

SEGREGATION DURING SOLIDIFICATION

IN THE MAR-M247 SYSTEM

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Abstract

Elemental segregation behavior was examined in the as-solidified microstructures of six directionally-solidified MAR-M247-derivative alloys with variations in the C, Hf, and Ta levels. Elemental segregation patterns were determined from elemental contour maps of dendritic cross-sections generated from electron microprobe data. Hf, Ta, Ti, and Al were found to segregate to the liquid, W and Co segregated to the solid, and Mo, Cr, and Ni did not segregate consistently to one phase during solidification. Initial distribution coefficients were calculated as the ratio of dendrite core composition to bulk alloy composition. Average distribution coefficients were determined from constructed solid composition profiles as a function of fraction solidified using a Scheil-type analysis. The distribution coefficients did not vary between the six alloys for a given element; mean values of the average distribution coefficients were found to be 0.12 for Hf, 0.77 for Ta, 0.73 for Ti, 0.94 for Al, 1.23 for W, and 1.07 for Co.

Introduction

The elemental segregation that accompanies solidification must be characterized quantitatively in order to understand the development of as-cast nickel-base superalloy microstructures. While a significant amount of work has been conducted in the area of dendritic microsegregation in these alloys [1-10], few studies have been concerned with determining distribution coefficients (defined as the ratio of solid composition to liquid composition at a given temperature) for multiple alloys derived from a single system with systematic variations in composition. Furthermore, most of the techniques used for determining distribution coefficients involved either specialized solidification methods that were not representative of actual casting practices or pertained only to part of the solidification interval rather than being descriptive of the solidification process as a whole.

Therefore, the goal of this research was to examine the segregation behavior as a function of variations in C and the refractory elements Hf and Ta in six directionally and dendritically solidified alloys derived from the MAR-M247 system. These variations were selected since the addition of C leads to the formation of carbides (if the C level exceeds the solubility limit) and the two refractory elements participate in carbide formation as well as segregate to the liquid during solidification. The addition of Hf has also been linked to the formation of the γ - γ' eutectic microconstituent [11,12] and has led to the formation of Hf-rich intermetallic compounds in some instances [2,12].

Distribution coefficients were calculated using two different procedures. Segregation patterns for all of the major alloying elements except C were first established from the as-solidified microstructures using electron microprobe data in the form of compositional contour maps of dendrite cross-sections. Distribution coefficients representative of initial solidification were calculated as the ratio of the dendrite core composition to the bulk alloy composition. Average distribution coefficients for the elements were determined using a Scheil-type analysis on solid composition data from entire sample cross-sections as a function of fraction solidified. The results for one alloy containing MC carbides and with a composition of 0.5 at% C, 0 at% Hf, and 1 at% Ta (which represents a case of intermediate complexity) will be presented in detail, while the results for the other five alloys will be summarized.

Materials and Experimental Procedure

The MAR-M247-derivative alloys were directionally solidified by Howmet Turbine Components Corporation using the withdrawal process. The compositions for the six alloys listed in Table I, with the exception of C, were determined using an electron microprobe with a wavelength dispersive spectroscopy system, software to correct for atomic number, absorption, and fluorescence effects, and pure elemental standards. The C contents from the original compositional analyses by Howmet were used rather than measuring them with the electron microprobe, due to the problems associated with low level light element analysis with this type of a system. The primary differences in composition between the six alloys are the levels of C, Hf, and Ta; 0.5 at% C, 0.4 at% Hf, and 1 at% Ta were substituted for Ni. Although alloy D has the nominal MAR-M247 composition, alloy F (0.5 at% C, 0 at% Hf, and 1 at% Ta) was chosen to illustrate the segregation analyses employed in this work.

