heat numbers beginning with 9 represent VIM/VAR ingots 61 cm (24 inches) in diameter. Wrought structures were produced by rolling ingot coupons 5.08 cm (2 inches) thick to plates 1.27 cm (0.50 inches) thick with a final rolling temperature of 1038°C (1900°F). Heat numbers beginning with D1 represent VIM ingots 6.4 cm (2.5 inches)

	Wt. % (Balance Ni)									
Heat	C	Cr	Co	Мо	Τi	A1	В	Zr	S	N
9-4747	.057	19.0	13.6	4.25	3.17	1.41	.005	.06	.004	.0030
9-5750	.034	18.9	13.5	4.10	3.05	1.34	.005	.07	.003	.0027
9-6130	.020	19.2	13.6	4.08	3.09	1.32	.005	.07	.002	.0022
9-1549	1.038	19.1	13.7	4.25	3.12	1.37	.005	.07	.003	
1	-									
D1-1650	1.035	19.4	13.2	4.05	3.07	1.35	.004	.06	.001	
D1-1653	1.036	19.3	8.1	3.99	3.01	1.33	.003	.06	.001	
D1-1730	1.040	19.5	0.0	3.94	3.01	1.35	.001	.06	.002	
D1-1654*	1.040	19.2	12.4	4.05	3.03	1.36	.003	.06	.001	
*0.41% Nb										

Table I. Chemistries

in diameter which were also rolled to plates 1.27 cm (0.50 inches) thick. Final rolling temperature was 1093°C (2000°F). Grain sizes for as rolled and selected heat treated conditions are given in Table II.

Table II. Typical Grain Sizes

	Final Rolling		
Heat	Temperature		Grain Size
		1010°C(1850°F)/ 4hrs.	
		1066°C(1950°F)/17hrs.	
9-5750	1038°C(1900°F)	1232°C(2250°F)/24hrs.	1000000-00000
D1-1650) 1093°C(2000°F)		$ 1-1\frac{1}{2}, 4-4\frac{1}{2} $

Specimens for extraction were trimmed to remove oxidized and depleted surfaces. The (TiMo)C carbides along with small amounts of TiCN, TiN, and $\text{Ti}_4\text{C}_2\text{S}_2$ were isolated by successive extractions in a 10% bromine-methanol solution. Also, an electrolytic extraction was done in a 10% hydrochloric acid-methanol solution to isolate the phases listed above plus the M23C6 type chromium carbide, if present. The residues from both extractions were separated from solution by filtering. Specimens were weighed before and after extraction and extracted residues were weighed.

Carbon analyses were made on the MC carbide residues isolated by bromine methanol to calculate the percent of total carbon present as MC. These results include the small amounts of carbon present as Ti(CN) and $Ti_4C_2S_2$. The weight percent of M23C6 carbide was determined by difference between the bromine and electrolytic extractions.

Based on previous determinations, 5 weight percent was used as the amount of carbon in $M_{23}C_6$ for calculating the percent of total carbon as $M_{23}C_6$. X-ray diffraction analyses were also conducted on the residues of the electrolytic extraction to confirm the presence of $M_{23}C_6$. All samples were done in duplicate.

RESULTS AND DISCUSSION

Basic carbon partitioning diagrams were determined from ingot samples heated to 1232°C (2250°F) for 24 hours and water quenched followed by precipitation at specific temperatures for 17 hours and water quenching.

Ingot Structure - 0.057% C. Figure 1 shows the basic carbon partitioning diagram for 0.057% C. The amount of C that did not go into solution at 1232°C (2250°F) has been designated primary MC over the entire temperature range. Although almost 80% of the C was in solution at 1232°C (2250°F), only about 3% was still in solution at 843°C (1550°F). Both MC, identified as (Ti.8Mo.2)C, and M23C6, which is primarily (Cr21Mo2)C6 precipitated intragranularly and on grain boundaries. Above about 1038°C (1900°F), M23C6 did not exist. Precipitation of M23C6 is profuse in the temperature range 954°C (1750°F) to 788°C (1450°F),

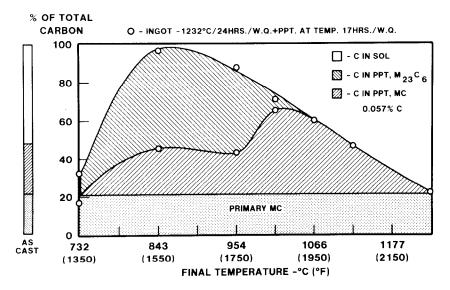


Figure 1. Carbon partitioning diagram for 0.057% C ingot.

apparently due to extreme supersaturation promoting extensive nucleation on dislocations, stacking faults and other defects. Note that $M_{23}C_6$ was not present as cast.

Holding in the MC precipitation range prior to cooling into the $M_{23}C_6$ temperature range reduced C supersaturation and, therefore, less $M_{23}C_6$ was precipitated. This is illustrated in Figure 2 where specimens were held at $1066^{\circ}C$ (1950°F) for 17 hours and water quenched before being held at various temperatures; the amount of $M_{23}C_6$ precipitated at $843^{\circ}C$ (1550°F) and $954^{\circ}C$ (1750°F) was greatly reduced. Also, a small amount of MC beyond that precipitated at $1066^{\circ}C$ (1950°F) precipitated at these two temperatures.

