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HOMOGENIZATION OF ARC-MELTED URANIUM-6 WEIGHT PERCENT NIOBIUM ALLOY INGOTS

W. B. Snyder, Jr

January 1978

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Prepared for the Department of Energy
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ABSTRACT

Microsegregation and macrosegregation in uranium-6 niobium arc-melted ingots were characterized by electron microprobe analysis. Homogenization studies determined that microsegregation can be eliminated by heat treating the alloy for six hours at 1100° C. Extensive homogenization did not eliminate macrosegregation (banding) from the as-cast alloy, but a mathematical model describing banding and coring indicated that banding could possibly be eliminated by working prior to homogenization.

CONTENTS

SUMMARY

During arc melting of uranium-6 weight percent niobium alloy ingots, both microsegregation (interdendritic coring) and macrosegregation (banding) occur during solidification of the ingot. The present study was undertaken to determine the extent of homogenization treatment necessary to minimize these chemical inhomogeneities. Using electron microprobe analyses of cast and homogenized material, it was determined that either six hours at 1100° C or ten hours at 1050° C was sufficient to essentially eliminate microsegregation. Extensive homogenization of the cast ingot had very little effect on the macrobanding segregation. However, a model developed to describe the effect of homogenization on the cast material predicted that extensive forging prior to homogenization could minimize banding segregation.

INTRODUCTION

During vacuum arc melting and solidification of uranium alloys, segregation occurs in essentially three patterns: gross ingot segregation, macrosegregation (banding), and microsegregation (dendritic coring). A portion of the present investigation was undertaken to measure the degree of macrosegregation and microsegregation found in 200-mm-diameter uranium-6.0 weight percent niobium alloy (U-6 Nb) ingots that were arc melted in the Oak Ridge Y-12 Plant.[a] Additionally, experiments were performed to determine the effects of homogenization treatments on both types of segregation of the as-cast ingots. Results of the homogenization experiment were compared to theoretically predicted niobium variations.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

HOMOGENIZING ARC-MELTED URANIUM-NIOBIUM INGOTS

EXPERIMENTAL PROCEDURE

A 3.2-mm-thick longitudinal slice was machined from a 200-mm-diameter arc-melted ingot. Two strips, 12 mm wide, were machined; one longitudinally from the ingot center and the other 25 mm from the outside edge, as illustrated in Figure 1. Each strip was cut into 12-mm squares, then the squares were degreased and sealed in evacuated quartz ampoules. Homogenization was performed in an air-atmosphere furnace with a control thermocouple adjacent to the specimens. After the specified homogenization treatment, the ampoules were dropped into a container of room-temperature water and broken. All samples were metallographically mounted in epoxy for microprobe examination. Microprobe analysis involved counting the niobium L_α radiation for 30 seconds at fixed intervals of distance. When examining microsegregation, counting was performed at 10-μm intervals over a space of 1500 μm, while macrosegregation was characterized by counting at 51-μm intervals over a length of 10.16 mm. No standard was available for an exact quantitative determination of the niobium content; therefore, all analyses are on a relative basis.

Grain size of the homogenized specimens was estimated by comparison with the ASTM untwinned grain-size charts. X-ray line broadening was measured by step scanning each of the homogenized specimens using CrK_α radiation from 45 - 86 degrees of 2θ in increments of 0.05 degree and for a count time of 40 seconds. Peak width at half maximum intensity was measured and averaged for the first seven peaks of the monoclinic alpha double prime structure.[1]

RESULTS

Microsegregation

Figure 2 shows the as-cast microstructure of the U-6 Nb alloy while Figure 3 gives the electron microprobe scans of similar areas from the center and edge of the ingot. The dark areas in the micrographs are believed to be niobium-rich areas which have undergone the monotectoid decomposition reaction during the slow cooling of the ingot. These regions would have been the first to solidify from the melt and are the primary dendrites. The interdendritic spacing of the center specimen is somewhat greater than that of the edge. The sinusoidal swings in niobium of Figure 3 are a

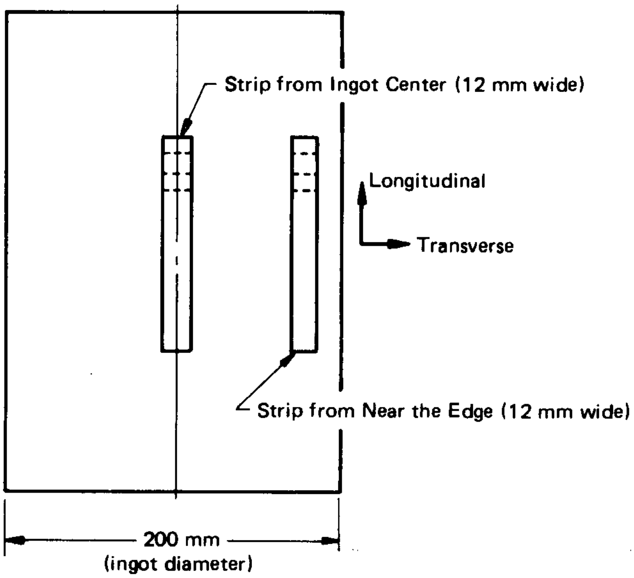
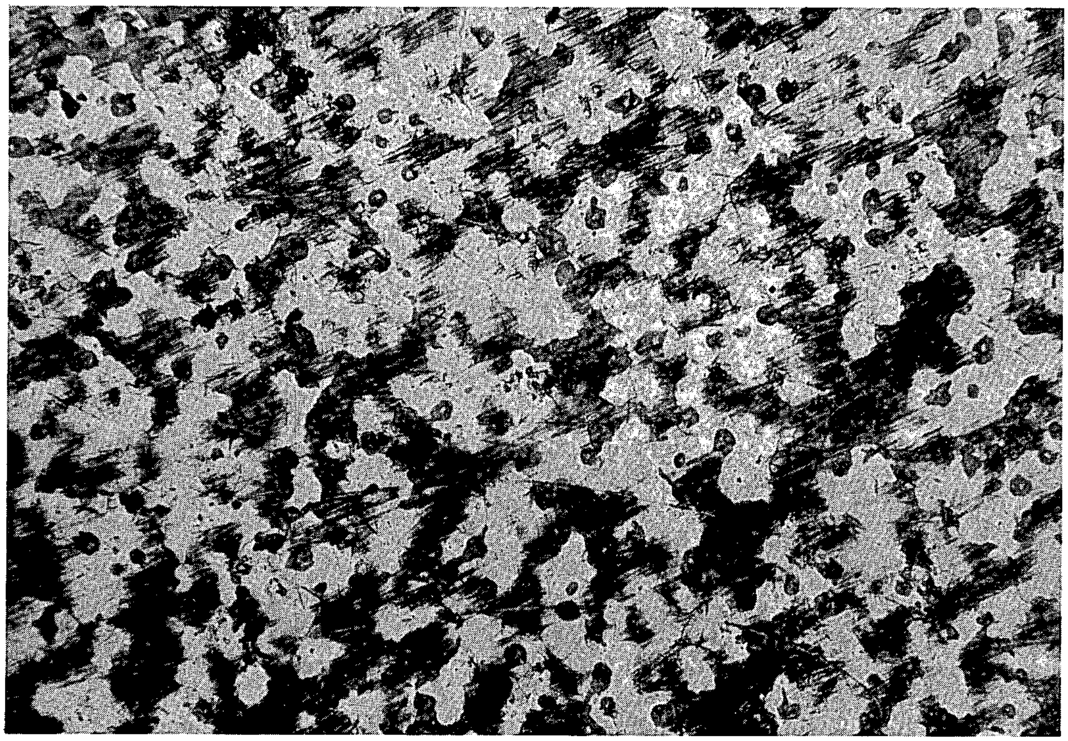
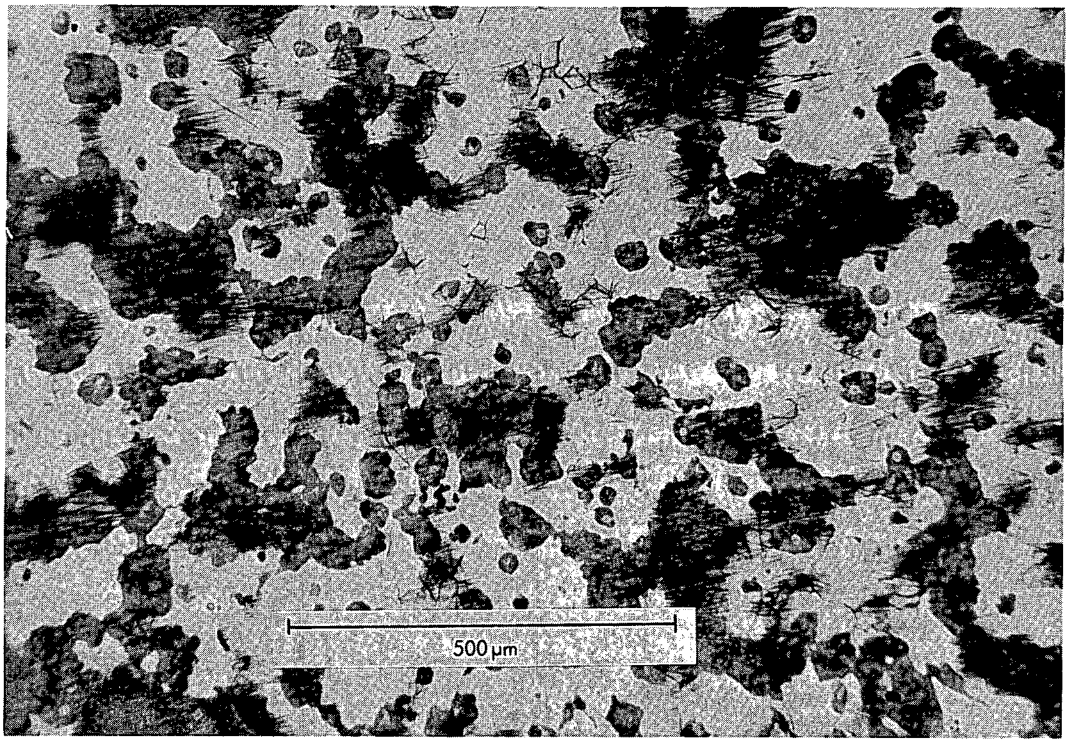


Figure 1. SAMPLE LAYOUT FOR THE HOMOGENIZATION STUDY.

