CONFIDENTIAL

UNCLASSIFIED

AEC RESEARCH AND DEVELOPMENT REPORT

Photostat Charge ~~14-000~~
Accession Number ~~14-000~~
\$4.93
Available from
Technical Information Service
P. O. Box 1003, Oak Ridge, Tennessee

Report A-2914

This document is
PUBLICLY RELEASABLE

Hugh Kinner
Authorizing Official

Date: 9-7-11

COMPARISON OF NORMAL PROCESS AND SINGLE PROCESS (XC) URANIUM

by

H. T. Cleaves

CLASSIFICATION CANCELLED

DATE 11-30-59

For The Atomic Energy Commission

H. T. Cleaves
Chief, Declassification Branch *ml*

CONTRIBUTION
from the

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

NATIONAL BUREAU OF STANDARDS
Division of Metallurgy
J. G. Thompson, Acting Chief

MADISON SQUARE AREA
MANHATTAN DISTRICT
CORPS OF ENGINEERS

7 October 1946

*Declassify w/o
H7C. 11/25/59*

691-1

UNCLASSIFIED **CONFIDENTIAL**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~CONFIDENTIAL~~

UNCLASSIFIED

Report A-2914

COMPARISON OF NORMAL PROCESS AND SINGLE PROCESS (XC) URANIUM

by

H. E. Cleaves*

Certain difficulties have been encountered in attempts to substitute a "one-step" casting process, developed at Iowa State College, for the "normal" process generally used for the production of extrusion billets. In the "one-step" process molten metal is delivered from the reduction bomb to the billet mold instead of allowing the metal to solidify in the bomb with subsequent vacuum remelting of the biscuit metal before casting in the billet mold.

Routine analyses had failed to establish significant differences in the composition of normal and one-step metal. The one-step billets had been extruded satisfactorily, and finished slugs were prepared and subjected to the usual canning operation. In subsequent tests however, it was found that a large percentage of the canned slugs were badly defective.

An investigation was requested to determine the differences in composition or structure of the X-C and normal metal which would account for the failure of the X-C slugs. Samples of the failed slugs and of metal from various stages of both the one-step and normal processes were supplied by Madison Square Area, for comparison on the basis of analyses, microstructure, or such other tests as seemed desirable.

Materials

One-step metal supplied for this investigation consisted of:

(A) Six failed slugs from ~~Madison~~, each 1.4" in diameter by 8" long. Three of these slugs had been selected to represent the best of the failed material and were assigned identification numbers 1, 2, and 3. The remaining three, representing badly defective material, were assigned the numbers 4, 5, and 6.

(B) Two pairs of 4 1/4" diameter billets from Ames, identified as billets B1 and B2, C1 and C2; and also identified respectively as billets XC-266, 271, 279, and 293. Each billet had been cut to form a series of disks, each 1 1/2" thick, and numbered consecutively from the bottom of the ingot (e.g. B1-1) to the top (B1-14). Billets B1 and B2 had been cast in steel molds, C1 and C2 in graphite molds.

* Work done under direction of Dr. J. G. Thompson, by H. E. Cleaves, W. E. Lindlief, H. G. MacKerrow, J. T. Sterling, Ruth Kimble, A. E. Lemper, and C. P. Saylor.

G 91 2

UNCLASSIFIED ~~CONFIDENTIAL~~

(C) Sections of extruded rod, each 1 1/2" in diameter and about 12" long, received from Metal Hydrides, Inc., and identified as follows: XC-72, 105, 122, 128, 143, and 144.

Normal process metal available for the investigation consisted of:

(D) Two billets from the Electro Metallurgical Corp., identified respectively as E 3690-1 (Billet D1) and E 3638-9 (Billet D2). Each billet was cut to form 16 or 17 disks, which were numbered consecutively from the bottom (e.g. D1-1) to the top (D1-16).

(E) Three slugs received in September, 1944 from the Metallurgical Laboratory, Chicago. These were designated slugs 7, 8, and 9.

Additional material investigated intermediate between one-step and normal process metal, consisted of the following:

(F) Transverse and longitudinal sections of biscuit AA913 from the Electro Metallurgical Corp.

(G) Two pairs of cast rods, RA and RB, RC and RD, each 1 1/2" diameter by 18" long, produced at NBS by vacuum remelts of portions of single process billets B and C.