Table I: Compositions of MAR-M247-Derivative Alloys (At%)

Alloy	C	Hf	Ta	Ti	Al	W	Mo	Cr	Co	Ni
H	0.05	—	—	1.07	11.37	3.08	0.40	9.84	10.31	63.89
J	0.04	—	1.08	1.19	11.92	2.95	0.34	10.02	10.27	62.20
E	0.52	—	—	1.13	11.19	3.00	0.40	9.80	10.13	63.84
F*	0.48	—	1.11	1.23	11.40	3.02	0.33	9.99	10.35	62.08
C	0.49	0.38	—	1.14	11.31	2.93	0.33	9.85	10.17	63.41
D†	0.51	0.44	1.08	1.18	11.57	3.00	0.41	9.89	10.20	61.73

* Alloy chosen for detailed description in this paper

† Nominal MAR-M247 composition

Segregation patterns and initial distribution coefficients were determined as follows. A grid consisting of at least 150 compositional analyses was located on the cross section of a dendrite in an unetched sample using the electron microprobe. Analyses near pores or carbides were eliminated, and the resulting set of compositions was transformed using contouring software into elemental contour maps. For those elements with segregation patterns that matched the shape of the dendrite, initial distribution coefficients were calculated as the ratio of the dendrite core composition to the overall alloy composition.

Average distribution coefficients were calculated for those elements with consistent segregation patterns following a procedure established for the Al-Cu system [13]. A grid of at least 200 compositional analyses was distributed over the cross section of an entire unetched sample; these analyses represented a statistical sampling of the changing solid composition during solidification. After subtracting any analyses located at pores or carbides, solid composition profiles for elements that segregated to the liquid were produced by plotting the analyses in order from lowest amount to highest amount measured. Each analysis was assigned an incremental number; dividing each of these numbers by the total number of analyses yielded a solid composition profile as a function of fraction solidified. For elements that segregated to the solid, solid composition profiles were produced with the same procedure, but the analyses were plotted from highest level to lowest level. The resulting solid composition profiles were modeled using the Scheil equation in order to obtain average values for the distribution coefficients.

Experimental Results

The as-cast microstructure of alloy F is shown in Figure 1. The phases present as a result of solidification are γ and MC. Based on the phase distribution and the solidification sequences reported for other alloy systems [7,14,15], solidification most likely occurred through the following reactions for this alloy:



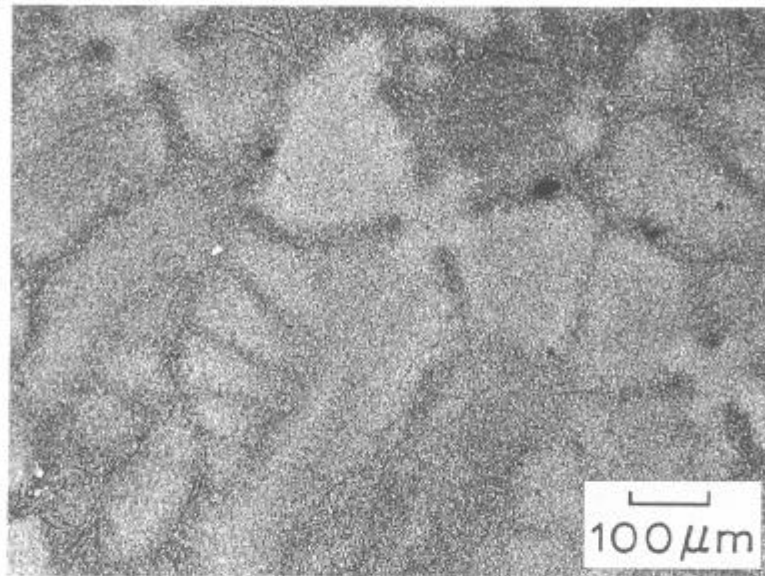
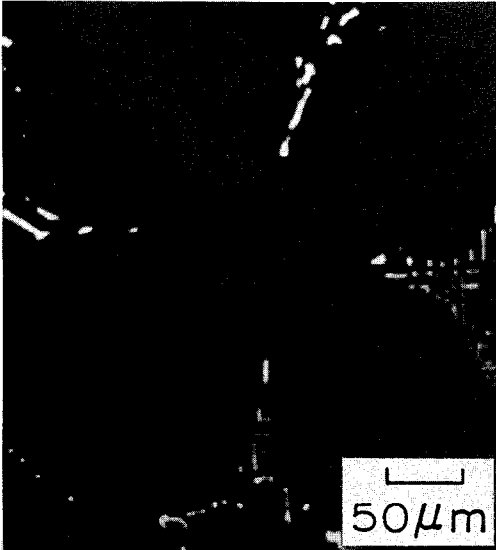


Figure 1: Optical micrograph of alloy F, showing the phases resulting from solidification and the differential etching due to dendritic microsegregation.