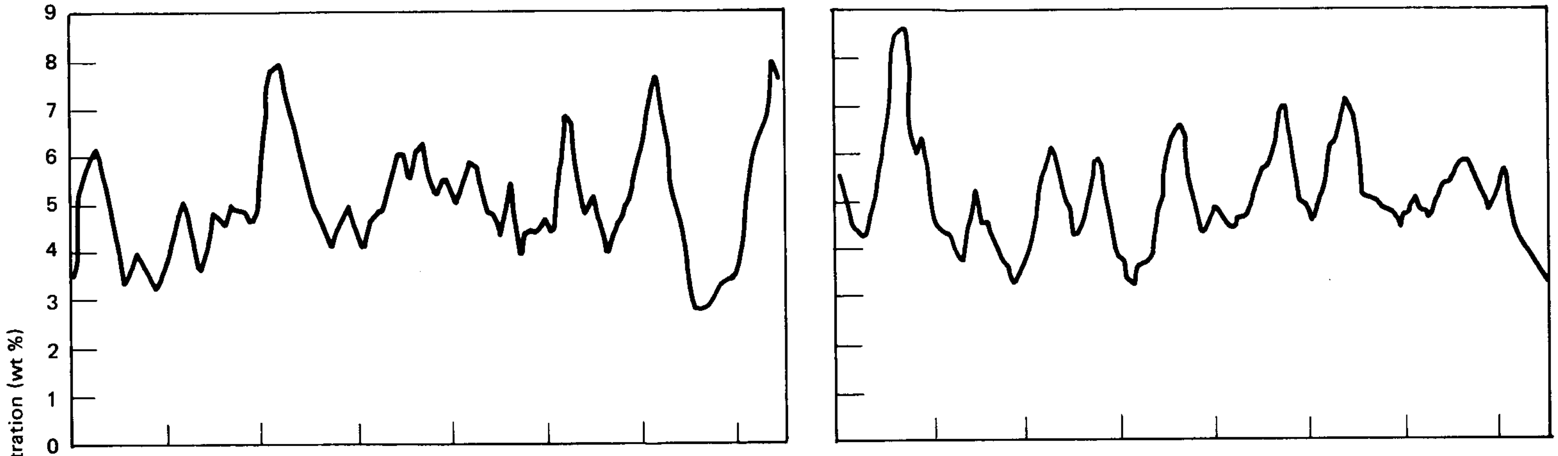


(a) Specimen from Near the Edge of the Ingot. M286-1



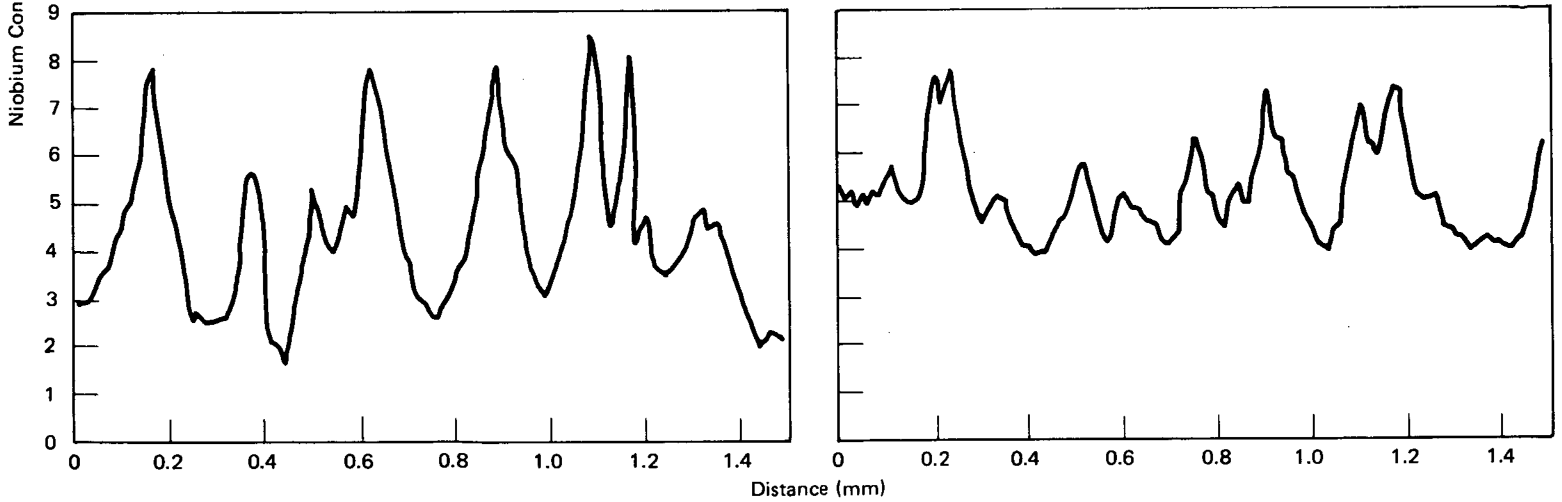
(b) Specimen from the Center of the Ingot. M286-2

Figure 2. OPTICAL MICROSTRUCTURE OF AS-CAST URANIUM-6 NIOBIUM ALLOY USED FOR THE HOMOGENIZATION EXPERIMENT. (Bright Field Illumination; 100X)



(a) Center; Transverse Scan.

(b) Edge; Transverse Scan.



(c) Center; Longitudinal Scan.

(d) Edge; Longitudinal Scan.

Figure 3. ELECTRON MICROPROBE SCANS OF AS-CAST MATERIAL FROM THE CENTER AND EDGE OF THE INGOT. (Refer to Figure 1)

result of the dendritic segregation shown in Figure 2. Both transverse and longitudinal scans of the edge sample (Figure 3, Views b and d) are similar, showing a maximum variation of approximately 5.0 weight percent niobium and an interdendritic spacing of 150 - 200 μm. View c shows that coring is more severe in the center of the ingot with a maximum variation of 8.6 weight percent niobium and a larger dendritic spacing of 200 - 300 μm.

Duplicate specimens of those used for Figure 3 were homogenized for 2, 6, and 12 hours at 1000, 1100, and 1200° C. Both edge and center specimens in either the transverse or longitudinal direction responded to homogenization in a similar manner. Therefore, only the edge-transverse scans are shown (Figure 4). Spikes of composition, such as shown for the two-hour, 1200° C specimen, were due to niobium carbide inclusions and do not represent the niobium dissolved in the uranium. Because existing production furances were only capable of a maximum temperature of 1050° C, a second series of specimens were run at 1050° C for 8, 10, and 12 hours. Electron microprobe results on the specimens are reported in Figure 5. Table 1 lists the X-ray-peak-width results on both series of specimens, while Table 2 gives the grain size of the first series of specimens. X-ray data for the 6 and 12-hour specimens at 1100° C were omitted because of the difficulty in separating the γ_0 and α'' diffraction peaks. The unusually large value for the 12-hour, 1200° C specimen was believed to be due to nitrogen contamination of the specimen during homogenization.

Interpretation of the electron microprobe results in quantitative terms is quite difficult, and a reliance on judgment must be made when the niobium concentration has smoothed to the instrument background. Examination of Figure 3 shows that six hours at 1100° C is the shortest time and lowest temperature at which the niobium response apparently reaches instrument background. A similar analysis of Figure 5 indicates that ten hours at 1050° C is approximately equivalent to six hours at 1100° C. The X-ray data of Table 1 show a decrease in peak width with time at 1000° C; at 1050° C, the peak width appears to decrease and then increase. However, within the scatter of the measurements, these values are probably not significantly different. At 1100° C, there is a further decrease in peak width, but increasing the temperature to 1200° C causes an apparent increase in peak width. These data do not correlate well with either the microprobe data or the X-ray data of Jackson.[1] Considering the variability of grain size, quenching stresses, and the uncertainty in separating the γ_0 and α'' peaks, the X-ray technique is of limited value in determining an optimum homogenization treatment.