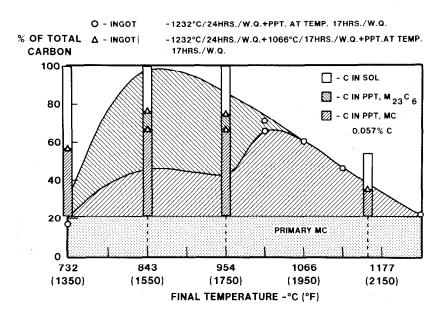


Figure 2. Carbon partitioning after holding at 1066°C before precipitating at various temperatures for 0.057% C ingot.

Wrought Structure - 0.057% C. The basic carbon partitioning diagram for ingots is also useful for wrought structures. Holding rolled specimens at solution temperatures between 1066°C (1950°F) and 1232°C (2250°F) for 4 hours resulted in essentially the same amount of MC as indicated on the ingot diagram. Also 10 minutes at 1121°C (2050°F) was equivalent to 4 hours, indicating that carbon goes into solution very quickly at these higher temperatures.

As shown in Figure 3, holding at 1066°C (1950°F) followed by precipitation at 843°C (1550°F) resulted in more $M_{23}\text{C}_{6}$ than for the ingot structure (Figure 2). This is attributed to the presence of more grain boundaries. Also, Figure 3 illustrates that more $M_{23}\text{C}_{6}$ precipitates at 843°C (1550°F) following 1010°C (1850°F) as compared to 1066°C (1950°F) because of finer grain size. Holding at 1232°C (2250°F) before holding at 1066°C (1950°F) resulted in essentially no $M_{23}\text{C}_{6}$ precipitating at 843°C (1550°F) in 17 hours because of extremely large grains. An indication of the rate of $M_{23}\text{C}_{6}$ precipitation at 843°C (1550°F) is given by data at 10, 100° and 1020° minutes in Figure 3.

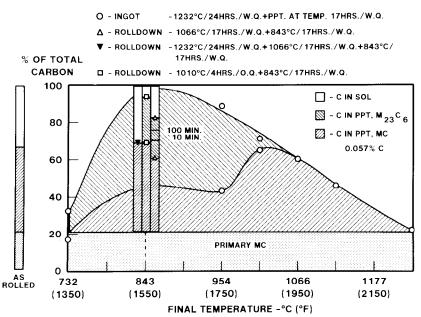


Figure 3. Carbon partitioning for wrought specimens with various heat treatments for 0.057% C.

Ingot Structure -0.034% and 0.020% C. Basic carbon partitioning diagrams are shown in Figures 4 and 5 for 0.034% C and 0.020% C, respectively. Again, M23C6 precipitates below about 1038°C (1900°F) and is a maximum between 843°C (1550°F) and 984°C (1750°F). However, the amount of M23C6 is significantly less than for 0.057% C. The higher percentage of primary MC for the lower C of 0.020% is attributed to the presence of TiCN, TiN, and Ti4C2S2 which contribute a greater proportion to the total extracted residue because fewer carbides are present.

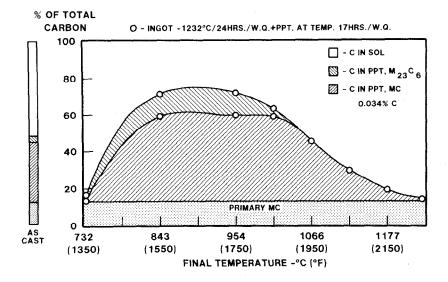


Figure 4. Carbon partitioning diagram for 0.034% C ingot.

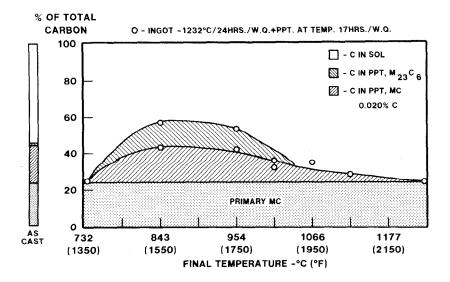


Figure 5. Carbon partitioning diagram for 0.020% C ingot.

These additional phases are more stable than MC and are not readily solutioned. The actual amount of precipitated MC was about the same for 0.057% C and 0.034% C in the 843°C (1550°F) to 954°C (1750°F) range. For example, multiplication of the fraction of total C as precipitated MC by the total C yields .014% C and .015% C as the actual amount of C as precipitated MC for 0.057% C and 0.034% total C, respectively, at 843°C (1550°F).

As illustrated in Figure 6, holding at 1066°C (1950°F) at 843°C (1550°F) resulted in less precipitated MC and $M_{23}C_6$ for 0.020% C.

