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RFP-1582

October 13, 1970

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HOMOGENIZATION OF URANIUM-BASE
NIOBIUM ALLOYS

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U.S. ATOMIC ENERGY COMMISSION
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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information

National Bureau of Standards, U. S. Department of Commerce

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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October 13, 1970

RFP-1582
UC-25 METALS, CERAMICS,
AND MATERIALS
TID-4500 — 56th Ed.

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Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

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HOMOGENIZATION OF URANIUM-BASE NIOBIUM ALLOYS

Ross J. Jackson and Clifford V. Kangas

Abstract. Three types of niobium segregation are considered in uranium-base niobium alloys: dendritic coring, macrobanding, and gross-ingot segregation. The origin and nature of these inhomogeneities are discussed, as are procedures for their identification and elimination.

TYPES OF NIOBIUM SEGREGATION

This study has revealed three types of niobium segregation in cast uranium-base niobium alloys: dendritic coring, macrobanding, and gross-ingot segregation.

Dendritic Coring:

Uranium-base niobium alloys core readily when cooled from the liquid state. According to the phase diagram of Rogers, and others,¹ the solidus temperature for a U-6.4 wt% Nb (15 at.% Nb) alloy is 1235°C and the liquidus temperature is 1320°C. On cooling from the single phase liquid region the first γ_1 that forms would have a composition of 12 wt% Nb (26 at.% Nb), whereas the last solid to form might be as low as 3 wt% Nb (6.5 at.% Nb).

Experimentally, in arc-cast U-6.4 wt% Nb alloys, the predicted large variation in niobium content from core-to-core is not observed. Microprobe analysis shows the niobium content to vary from 7.5 wt% Nb (17 at.% Nb) at the center of the core to ~5.0 wt% Nb (12 at.% Nb) at the edge. The apparent discrepancy does not imply that the phase diagram is incorrect but only that appreciable diffusion takes place during the cooling of an arc-cast ingot. Some lessening of the gradient is to be expected since the diffusion distances are not great. The average shortest distance from center to edge of a core was 30 microns.

Macrobanding:

The second type of niobium segregation is referred to as macrobanding. The bands are continuous and oxidize nonuniformly in certain environments to form alternating dark and light layers having a repeat distance of approximately 1/8 inch. Microprobe analysis shows

the maximum niobium variation to be approximately 0.3 wt% Nb in a U-6.3 wt% Nb alloy. The homogenizing parameters prescribed in this report do not eliminate macrobanding in arc-castings. Macrobanding in induction castings can be minimized, if not eliminated, by slow cooling the casting.

The origin of the macrobands is not clear, but it is undoubtedly caused by constitutional supercooling. A line parallel to any band would represent a single freezing interface. On cooling, the first infinitesimally thin sub-layer to freeze would be niobium rich. As additional sub-layers freeze, the liquid ahead of the interface becomes progressively depleted in niobium. A point is soon reached at which time the combined effects of the heat of solidification and the reduced niobium content prevent additional solidification, and the interface liquid must enrich in niobium by diffusion before continued freezing can occur. This occurrence would be the start of the formation of a new macroband and the described cycle would repeat itself. The mechanism can be looked upon as a minaturized and cyclic single-stage zone-refining operation. It is likely that impurity atoms are also segregated by this process.

Gross-Ingot Segregation:

The third type of niobium segregation is a continuous gross segregation from top-to-bottom and center-to-edge of an ingot. In a U-6.3 wt% Nb alloy arc-cast into a cylindrical shape, the ingot is niobium rich at the top and edge with a maximum variation of ~1.0 wt% Nb. If the same alloy is induction cast, the resulting cylinder is niobium rich at the top and center with a maximum niobium variation of ~0.5 wt%. Reducing the niobium content significantly reduced the maximum variation in a casting. For example, a U-4.5 wt% Nb arc-casting has a maximum variation of ~0.5 wt% Nb. This is half the variation observed in the arc-cast U-6.3 wt% Nb alloy. The homogenizing parameters described in this report do very little towards removing this type of ingot segregation. Slow cooling the liquid casting seems to be the best means of minimizing this type of segregation.