Macrosegregation

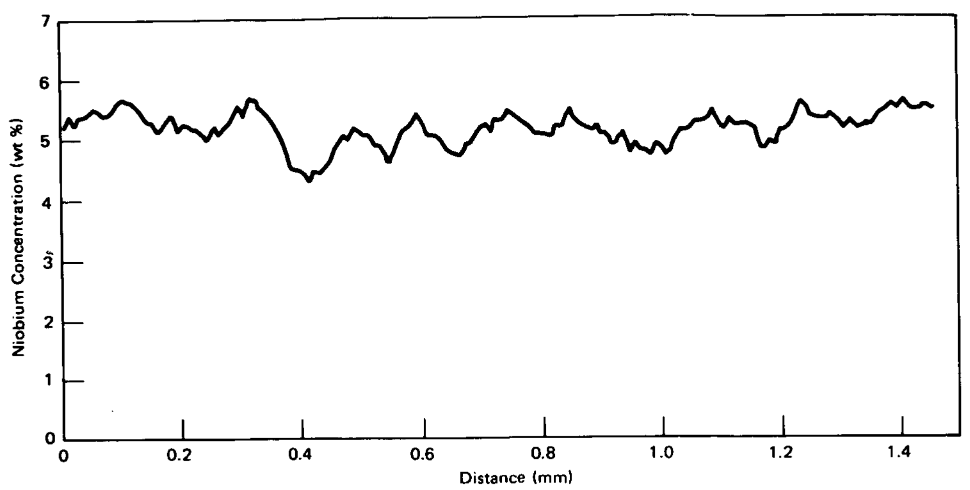
Macrosegregation, or banding, is a form of segregation which is best illustrated by the positive reproduction of a radiograph of an ingot section (Figure 6). A round penetrameter in the lower right portion of the radiograph indicates a higher-density area. Thus, the light areas of the radiograph represent niobium-depleted regions. Near the edge of the ingot, these regions occur as regularly spaced bands of 3 - 5-mm separation, while at the center they become poorly defined. The mechanism for formation of these bands is not well understood. Some investigators believe banding is due to a variation in solidification rate during arc melting,[2] while others feel it is due to a form of constitutional supercooling.[1]

Homogenization Time - 2 Hours

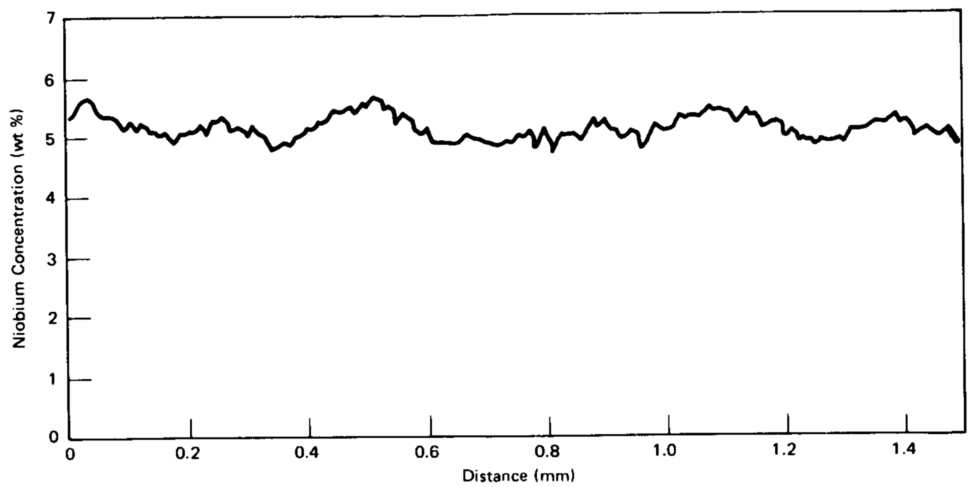
Homogenization Time - 6 Hours

Homogenization Time - 12 Hours

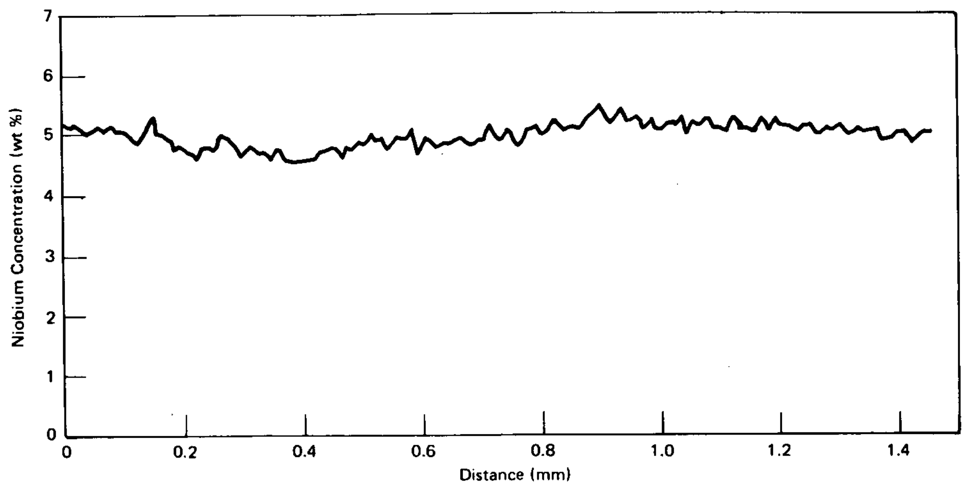
Homogenization Temperature - 1000° C



(a) Sample E1.

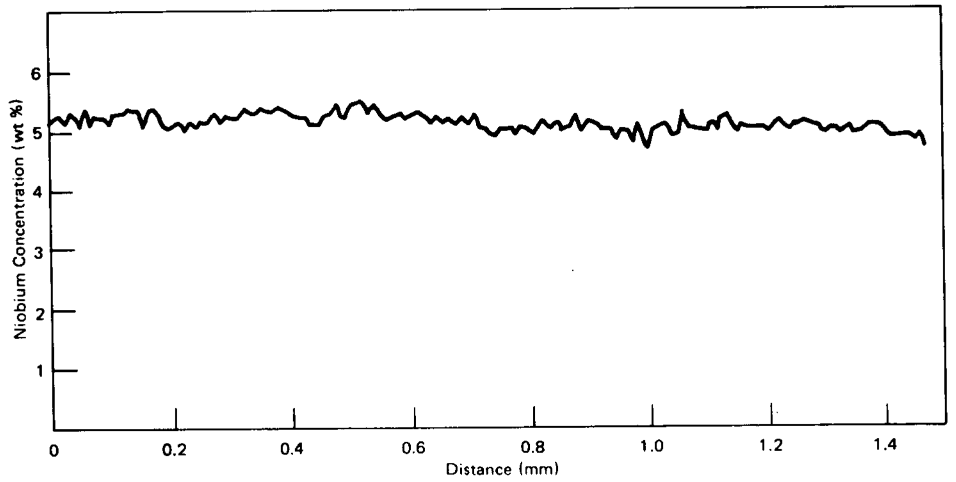


(b) Sample E3.

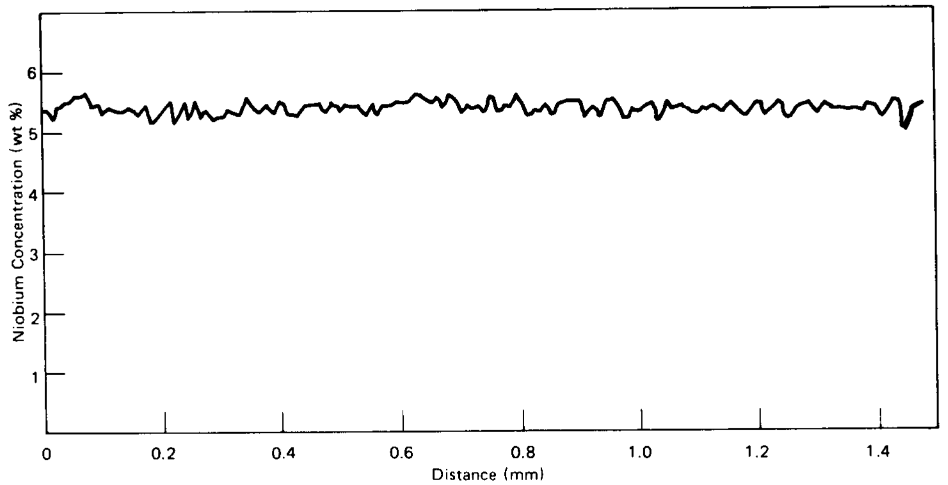


(c) Sample E6.

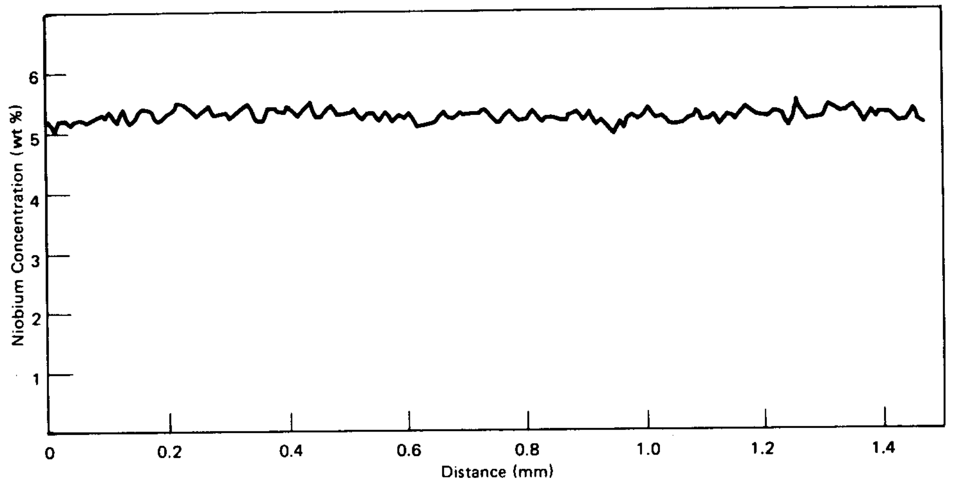
Homogenization Temperature - 1100° C



(d) Sample E2.