Sampling Method

A slice 4 1/4" x 1 1/2" x 1/2" was cut through the center of each of the top, center, and bottom disks from each of the six billets. One half of each slice was used for chemical and spectrochemical examination, and the other half furnished samples for metallographic examination.

Disk samples 1/4" or less in thickness were cut near each end of each of the extruded rods, slugs, and rod specimens of biscuit metal.

Results of Macroexamination

Visual inspection of the various lots of metal yielded results as follows:

Billets. Prior to cutting for the purpose of sampling, the surfaces of all sections of the six billets were examined for defects. Three or four inches of XC billets were sound; the remaining sections contained cavities ranging from pinholes to 5/8" in diameter. A greater portion, about 7 1/2", of the bottom of the normal process billets (D1 and D2) was sound, but cavities were as prevalent in the remainder of these billets as in the XC billets.

691 3

REF ID: A66188

Edge cracks and large non-metallic inclusions were present in the top sections of the XC billets but were not observed in the normal process billets.

Slugs and Extruded Rods. The appearance of the six slugs which failed during processing is shown, as received, in Figure 1. Slugs 1, 2 and 3 appeared sound to visual inspection, although they contained a few white specks or inclusions, the worst of which is shown in the photograph of slug 3. Slugs 4, 5, and 6 were visibly cracked and contained more white inclusions, particularly No. 4, which had the worst cracks.

Removal of tarnish from these slugs by pickling in nitric acid revealed numerous small cracks in slugs 1, 2, and 3. The slugs tarnished too rapidly to permit photographing satisfactorily. They were then cleaned electrolytically in a 1:1 phosphoric acid-glycerine mixture. The rate of tarnishing was retarded sufficiently by the anodic cleaning to permit photographing. The pickle in nitric acid plus the electrolytic cleaning altered the appearance of the slugs in several respects, as is shown by Figure 2. The white inclusions and some of the other large inclusions disappeared, leaving pits in the surface. The large cracks on slugs 4, 5, and 6 were unchanged. The cracks revealed on slugs 1, 2, and 3 by removal of the tarnish film were most prominent on No. 1, less noticeable on No. 3, and barely discernible on No. 2.

Examination of the sections cut from the six XC slugs that failed during processing showed that cracks extending to the surface were filled with a white metal which was more resistant to tarnishing than uranium. Microanalysis showed the principal constituents of this white metal to be tin and copper. The appearance of cracks in sections of slugs 4, 5, and 6 is shown in Figure 3. Macro-inclusions were observed in most sections of slugs 4, 5, and 6, but not in the sections of slugs 1, 2, and 3, nor in slugs of recast metal 7, 8, and 9. Micro-inclusions present in a section of slug 4 are shown in Figure 4 magnified about 4 times. Frequently particles of uranium were trapped in these inclusions. Microanalysis showed that these inclusions consisted principally of magnesium and fluorine, indicating that the inclusions are globules of magnesium fluoride slag entrapped in the tuballoy. Cracks frequently started from or passed across these inclusions.

The billets and slugs of normal metal and the extruded XC rods were free from macro-inclusions.

Microexamination

Grain Size. The XC metal and the normal process metal appeared equally coarse-grained, whether examined by polarized light on the polished metal, or by bright-field illumination of the electrolytically etched surface as is seen in Figures 5 to 9. Exceptions to the prevalence of coarse-grained structures were two of the three normal metal slugs. Slug No. 7 was relatively fine-grained as shown in Figure 10, and No. 9 was intermediate in grain size; but No. 8 had the usual coarse structure.

The cracks were generally intercrystalline, although occasionally a crack appeared to cross a grain as is seen in Figure 11.

Inclusion

The outstanding difference between the normal process metal and the XC metal observed in micro-examination was in the number and type of inclusions. Only carbide inclusions were prevalent in the normal metal, as shown in Figure 12, whereas in the XC metal a variety of inclusions were present in addition to the carbides. Circular or globular inclusions of the type shown in Figure 13 were the most frequent. These were smaller versions of the macroscopic inclusions illustrated in Figure 4, and presumably were the same material, magnesium fluoride. The micro-inclusions, like the larger inclusions, occasionally contained particles of entrapped metal, as shown for example in Figure 14. Such inclusions probably represent a small particle of the combined products of the reduction reaction, where the amount of metal to mold is not enough to break through the layer of slag and agglomerate with the rest of the metal. Elongated inclusions, types of which are shown in Figures 15 and 16, were frequently observed. Another of the assorted types of inclusions present in the XC metal is seen in Figure 17.