EXPERIMENTAL APPROACH

Composition gradients caused by solidification can generally be eliminated by heat treating near (but below) the

solidus temperature. The intent of the present study is to first determine the times and temperatures necessary to homogenize a U-15 at.% Nb alloy, and then to develop the best procedures for determining homogeneity in uranium-base niobium alloys.

Preliminary studies indicated approximate times and temperatures necessary for homogenizing. Individual arc-cast samples weighing 6 grams each were wrapped in tantalum foil and individually sealed in evacuated quartz capsules. The capsules were homogenized for various lengths of time at 1100°, 1150°, and 1200°C. The samples were quenched directly from the homogenizing temperature by crushing the capsule at the same time it was immersed in ice water. The water-quenched samples were examined by X-ray diffraction and optical metallography, and then tested for hardness. Specifics of these procedures are discussed in the following sections.

The samples used in the study were from a 4-inch i.d. by 5-inch o.d. by 1/4-inch-thick concentric ring machined from the lower portion of a 6-inch-diameter arc-cast cylindrical ingot weighing approximately 150 kg. All the samples were cut from this ring and would therefore have identical composition and thermal history.

HOMOGENEITY AND X-RAY METALLOGRAPHY

Half-Height Peak Width:

As the composition gradients in the cored alloys diminish on homogenization, there is a corresponding lessening of X-ray peak width. Figure 1 shows average X-ray half-height peak widths as a function of homogenizing time and temperature. The listed peak width is an average of the first seven significant peaks in the monoclinic a'' structure.² The first seven significant peaks are from the $(\bar{1}10)$, (110) , $[(021), (002)]$, $(\bar{1}11)$, (111) , $(\bar{1}12)$, and (112) planes.

Using peak width as a criteria for completion of homogenization, one can conclude that 2 hours at 1200°C, 4 hours at 1150°C, or 24 hours at 1100°C is sufficient to homogenize the arc-cast U-15 at.% Nb alloy. The peak width criteria is a valid one since the "d" spacings of the a'' structure are a direct function of niobium composition. As the niobium gradient diminishes, the peak width would diminish and reach a constant minimum value for the fully homogenized alloy.

Figure 1. Average Half-Height X-Ray Peak Widths as a Function of Homogenizing Time and Temperature.

X-ray Peak Intensity:

The peak intensity of the monoclinic α'' alloys quenched from 1200°C was significantly greater than those quenched from 1150°C and 1100°C. The area under the first seven significant α'' peaks averaged 4.5 in² for the 1150°C and 1100°C quench; whereas, for the 1200°C quench the average was 7.7 in². This is a 70% increase.

This intensity increase is probably the result of a much higher vacancy concentration at 1200°C than at 1150°C or 1100°C. On quenching, the vacancies are partially entrapped giving rise to lattice imperfections of various types. These lattice imperfections result in a stronger mosaic pattern, i.e., a more imperfect lattice. X-ray peak intensity is proportional to the extent of the mosaic structure. Hence, the significant increase in peak intensity would be expected.

α'' - γ^0 Peak-Intensity Ratio:

The gamma-quenched, nonhomogeneous alloys consist of two coherent phases. The phases are monoclinic α'' and tetragonal γ^0 .² The relative amount of these two phases is proportional to the ratio of their X-ray peak intensities. Figure 2 shows the relative ratio of intensities for γ^0 and

α'' as a function of time at temperature. The α'' intensity was the sum of the areas under the first seven significant α'' peaks. The γ^0 intensity was the area under the intensity curve from 18.40° to 18.75° theta (CuK α radiation) and corresponds to the areas under the (220) and (201) γ^0 peaks.