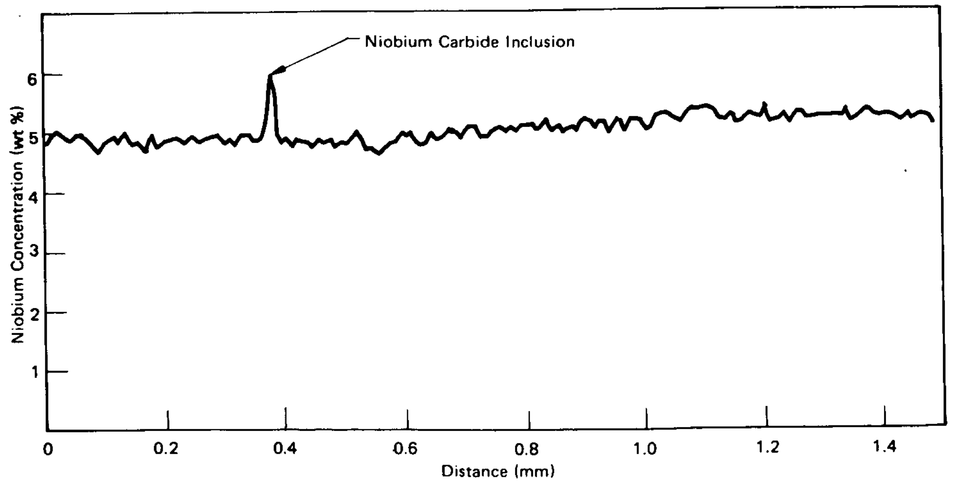


(e) Sample E4.

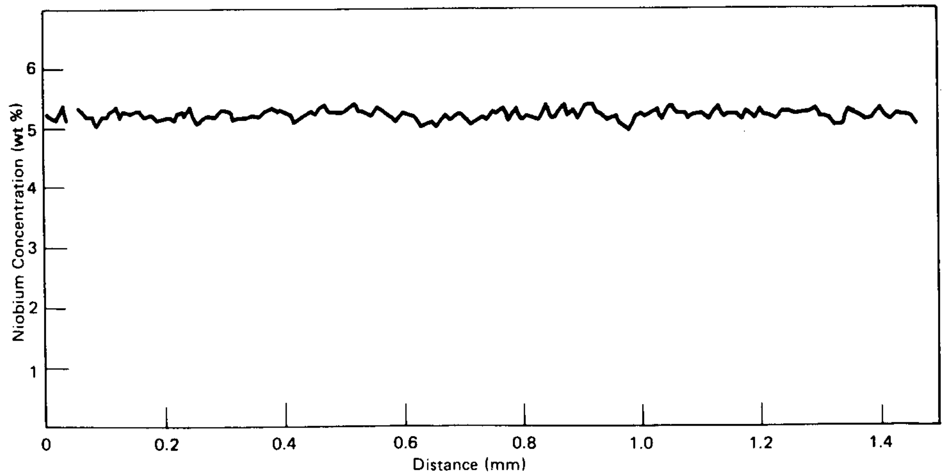


(f) Sample E14.

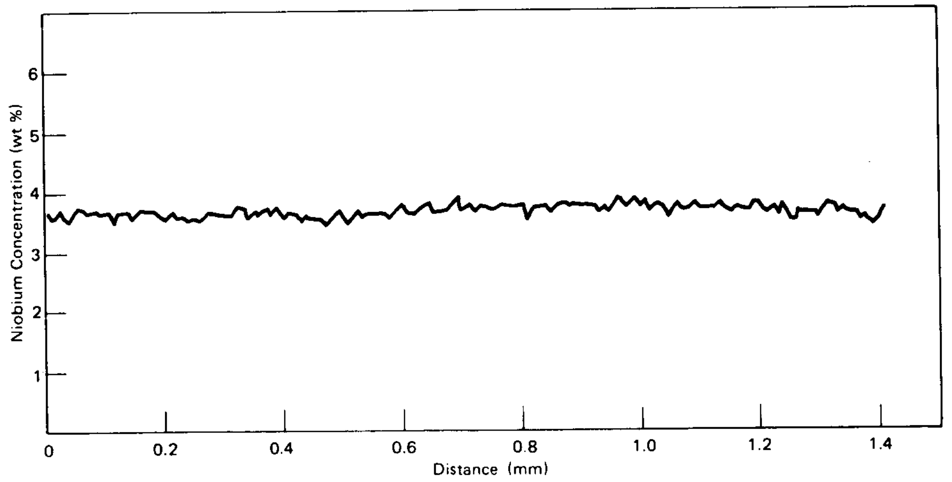
Homogenization Temperature - 1200° C



(g) Sample E8.

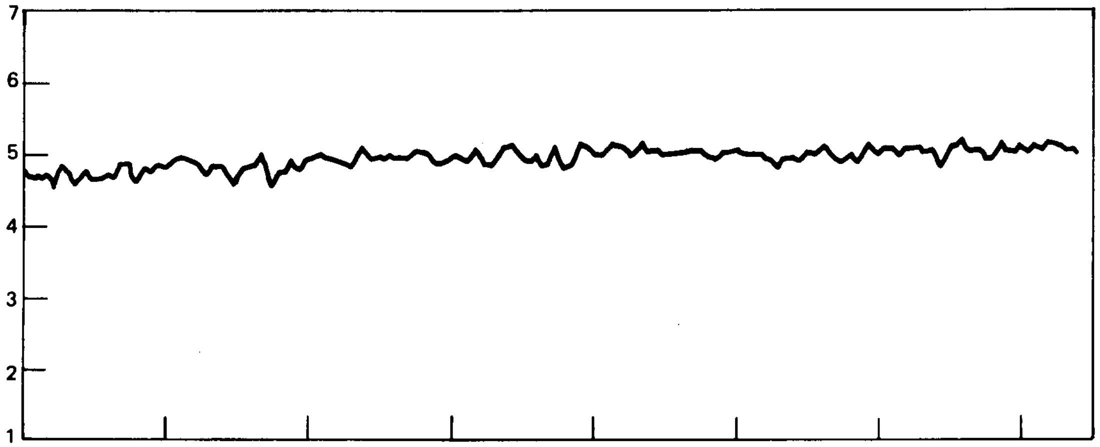


(h) Sample E12.

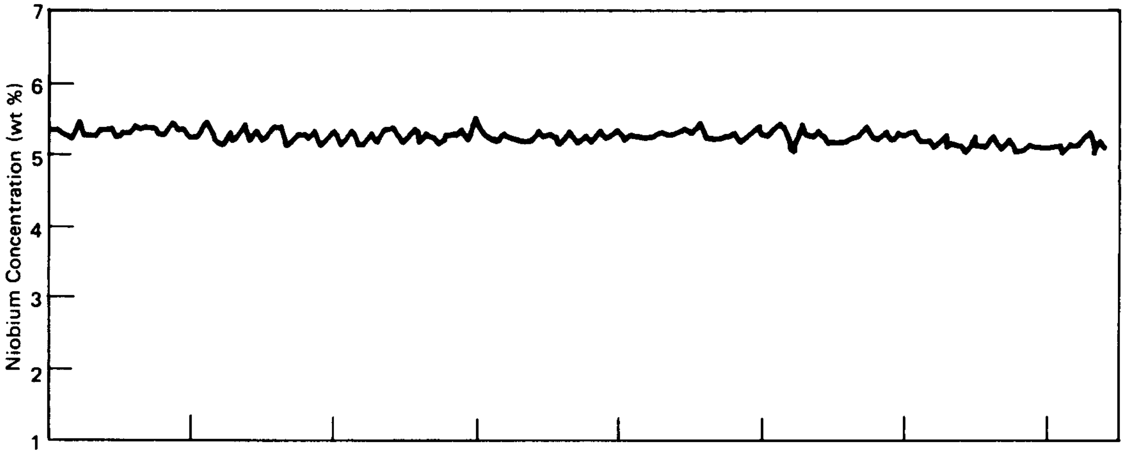


(i) Sample E15.