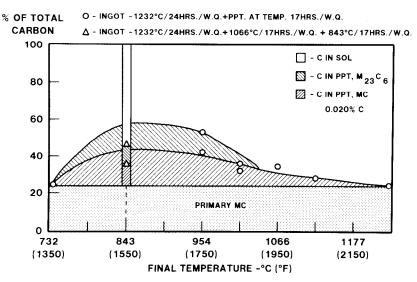


Figure 6. Carbon partitioning after holding at 1066° C before precipitating $M_{23}C_{6}$ for 0.020% C ingot.

Wrought Structure - 0.034% and 0.020% C. Figure 7 shows that precipitation in the 843°C (1550°F) to 954°C (1750°F) range after holding at 1010°C (1850°F) or 1066°C (1950°F) resulted in more $M_{23}C_6$ than for ingot samples. Also, holding at 1010°C (1850°F) resulted in more $M_{23}C_6$ than holding at 1066°C (1950°F). Solutioning at 1232°C (2250°F) resulted in less precipitated $M_{23}C_6$ than for ingot samples. Again, these differences in $M_{23}C_6$ precipitation are attributed to grain size differences since $M_{23}C_6$ precipitates preferentially on grain boundaries. The rate at which $M_{23}C_6$ forms is shown in Figure 7 for short times and in Figure 8 for long exposures where MC reacts to form $M_{23}C_6$. The values of 29% C as MC and the remaining 71%

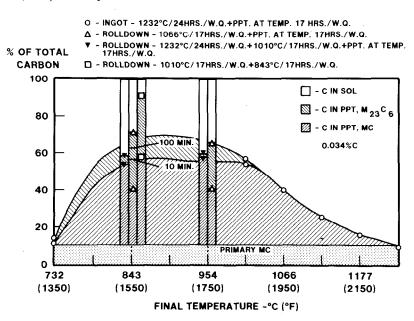


Figure 7. Carbon partitioning after holding at 1010°C, 1066°C, or 1232°C before precipitating M23C6.

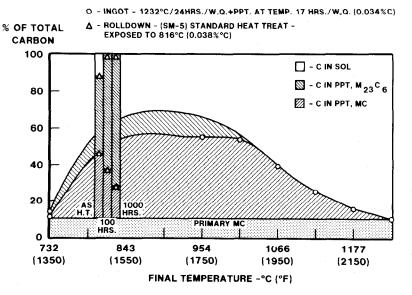


Figure 8. Carbon partitioning after long exposure times for 0.038% C rolldown. Standard heat treatment is 1010°C/4 hrs./OQ + 834°C/4 hrs./AC + 760°C/16 hrs./AC.

of total carbon as $M_{23}C_6$ for 1000 hours is in good agreement with the corresponding values of 27% C and 73% C calculated from R. F. Decker's (1) regression analysis. These data are also consistent with that of H. E. Collins (2).

Reduced Cobalt. Recent and projected shortages of Co have prompted programs directed towards lowering Co in Waspaloy. One mechanism by which decreased Co may influence properties is by altering the amount and distribution of Therefore, carbon partitioning was evaluated for rolldowns from small ingots with various Co levels. results are presented in Figure 9 where they are compared to the basic carbon partitioning diagram for 0.034% C. Lowering Co did not affect solutioning at 1232°C (2250°F) but did increase precipitation of MC during rolling and increased the amount of $M_{23}C_6$ at $843^{\circ}C$ (1550°F). dency towards increased M23C6 formation at 843°C (1550°F) continued with precipitation times of 100 and 1000 hours for other experimental heats with about 0.025%C; at 1000 hours, 13.1% Co had 72% M23C6 compared to about 88% for 8.0% and 0.0% Co. Additional data are needed to determine if increasing MC with decreasing Co in the as-rolled condition is due to an increase in the rate of MC precipitation or an increase in the equilibrium amount of MC at the rolling temperatures.

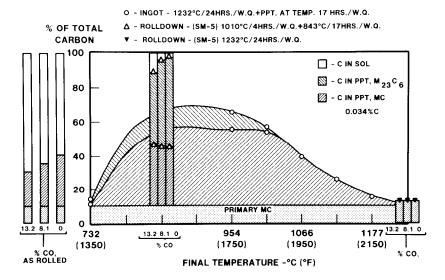


Figure 9. Effect of reduced cobalt on carbon partitioning of rolldowns with about 0.035% C.

Nb Addition. As shown in Figure 10, the addition of only 0.41% Nb significantly increased MC stability. Less MC went into solution at 1232°C (2250°F). Also, more MC was present after rolling and after precipitation at 843°C (1550°F) following a 1010°C (1850°F) hold for 4 hours. Apparently the entire MC field of the carbon partitioning diagram was raised.

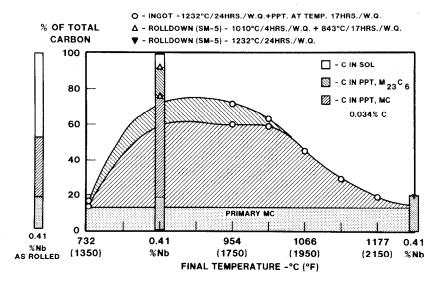


Figure 10. Effect of 0.41% niobium on carbon partitioning of rolldown with 0.040% C.

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