The above intensity ratio is not a criteria for completion of homogenization. The reason for this is that the α'' - γ^0 phase boundary occurs at approximately 16 at.% Nb. Thus, the γ^0 structure disappears before the composition gradient is eliminated. Times required for elimination of the γ^0 structure were 1, 2, and 4 hours for homogenization temperatures of 1200°, 1150°, and 1100°C, respectively.

HOMOGENEITY AND HARDNESS

The hardness of the starting as-cast material was 230 DPN. The hardness of samples water quenched after homogenizing at 1100°, 1150°, and 1200°C was 145, 146 and 155 DPN, respectively. The hardness of a sample air quenched after 3 hours at 1100°C was 236 DPN; whereas a sample furnace cooled from 1100°C was 447 DPN. All samples were heat treated to the desired condition,

Figure 2. Ratio of Selected X-Ray Peak Intensities for γ^0 and α'' as a Function of Homogenizing Time and Temperature.

metallographically polished and etched, and then tested for hardness. The quoted hardness values are an average of five indentations.

Figure 3 shows the DPN hardness of samples homogenized for various lengths of time at 1100°, 1150°, and 1200°C. The samples were water quenched directly from the homogenizing temperature. The constancy of hardness values as a function of time at temperature was somewhat

unexpected. This does show that hardness cannot be used as a measure on inhomogeneity. The hardness change between niobium-rich and niobium-poor regions is probably linear. Thus, the average hardness of the niobium-rich and niobium-poor region is the same as the hardness of the overall composition. The softness of the inhomogeneous alloy also indicates that only small strains are necessary to maintain coherency between the niobium-rich and niobium-poor regions.

Figure 3. Diamond Pyramid Number Hardness following Homogenization Treatments at Indicated Time and Temperatures.
All samples were water quenched directly from the homogenization temperature.

Figure 3 also shows that the hardness of the alloys homogenized at 1200°C was greater than the hardness of those alloys homogenized at 1150°C and 1100°C (DPN 155 versus DPN 145). This is probably caused by the significantly higher vacancy concentration at 1200°C . On quenching, these vacancies are partially entrapped giving rise to a higher concentration of lattice imperfections and a correspondingly higher hardness.

HOMOGENEITY AND MICROSTRUCTURE

As-Quenched Microstructures

The as-quenched, cored microstructures are best viewed in the as-polished condition. The cored structure is easily relief polished and shows up well when viewed under oblique light. Figure 4 illustrates various degrees of

Figure 4. Photomicrographs of As-Polished Samples Illustrating Various Degrees of Homogenization (a) as-cast sample held 30 minutes at 850°C and water quenched, (b) partly homogenized sample after 30 minutes at 1100°C , (c) partly homogenized sample after 2 hours at 1100°C , and (d) fully homogenized sample after 2 hours at 1200°C All 100X

homogeneity in as-polished samples viewed under oblique illumination.

This method of determining the degree of homogeneity gave results which agreed well with the X-ray line broadening studies. However, in the latter stages of homogenization, it takes considerable experience in differentiating a homogenized and nonhomogenized sample. Therefore, this procedure is not recommended as a test for homogeneity.

Prior Gamma Grain Size:

At the homogenizing temperature, the alloys are single phase bcc gamma with some undissolved NbC, Nb₂C, and UO₂ inclusions. The gamma grains can reduce their total surface energy by growing in size. This growth is impeded by the pinning action of the undissolved inclusions. The maximum obtainable grain size is, of course, limited to the minimum thickness of the sample

Figure 5 shows the average prior gamma grain diameter at 100X as a function of homogenizing time and temperature. The grain size is seen to increase significantly with increasing homogenizing time and temperature.

Figure 5. Average Prior Gamma Grain Diameter at 100X as a Function of Homogenizing Time and Temperature.