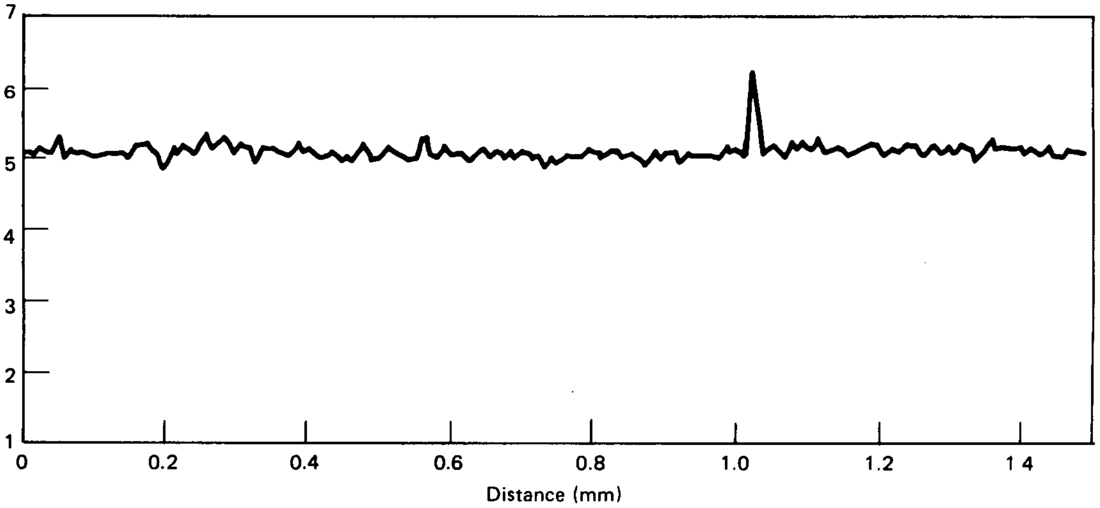
Figure 4. ELECTRON MICROPROBE SCANS OF THE EDGE, TRANSVERSE SPECIMENS THAT WERE HOMOGENIZED AT THE INDICATED TIME AND TEMPERATURE. (Compare with Figure 3, Graph b)



(a) For 8 Hours.



(b) For 10 Hours.



(c) For 12 Hours.

Figure 5. ELECTRON MICROPROBE SCANS OF EDGE, TRANSVERSE SPECIMENS THAT WERE HOMOGENIZED AT 1050° C FOR VARIOUS LENGTHS OF TIME.

Table 1

AVERAGE PEAK WIDTH AT HALF MAXIMUM INTENSITY OF THE ALPHA DOUBLE PRIME STRUCTURE

Homogenization Temperature (° C)	Homogenization Time (hr) 2	6	8	10	12
1000	85.7(1)	81.1	-	-	72.6
1050	-	-	82.0	79.4	80.7
1100	66.4	-	-	-	-
1200	68	55.4	-	-	71.4

(1) Values are in mm; 1 mm = 0.1 degree of 2θ.

Table 2

GRAIN SIZES OF HOMOGENIZED CAST URANIUM-6 NIOBIUM SPECIMENS

Homogenization Temperature (° C)	Location	Homogenization Time (hr) 2	6	12
1000	Edge	1 - 3(1)	1 - 3	2 - 3
	Center	3	2	3 - 4
1100	Edge	2	1 - 2	1
	Center	2 - 3	4 - 5	1
1200	Edge	1 - > 1	1	1
	Center	1 - > 1	1 - > 1	1 - > 1

(1) As-cast ASTM grain size, 3 - 4.

Undoubtedly, both effects combine to control macrosegregation during melting. In order to cover an interval that is wide enough to encompass the macrobands, microprobe data were taken at 0.05-mm intervals that extended over a length of 10.16 mm. Figure 7 is an electron microprobe scan of an as-cast specimen. Close examination of the scan reveals a long-wavelength component (dotted line) with coring superimposed. To determine the effects of homogenization upon banding, specimens were heat treated for 12 hours at 1050, 1100, and 1200° C. Electron microprobe results from these specimens are given in Figure 8. Initial analysis of the results led to the conclusion that banding was considerably reduced by high-temperature, long-time heat treatment. However, these results did not agree with the theoretical calculations, as will be discussed later.

To test the initial conclusion, the specimen of Figure 8, View a, was marked and a reference scan made. The specimen was then given a 12-hour homogenization at 1200° C, remounted, and a second microprobe scan made in exactly the same location as the first. Both the initial scan and the scan made after heat treatment are presented in Figure 9. Note that though some smoothing occurred, the long-wavelength banding segregation still persisted. Thus, the initial conclusion was due to a fortuitous selection of specimens which exhibited different degrees of macrobanding and not to the heat treatment used.

Discussion of Results

As a check on the experimental results and as a tool for further exploring the possibility of eliminating banding, a model was developed that exemplified both types of segregation. Microsegregation was approximated in one dimension by the equation:

$$C(x) = C_o + C_m \cos \frac{\pi x}{\ell} \,, \tag{1}$$

where the average concentration, C_o, was set equal to 6.0%; the amplitude, C_m, was set at 2.5 wt %, and the half wavelength, ℓ, was set equal to 75 μm—half of the interdendritic spacing. Macrosegregation was described by a similar equation with $C_o = 6.0$, $C_m = 1.0$, and

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Figure 6. POSITIVE PRINT OF THE RADIOGRAPH OF A THREE-MILLIMETER-THICK SLICE OF THE 210-MILLIMETER-DIAMETER INGOT USED FOR THE HOMOGENIZATION STUDY.

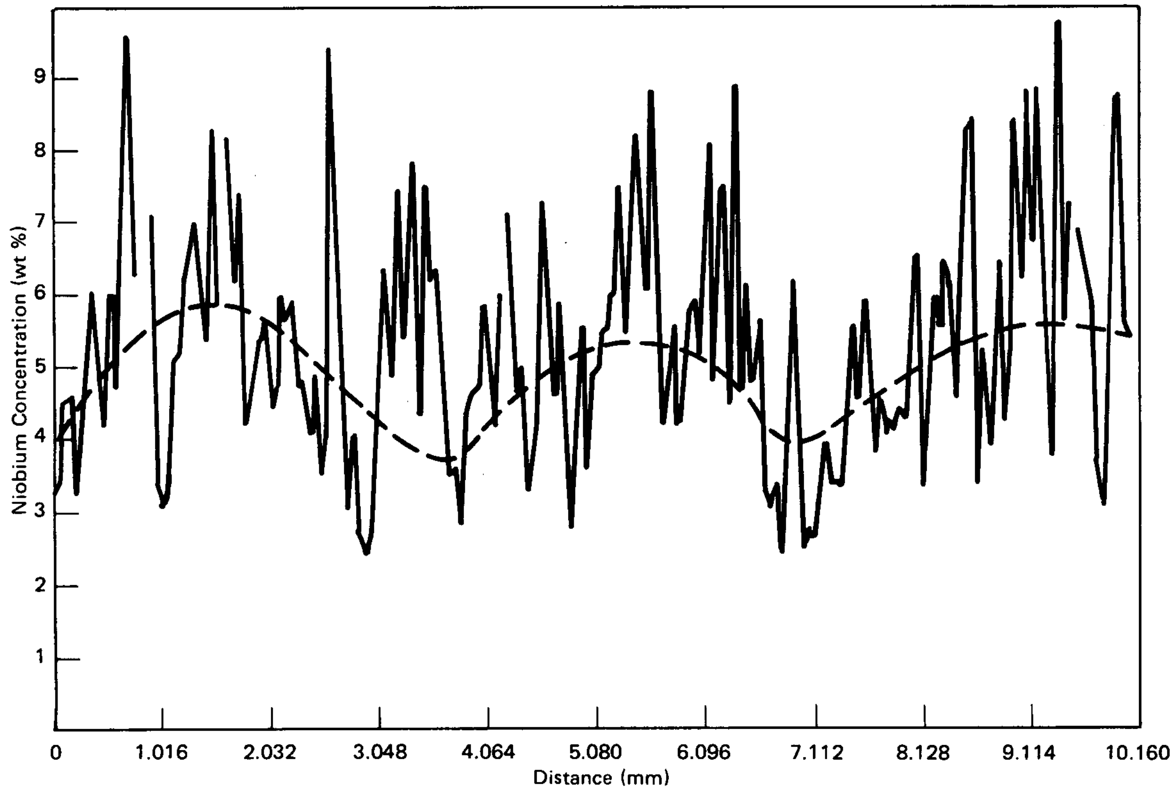


Figure 7. ELECTRON MICROPROBE SCAN FOR NOIBIUM ON AN AS-CAST SPECIMEN OF URANIUM-6 NIOBIUM. (Dotted Line Indicates an Approximate Long Wavelength Variation to the Data)

$\ell = 2500\ \mu\text{m}$ for half the banding spacing. A combination of these two equations yielded an equation describing the overall niobium segregation:

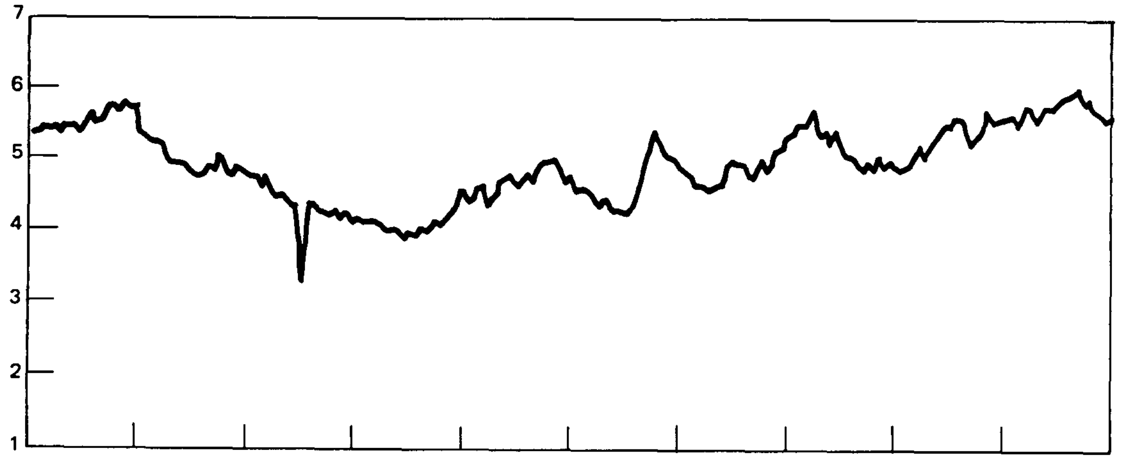
$$C(x) = 6.0 + 2.5 \cos \frac{\pi x}{75} + \cos \frac{\pi x}{2500} , \qquad (2)$$

where the term C(x) represents the niobium concentration at an x distance, given in micrometers. A graph of this function on two scales is given in Figure 10. The 10,000-μm scale corresponds to the scale of Figures 7 - 9, while the 1500-μm scale corresponds to Figures 3 - 5. Although the model is not an exact duplication of the actual conditions, it is sufficiently close for calculational purposes.