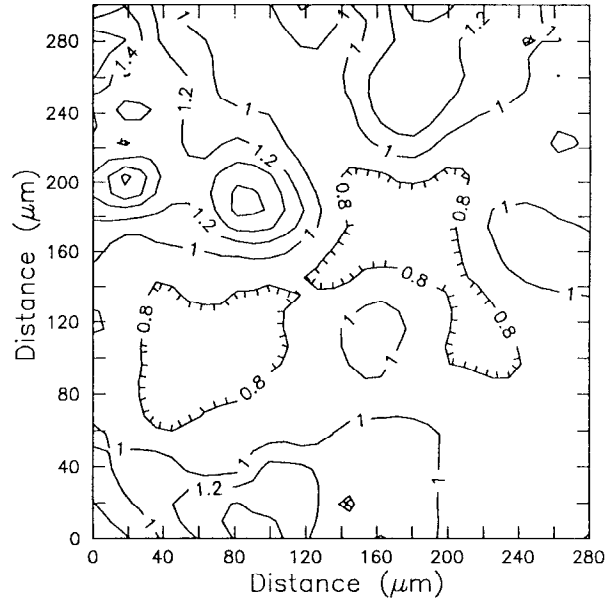
The microsegregation that occurred during solidification in alloy F is illustrated more clearly by the backscattered electron image in Figure 2. The segregation patterns shown by the elemental contour maps for some of the elements, namely Ta, Ti, Al, W, and Co, conformed to the shape of the dendrite. The levels of Ta, Ti, and Al are lowest at the location of the dendrite core and increase with proximity to the interdendritic regions (see Ti contour map in Figure 2). Conversely, the levels of W and Co are highest at the dendrite core and decrease with distance toward the interdendritic regions (see W contour map in Figure 2). The segregation patterns for Ta, Ti, and Al result from segregation to the liquid during solidification, while those for W and Co result from segregation to the solid γ . The elemental contour maps for Mo, Cr, and Ni do not conform to the shape of the dendrite (see Ni contour map in Figure 2). This lack of correspondence indicates that Mo, Cr, and Ni did not consistently segregate to one phase or the other during solidification. The same segregation tendencies were observed for these elements in the other five alloys. In addition, Hf was found to segregate to the liquid when present in alloys C and D.

Distribution coefficients pertaining to initial solidification were calculated from the ratio of the dendrite core composition to the overall alloy composition (ratio of the composition of the first solid that formed to the composition of the liquid from which it formed). Values of these initial distribution coefficients are listed in Table II for alloy F along with the average values based on all six alloys. As shown by the low standard deviations, these values are highly consistent for any one element between the six alloys. These standard deviations are equal to or less than 5% of the mean values with the exception of that for Hf, which was the most severely segregating element present.