Aging-Etch Test for Homogeneity:

A metallographic procedure was developed that readily distinguishes between homogenized and nonhomogenized samples. In this procedure, the quenched sample is aged

10 minutes at 450°C. After polishing, the sample is stain etched in a freshly prepared chromic-chromate solution at 2 volts for 10-20 seconds. The electroetch solution consists of equal portions of two stock solutions: 118 g CrO₃ in 100 ml of water, and a saturated solution of Na₂Cr₂O₇·2H₂O in water.

Figure 6 contrasts the appearance of a homogenized and nonhomogenized sample after the aging-etch procedure. Precipitation in the nonhomogenized sample is enhanced in the regions of low niobium content and also in the region separating the α'' and γ^0 phases. In the homogenized sample, alpha precipitation does not occur in the low niobium region during the 10 minutes at 450°C; or if it does occur, it occurs uniformly. The sensitivity of the method is illustrated in Figure 7. In the sample homogenized 3 hours at 1150°C, alpha precipitation occurred during the 10 minute age; whereas in the sample homogenized 4 hours at 1150°C, alpha precipitation did not occur. This indicates that 4 hours at 1150°C is necessary for homogeneity. The overall results of the aging-etch procedure agrees well with the X-ray line broadening studies.

Macrobanding is also well delineated by the aging-etch procedure. Figure 8 shows macrobanding in U-15 at.% alloy given the aging-etch treatment. The alloy was homogenized 15 minutes at 1150°C and water quenched followed by 20 minutes at 450°C. The layers of enhanced precipitation are quite obvious. The homogenizing times and temperatures used in this study were not sufficient to eliminate macrobanding but the longer times and higher temperatures did significantly reduce the magnitude of macrobanding. Rough calculations indicate that several thousand hours at 1150°C would be required to eliminate macrobanding in an arc-casting. Thus, the procedure described earlier for preventing the formation of macrobands is the preferred method of treatment.

SUMMARY

In uranium-base niobium alloys there are three types of niobium segregation: dendritic coring, macrobanding, and gross-ingot segregation. The origin, extent and elimination of these inhomogeneities in a U-6.4 wt% Nb alloy was considered.

Dendritic coring results in niobium gradients having a composition span of 2.5 wt% Nb over an average minimum distance of 30 microns for arc-castings. Two hours at 1200°C, 4 hours at 1150°C, or 24 hours at 1100°C is sufficient to eliminate dendritic coring.

Figure 6. Photomicrographs Illustrating the Appearance of a Nonhomogenized and Homogenized Sample after the Aging-Etch Procedure. (a) As-cast sample held 30 minutes at 850°C , water quenched, and aged 10 minutes at 450°C . Alpha precipitation has occurred in the low niobium regions and in the region separating the α'' and γ^0 phases. 100X; (b) Sample homogenized 2 hours at 1200°C , water quenched, and aged 10 minutes at 450°C . No alpha precipitation is apparent. 125X.

Figure 7. Photomicrographs Illustrating the Sensitivity of the Aging-Etch Procedure for Determining Homogeneity in a U-15 at.% Nb Alloy. (a) Sample Homogenized 3 hours at 1150°C and aged 10 minutes at 450°C . Alpha is precipitating in low niobium regions (grain boundaries) indicating a partly homogenized alloy; (b) Sample homogenized 4 hours at 1150°C and aged 10 minutes at 450°C . No alpha precipitation has occurred indicating an homogenized alloy. Both 100X.

Figure 8 Photomicrograph Illustrating the Aging-Etch Procedure for Delineating Macrobanding in a U-6 4 wt% Nb Alloy Sample homogenized 15 minutes at 1150°C, water quenched and aged 20 minutes at 450°C 10X

Macrobanding is a layered inhomogeneity with a 0.3 wt% Nb gradient over a distance of one sixteenth inch. The times and temperatures for removal of dendritic coring do not eliminate macrobanding. However, macrobanding can be made insignificant by slow cooling the liquid ingot through the solidification range.