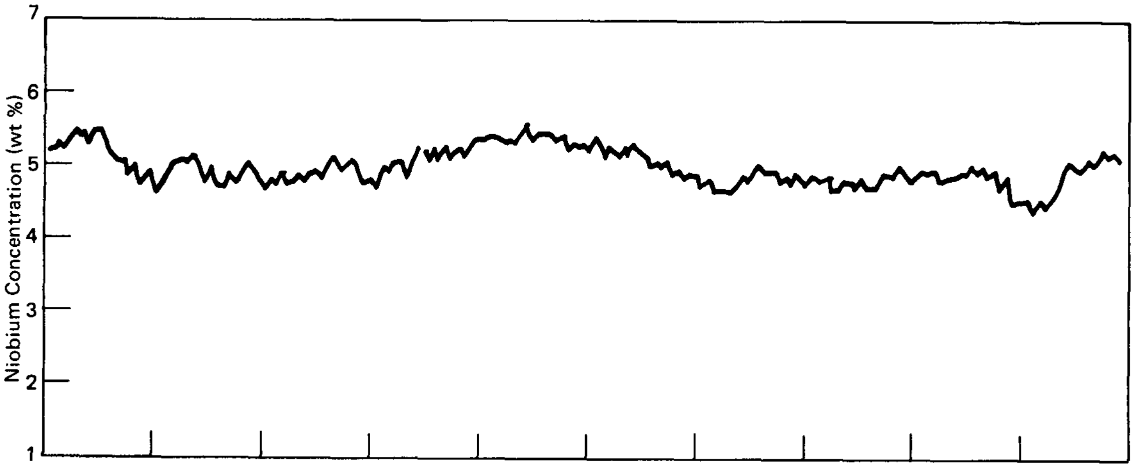
In order to determine the effects of homogenization upon the initial concentration profile, it is necessary to have a solution to Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x}\right) ,^{3,4} \qquad (3)$$

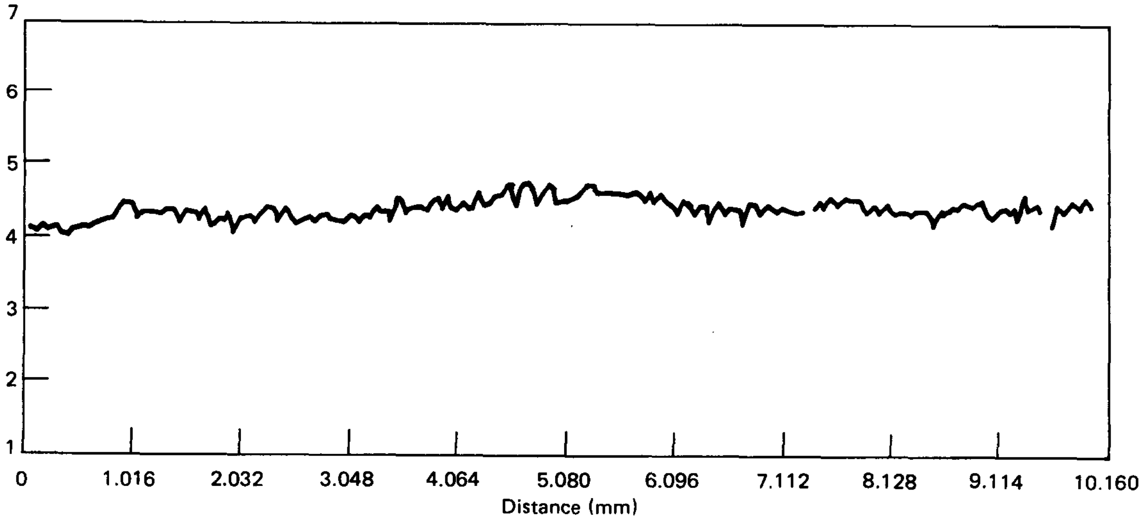
where C represents the concentration of niobium; t, the time; D, the diffusion coefficient, and, x, the distance parameter.



(a) At 1050° C.

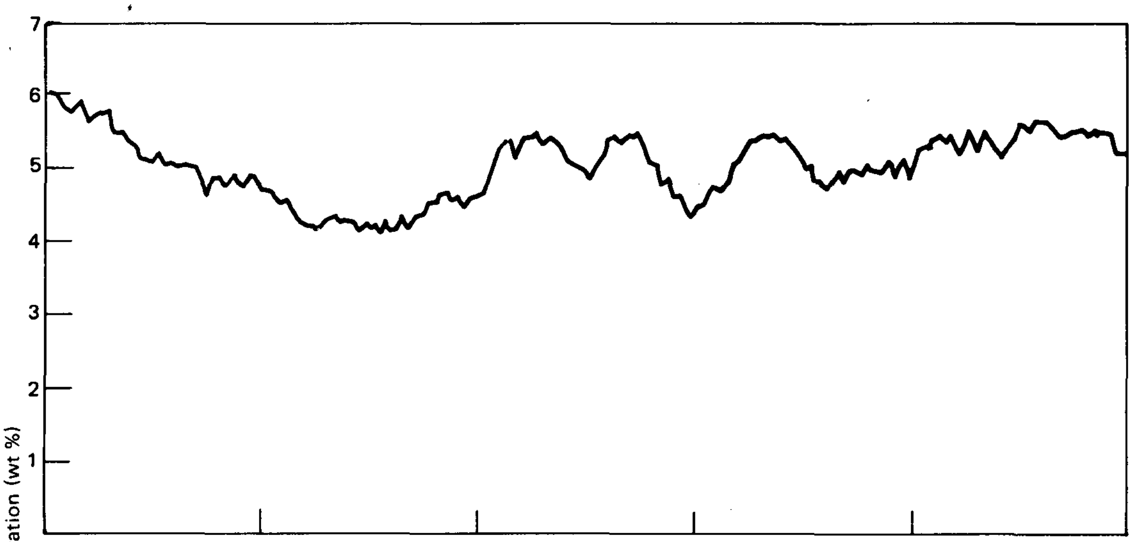


(b) At 1100° C.

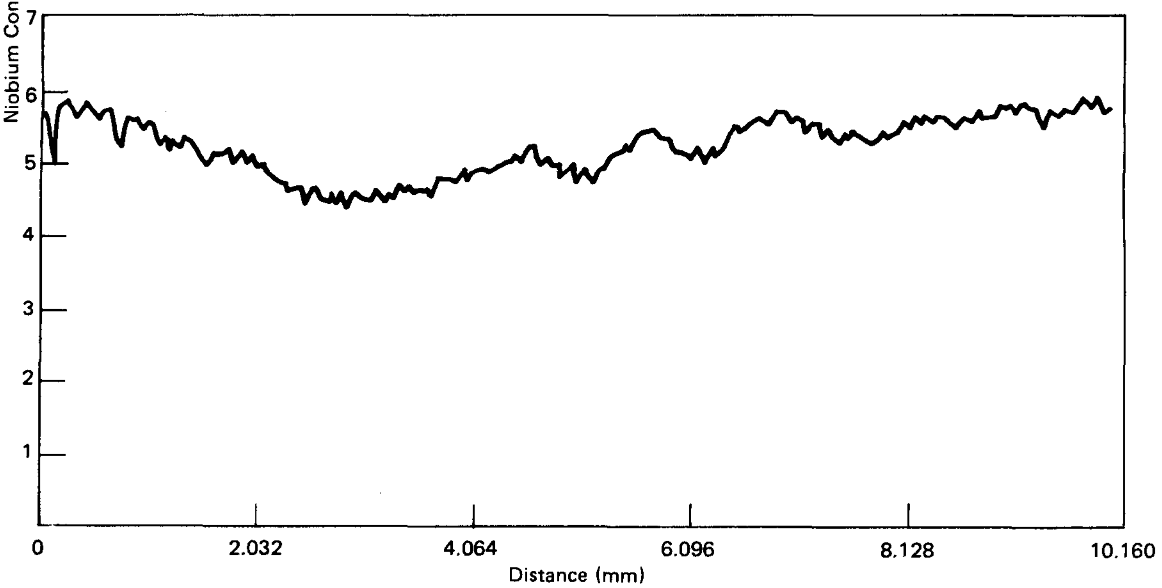


(c) At 1200° C.

Figure 8. ELECTRON MICROPROBE NIOBIUM RESPONSE TO SPECIMENS THAT WERE HEAT TREATED FOR 12 HOURS AT THREE DIFFERENT TEMPERATURES.



(a) Scan after 12 Hours at 1050° C.