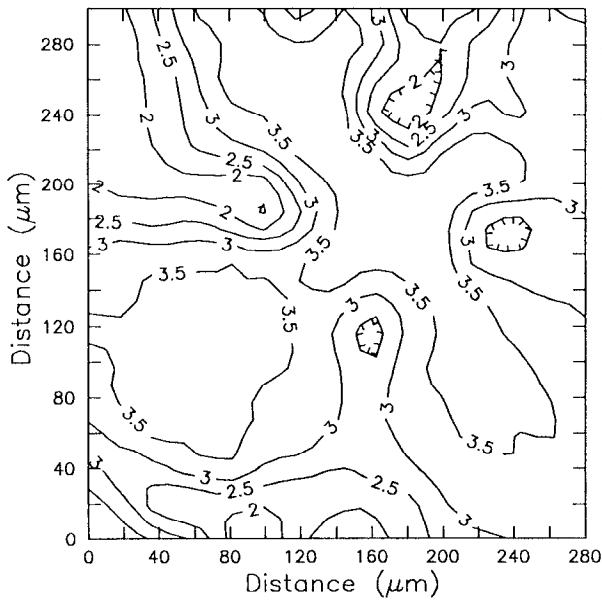
Backscattered Electron Image



Ti Contour Map



W Contour Map



Ni Contour Map

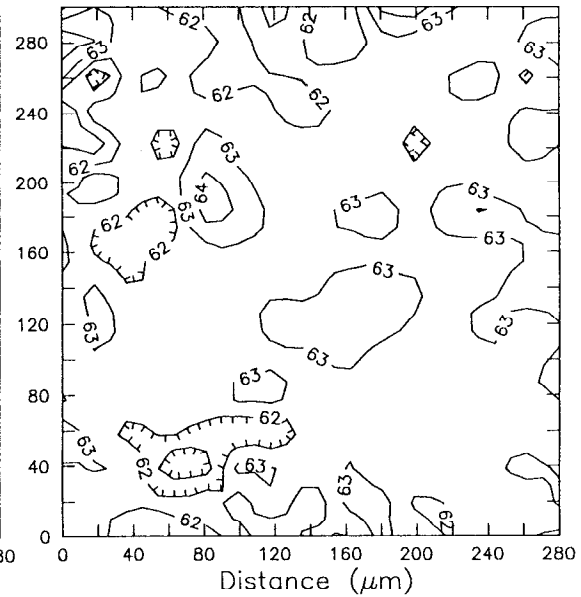


Figure 2: Backscattered electron image of a dendritic cross-section in alloy F, unetched, and elemental contour maps (at%) of the same area for Ti, W, and Ni.

Distribution coefficients averaged over the entire solidification interval were obtained through a Scheil-type analysis of the solid composition profiles (see Figure 3). The Scheil equation describes the solid composition as a function of fraction solidified:

$$C_s = k C_0 (1 - f_s)^{(k-1)} \quad (3)$$

where C_s is the solid composition at a given temperature, C_0 is the overall composition, k is the distribution coefficient, and f_s is the fraction solidified. This equation was developed with the following assumptions: 1) equilibrium is maintained at the solid-liquid interface, 2) distribution coefficients are not a function of temperature, 3) solid state diffusion is insignificant, and 4) the composition of the liquid is uniform. Average values for the distribution coefficient were obtained by fitting the solid composition profiles by linear regression to a modification of the Scheil equation:

$$\ln(C_s/C_0) = (k - 1)(\ln(1 - f_s)) + \ln(k) \quad (4)$$

Initial compositions in some of the solid composition profiles were not linear when plotted as a function of $\ln(1 - f_s)$; these compositions were not used when determining distribution coefficients. The average distribution coefficients for alloy F and the mean values based on all six alloys are listed in Table III; these values show the same relative segregation tendencies as were found with the initial distribution coefficients. The average distribution coefficients for a given element are again very similar from alloy to alloy, as indicated by the low levels of the standard deviations. The solid composition profiles were modeled using equation 3 and the average distribution coefficients; these curves are labeled Solid-Scheil in Figure 3. The solid composition profiles calculated with the Scheil equation show a reasonably close fit to the solid composition profiles except for the initial solidification regions.