The third type of niobium segregation is a continuous gross segregation from top to bottom and center-to-edge of an ingot. The maximum niobium variation of 1 wt% was separated by a distance of 24 inches in an arc casting. Realistic homogenization times and temperatures have little effect on this composition gradient. The best means of controlling this type of segregation is to slow cool the ingot through the liquid solidification range.

The most effective means of preparing an homogenized alloy free of macrobanding and with reduced gross ingot

segregation is to first arc-cast the constituent metals. The arc-casting step is necessary to dissolve the higher melting niobium (2415°C) in the lower melting uranium (1133°C). After arc-casting, the alloy is induction melted in a zirconia-coated graphite mold and immediately poured into a preheated zirconia-coated graphite mold. For the U-15 at % Nb alloy, the casting is then homogenized 4 hours at 1150°C to remove inhomogeneity caused by coring.

The results of this study are primarily from a U-6 3 wt% Nb alloy. Alloys with lower niobium contents yield ingots which show smaller variations in niobium content, whereas alloys containing more than 6.3 wt% Nb yield ingots having larger variations in niobium content. Correspondingly, shorter times and/or lower temperatures are required to homogenize the hypo U-6 3 wt% Nb alloys, whereas longer times and/or higher temperatures are required to homogenize the hyper U-6 3 wt% Nb alloys. Thus, a low niobium content alloy is easier to homogenize than a high niobium content alloy, and this should be considered when selecting a given alloy for a given application.

The best procedures were considered for determining homogeneity in uranium-base niobium alloys. The X-ray half-height peak width was found to be the most sensitive method for determining the degree of homogeneity. Since the "d" spacings of the monoclinic α'' structure are a direct function of composition, the peak width diminishes as the niobium gradient diminishes and it reaches a constant minimum value for the fully homogenized alloy. Other X-ray diffraction effects were considered. The peak intensity of the monoclinic α'' alloys quenched from 1200°C was 70% greater than those quenched from 1150°C or 1100°C. This significant increase was attributed to lattice defects arising from quenched-in vacancies. The relative amounts of the coherent α'' and γ^0 structures during homogenizing were followed by determining the α''/γ^0 peak intensity ratio. The times necessary for elimination of the γ^0 phase was found to be 1, 2, and 4 hours for homogenizing temperatures of 1200°, 1150°, and 1100°C, respectively.

It was found that hardness did not vary significantly with degree of homogeneity. This effect was attributed to a linear hardness-composition relationship. The softness (DPN 145) of the quenched, inhomogeneous, coherent, two phase alloys indicates that only small strains are necessary to maintain coherency between the α'' and γ^0 phases. The hardness of the alloys homogenized at 1200°C was greater than those homogenized at 1150° and 1100°C (DPN 155 versus DPN 145). The

effect was attributed to the higher vacancy concentration at 1200°C.

The relation between hardness and microstructure was considered. The as-quenched, cored microstructure is best viewed in the relief polished condition under oblique illumination. This method of determining homogeneity gave results which agreed well with the X-ray line broadening studies. However, in the latter stages of homogenization, interpretation is often difficult and this procedure is not recommended as a test for homogeneity.

An aging-etch metallographic procedure was developed that readily distinguishes between homogenized and non-homogenized samples. In the nonhomogenized sample, precipitation is enhanced in the regions of low niobium content and also in the regions separating the α'' and γ^0 phases. In the homogenized sample, alpha precipitation does not occur in the low niobium region during the age, or if precipitation does occur it occurs uniformly. The results of the aging-etch procedure agrees well with the X-ray line broadening studies.

It is concluded that either the aging-etch procedure or the X-ray line broadening approach is a sufficient test for homogeneity.

The benefits of a homogenized uranium-niobium alloy are several. Primary among these is improved corrosion resistance and dimensional stability. Care should be taken in the preparation of all U-Nb alloys to see that inhomogeneity arising from macrobanding and dendritic coring are eliminated. This can be done by the proper choice of melting, casting, and heat-treating procedures.

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