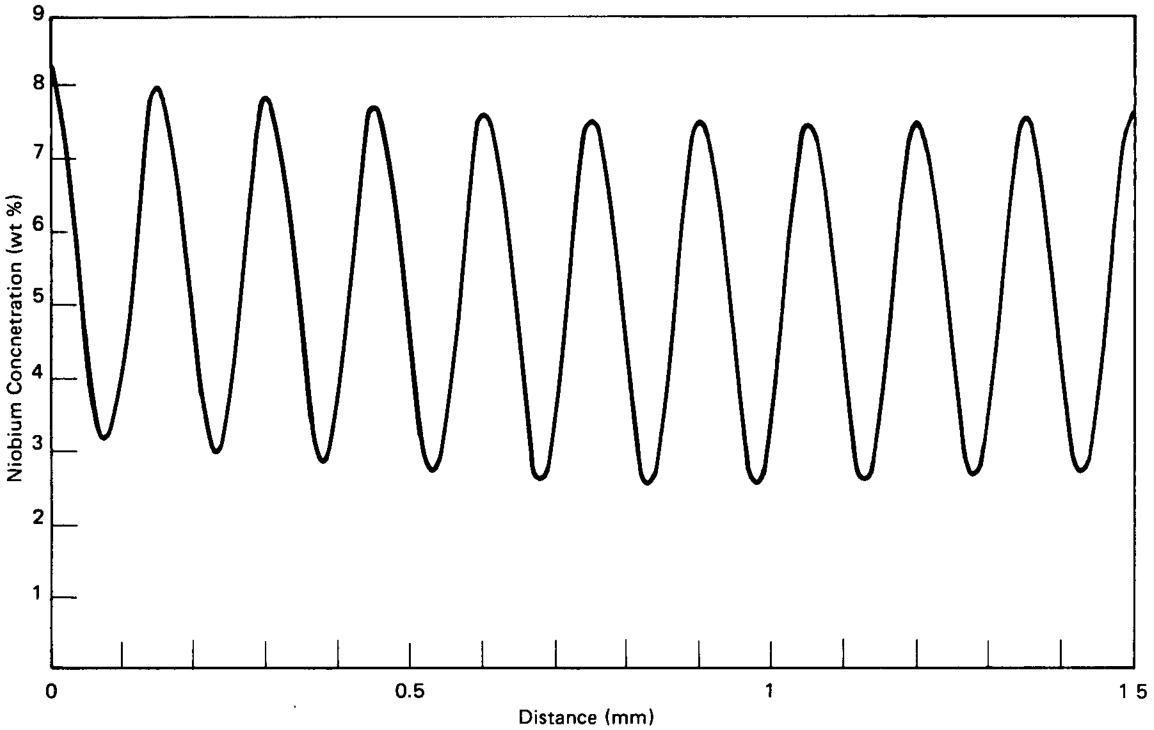
(b) Second Scan after an Additional 12 Hours at 1200° C.

Figure 9. MICROPROBE SCAN AFTER AN INITIAL HOMOGENIZATION TREATMENT, AND A SECOND SCAN AFTER AN ADDITIONAL HOMOGENIZATION TREATMENT.

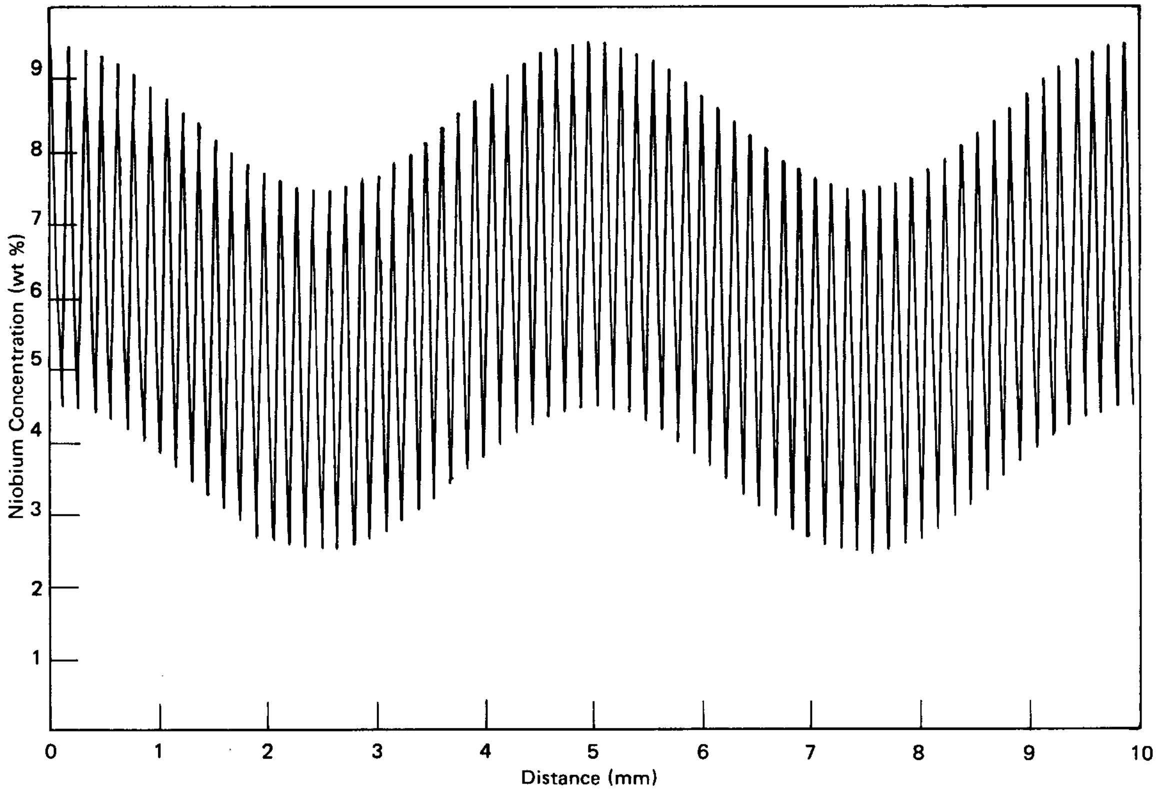
A suitable solution for the boundary conditions of the present problem is:

$$C(x,t) = 6.0 + 2.5 \cos\left(\frac{\pi x}{75}\right) \exp\left(\frac{-\pi^2 Dt}{(75)^2 10^{-8}}\right) + \cos\left(\frac{\pi x}{2500}\right) \exp\left(\frac{-\pi^2 Dt}{(2500)^2 10^{-8}}\right), \quad (4)$$

where x represents the distance, given in micrometers and t, the time in seconds. The other parameters have their previously described meanings.



(a) Niobium Concnetration over 1.5 mm.



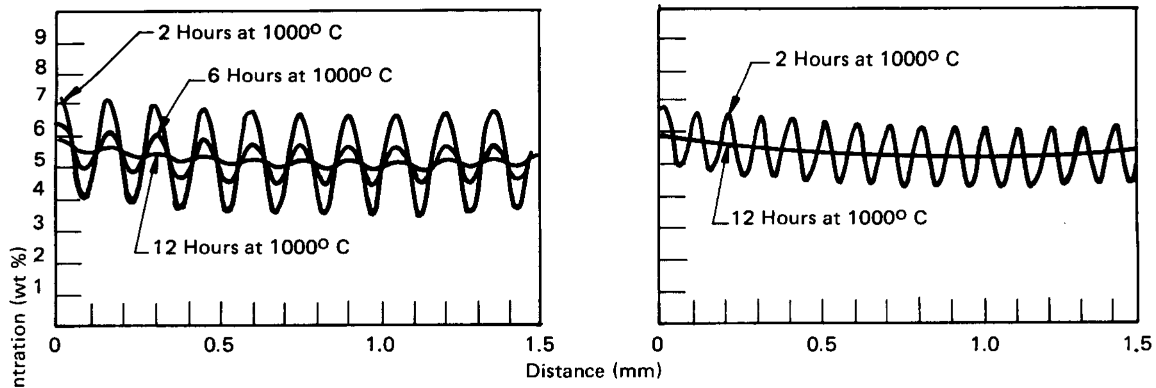
(b) Niobium Concentration over 10 mm.