Table II: Initial Distribution Coefficients
(C_s in at% / C_L in at%)

Alloy	Hf	Ta	Ti	Al	W	Co
F	—	0.63	0.58	0.88	1.27	1.10
Average of 6 alloys	0.10	0.65	0.60	0.88	1.31	1.11
Std. dev. for 6 alloys	0.01	0.02	0.03	0.04	0.06	0.04

Table III: Average Distribution Coefficients
(C_s in at% / C_L in at%)

Alloy	Hf	Ta	Ti	Al	W	Co
F	—	0.76	0.70	0.94	1.20	1.07
Average of 6 alloys	0.12	0.77	0.73	0.94	1.23	1.07
Std. dev. for 6 alloys	0.04	0.03	0.03	0.01	0.04	0.02

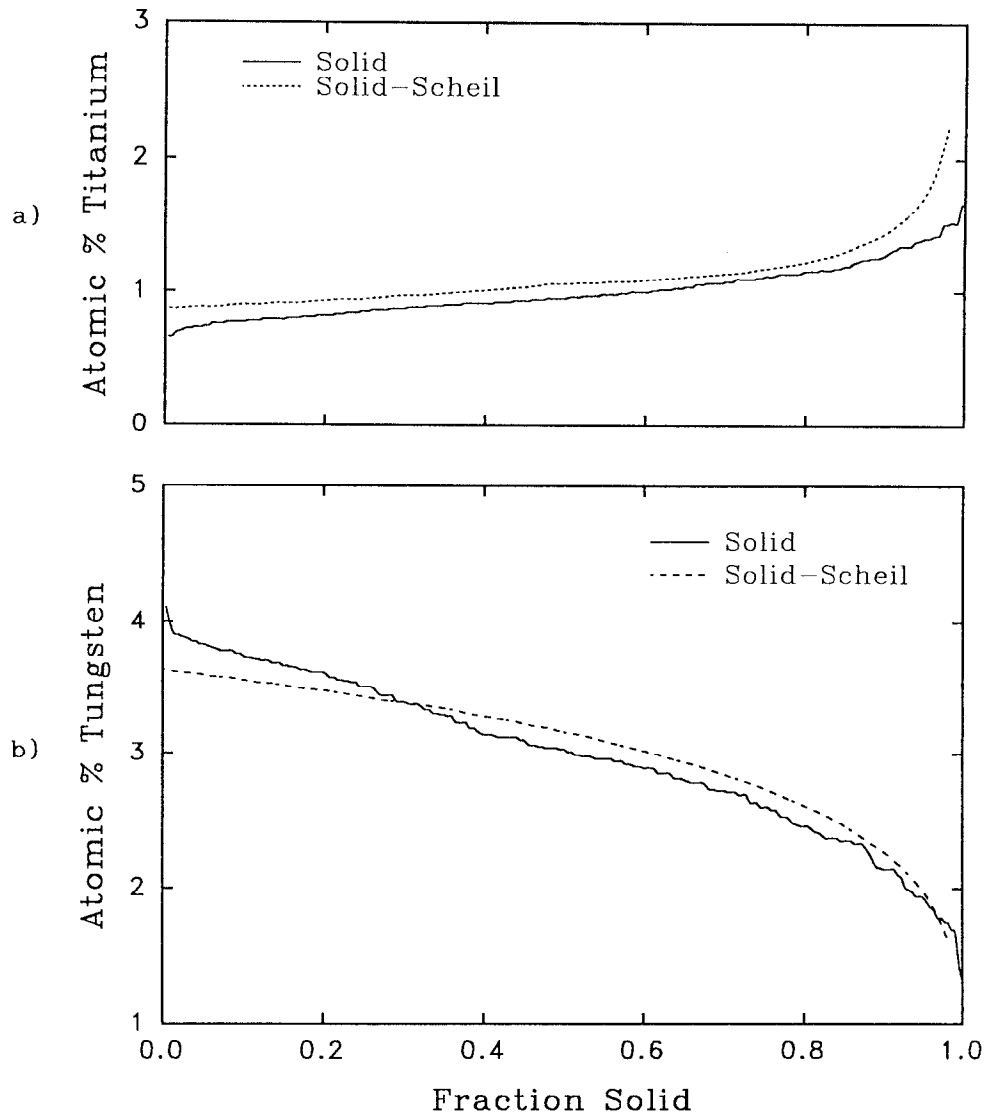


Figure 3: Solid composition profiles from alloy F and Scheil-type modeling for a) Ti and b) W.