Figure 10. INITIAL THEORETICAL CONCENTRATION PROFILES THAT ILLUSTRATE BANDING AND CORING EFFECTS. (Banding Wavelength, 5000 μm; Coring Wavelength, 150 μm)

Using a value of:

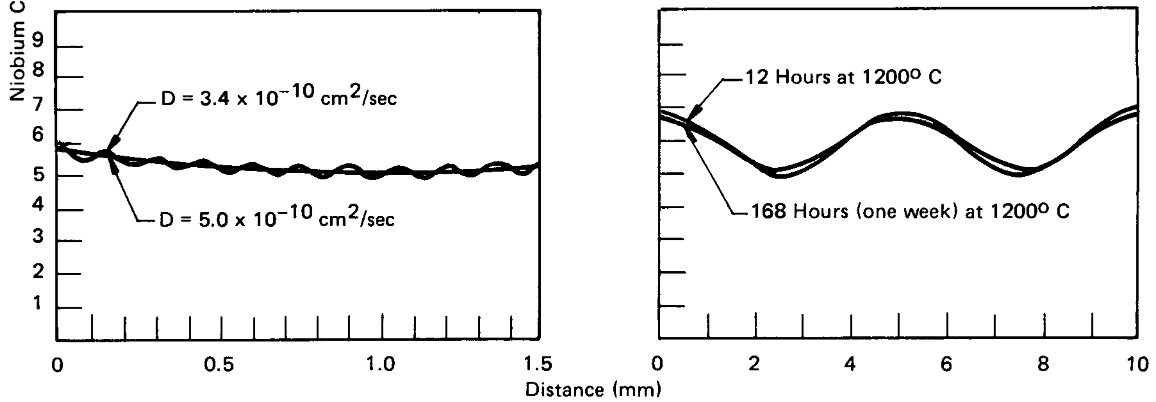
$$D = 1.4 \times 10^{-4} \exp(-36{,}200/RT)\ \mathrm{cm^2/sec}, \qquad (5)$$

for the interdiffusion coefficient of niobium in uranium,[5] concentration profiles can be calculated for given conditions of temperature and time. At 1000° C, for times of 2, 6, and 12 hours, the niobium concentration varies, as revealed in Figure 11, Graph a, which compares directly with Figure 4. The calculated concentration profiles are in reasonable agreement with the observed profiles. However, the measured profiles converge to a smooth line more rapidly than the theoretical curves. One reason for this difference may be the assumption that the diffusion coefficient is independent of concentration, while another reason may be that both the wavelength and amplitude of the measured coring are, at some points, less than those of the mathematical model. As the wavelength and amplitude decrease, the time necessary for homogenization also decreases. Complete homogenization is also achieved in less time if the diffusion coefficient is increased in magnitude.



(a) Interdendritic Spacing of 0.15 mm.

(b) Interdendritic Spacing of 0.1 mm.



(c) Effect of 50% Increase in the Diffusion Coefficient in 12 Hours at 1000° C.

(d) Effect of 12 and 168 Hours at 1200° C on Banding.

Figure 11. EFFECTS OF HOMOGENIZATION ON CORING AND BANDING.

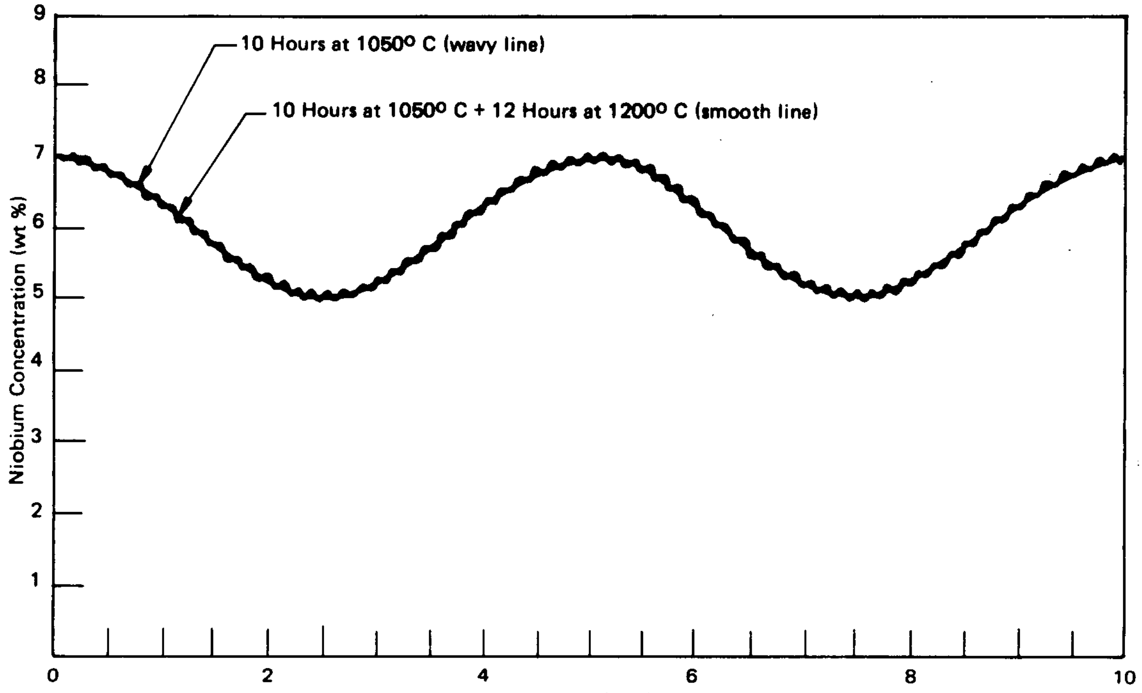
To illustrate the sensitivity of the model to interdendritic spacing and diffusion coefficient, the curves of Graph a (Figure 11) were recalculated in Graphs b and c, using different constants. Using a smaller interdendritic spacing of 100 μm allows for complete homogenization in 12 hours at 1000° C. Increasing the diffusion coefficient by 50% at 1000° C also smooths the curve in 12 hours (Graph c). Changes in both the diffusion coefficient and interdendritic spacing allow the calculated profiles to more closely approach the experimental results. It is quite probable that both effects are realized in practice.

Note that the long-range curvature in the graphs of Parts a - c, which exists in the smoother graphs, is due to banding. Part d further illustrates the effects of a 12-hour, 1200° C homogenization on banding. Coring is completely eliminated, but there is virtually no effect on the much longer-range segregation. Increasing the time at temperature to one week (Graph c) still doesn't affect the banding substantially. For a comparison with the experimental results of Figure 9, a profile (Figure 12) was calculated for 12 hours at 1050° C and a second profile calculated for 12 hours at 1050° C plus 12 hours at 1200° C. Note that the two curves are very close to one another and agree with the experimental results quite well, though the banding intervals are not the same.

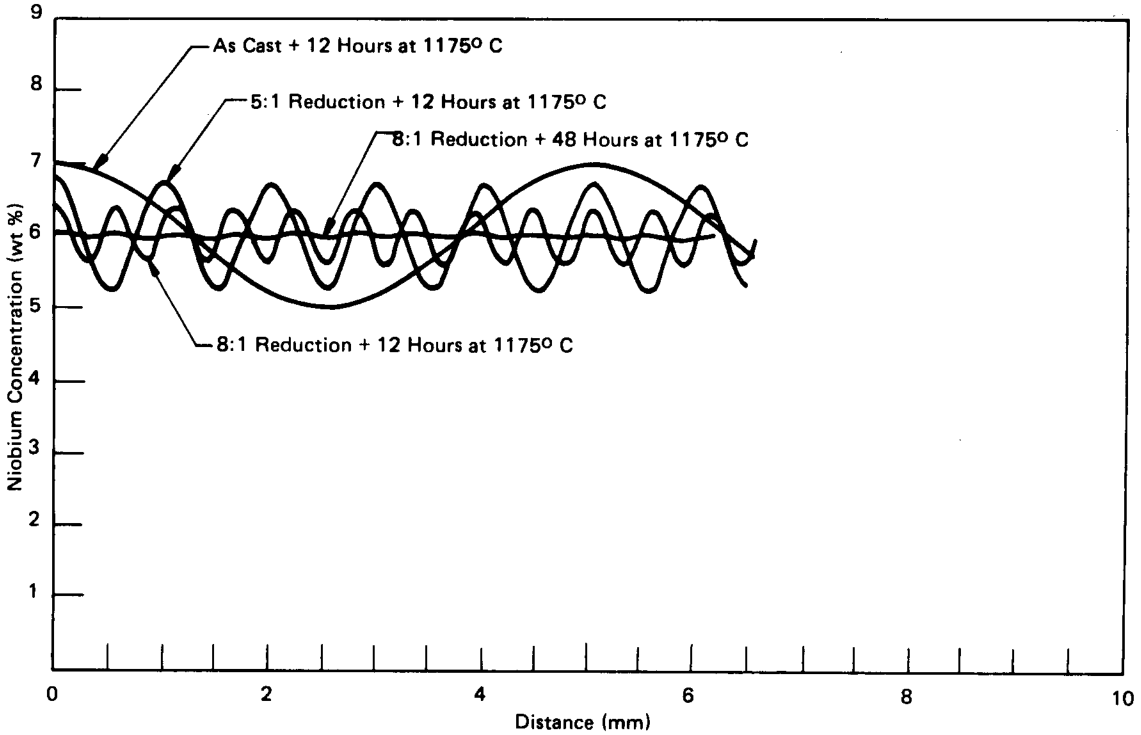
CONCLUSIONS

Based upon the results of this experiment, it is apparent that coring segregation can be eliminated by sufficient homogenization of the cast ingot for either six hours at 1100° C or ten hours at 1050° C. However, banding cannot be affected by any reasonable homogenization of the as-cast ingot. Aside from perhaps control of the melting parameters, working of the ingot appears to be the only probable means of eliminating banding. Working decreases the distance between bands in proportion to the reduction from the as-cast ingot.

Graph b of Figure 12 depicts the calculated effects on banding segregation due to forging and rolling an ingot to the given reduction ratios followed by homogenizing for 12 and 48 hours at 1175° C. Such a sequence of operations would appear to produce a reasonably chemically uniform product with a large grain size which could be subsequently worked to a finer grain size.



(a) Homogenization of 12 Hours at 1050° C plus 12 Hours at 1200° C.



(b) Effects of Homogenization at 12 Hours at 1175° C on As-Cast, 5:1 Reduction, and 8:1 Reduction Material.

Figure 12. THEORETICAL CONCENTRATION PROFILES THAT ILLUSTRATE EFFECTS OF MULTIPLE HOMOGENIZATION AND WORKING ON BANDING SEGREGATION.

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