Discussion

The initial distribution coefficients were calculated directly from the microsegregation measured in the as-cast microstructure, whereas the average distribution coefficients were determined from a constructed solid composition profile. In order for the second method to be considered a valid technique for measuring microsegregation, a correlation must be shown between the two types of distribution coefficients. A comparison of the values in Tables II and III indicates that the two methods for determining distribution coefficients produce consistent results, so that the second method is indeed valid. The average distribution coefficients are also closer to the value of one than the initial distribution coefficients for all of the elements. This difference can be explained through an examination of the solid composition profiles in Figure 3. The dendrite core compositions used to calculate the initial distribution

coefficients occurred early in the solidification interval where the degree of segregation appeared to be greater. These initial solid compositions did not fit the Scheil equation, which suggests that some of the assumptions inherent to the development of this equation were violated; most likely, the distribution coefficients varied with temperature or mixing was incomplete in the liquid.

The distribution coefficients for a given element did not vary significantly from alloy to alloy. This result indicates that low level additions of C, Hf, and Ta did not affect the segregation tendencies of the other elements. From a comparison of the average distribution coefficients, the relative segregation tendencies of the elements in these alloys can be ranked (see Table IV). In addition, distribution coefficients were estimated for dilute Ni-X binary systems by approximating the liquidus and solidus curves from Reference 16 as straight lines; the relative segregation tendencies and the distribution coefficients for these systems are also listed in Table IV. The elemental segregation behavior and distribution coefficients are very similar between the MAR-M247-derivative alloys and the dilute binary Ni-based systems for Hf, Ta, Ti, Al, Co, and W. C contents were not measured in the MAR-M247-derivative alloys, so no comparison can be made for this element. Mo was present at very low levels in the MAR-M247-derivative alloys, which may have caused difficulty in detecting moderate segregation to the liquid as observed in the binary system. The segregation behavior of Ni in dilute binary systems depends upon the specific solute, so the lack of consistent segregation pattern for Ni in the MAR-M247-derivative alloys is not unexpected. Cr segregates weakly to the liquid in dilute Ni-Cr alloys but did not consistently segregate to either phase in the MAR-M247-derivative alloys; this result is most likely a consequence of the large number of other alloying elements that segregated more strongly to the liquid. In general, these data suggest that little interaction occurred between the various alloying elements in the liquid phase of the MAR-M247-derivative alloys.

Table IV: Segregation Tendencies for MAR-M247 and Binary Ni-X Systems [16]

MAR-M247 System	Ni-X Systems
Hf (0.12) liquid	Hf (0.08) liquid
Ti (0.73) liquid	C (0.34) liquid
Ta (0.77) liquid	Mo (0.78) liquid
Al (0.94) liquid	Ta (0.81) liquid
Cr neither*	Ti (0.83) liquid
Mo neither	Al (0.85) liquid
Ni neither	Cr (0.89) liquid
Co (1.07) solid	Ni varies w/solute
W (1.23) solid	Co (≈ 1) solid
	W (≈ 1.4) solid

*Neither--did not segregate to solid or liquid

Conclusions

1. Elemental contour maps derived from electron microprobe data indicated that for the six alloys, Hf, Ta, Ti, and Al segregated to the liquid during solidification, W and Co segregated to the solid, and Mo, Cr,

and Ni did not exhibit consistent segregation patterns.

2. The values for the distribution coefficients determined from the dendrite core and alloy compositions (initial distribution coefficients) were quite similar to the values determined from constructed solid composition profiles using the Scheil equation (average distribution coefficients), which indicated that the latter method was a valid means for assessing microsegregation.
3. The distribution coefficients for a given element did not vary significantly among the six alloys, which suggested that low level additions of C, Hf, and Ta did not affect the segregation of the other elements. The mean values of the average distribution coefficients for the six alloys are 0.12 for Hf, 0.77 for Ta, 0.73 for Ti, 0.94 for Al, 1.23 for W, and 1.07 for Co.
4. The elemental segregation behavior in the MAR-M247-derivative alloys was very similar to that found in dilute binary Ni-based systems, which suggested that few interactions took place between these elements in the liquid.

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