The carbides were not uniformly distributed in the XC billets and in cross sections of the XC slugs and rods, but tended to cluster around other inclusions, as shown in Figure 15. In longitudinal sections of the XC slugs and rods the inclusions appeared striated, an effect not observed in the normal slugs. The appearance of longitudinal sections of normal slug 7 and extruded rod XC 72 at 1 1/2 diameters is shown in Figure 18. At high magnification, inclusions in longitudinal sections of the normal metal appear randomly distributed (Figure 19A), whereas the striations in the XC metal rods appear to be similar inclusions but arranged in columns parallel to the rod axis (Figure 19E).

The metal from biscuit AA913 appeared relatively clean except

at the top, where there was a concentration of carbide inclusions, and an occasional circular inclusion (Figure 20). In the body of the metal the carbide inclusions were surrounded by a skin of gray material, a type of inclusion not observed in the other specimens.

The cleanliness of the biscuit metal as compared with the XC metal may be ascribed to: 1. The additional time that the metal remained molten in the reaction chamber, permitting more of the slag particles to float to the surface, 2. Mixing of slag with the XC metal by vortex action as the metal flowed into the mold.

Hardness Determinations

In a survey of the billet material, it was found that the presence of spongy areas and small pits led to low Rockwell B readings, whereas an occasional large inclusion, for example of hard carbide, caused a high Rockwell reading to be obtained. For these reasons a series of Rockwell B readings on the surface of a cross section of a billet might cover a range of 20 or 25 Rockwell C numbers. Results of several hundred Rockwell B readings, after eliminating some of the obviously unreliable results, indicated that the average Rockwell B values for the four XC billets were 91, 90.5, 88.5, and 88 whereas the averages for the two normal process billets were 86.5 and 87.5. The XC metal may be a trifle harder than the normal process metal, but in view of the variation in any series of readings, it is doubtful that even this conclusion is justified. In each ingot the variation in hardness from top to bottom, or from center to circumference, was less than the uncertainty of the determinations.

Remelting the XC billet metal to form bars RA, etc., did not appreciably alter the hardness of the metal, although the spread in hardness values on each specimen was less for the bars than for the billets.

The average of the Rockwell B numbers obtained on the slugs of normal metal (91.5) was higher than the average of the numbers obtained on the XC slugs (87.1). However, the XC slugs had been canned and then stripped, whereas the normal metal had not been subjected to the canning process. Hence, the lower hardness numbers obtained on the XC slugs may be the result of temperature changes incidental to the canning process, rather than of fundamental differences in the metal.

The results of the hardness measurements indicated that any differences in composition of the two types of metal were without marked effect on the Rockwell B hardness.

Composition

Results of analyses of the materials used in the investigation are shown in Table 1. Carbon and fluorine were determined by chemical

analysis, and oxygen, nitrogen, and hydrogen by vacuum fusion. Hydrogen determinations on several samples by the vacuum extraction method were in satisfactory agreement with the vacuum fusion values. The other elements were determined by spectrochemical analysis. Some elements, carbon especially, were not determined on all specimens of a group when metallographic examination showed similar amounts of carbon inclusions in the different specimens of the group. (See footnote to Table 1 regarding fluorine determinations).

The presence of tin and abnormal amounts of copper in some of the failed slugs is ascribed to penetration of bronze into cracks open to the surface. Apparently the analytical samples of the different failed slugs included different amounts of large cracks filled with copper-tin bronze. The higher carbon contents of the normal and remelted metal resulted from pickup of carbon from the **graphite** crucible in remelting. There is no significant difference in the carbon content of XC billets cast in graphite or in steel molds. (This was confirmed by metallographic examination). Oxygen and nitrogen are present in abnormal amounts in the top section of the XC billets, but in other portions of the XC billets and in the XC slugs and rods the oxygen and nitrogen contents are similar to those of normal metal.

The outstanding and probably only significant difference observed between the XC and normal metal was in the content of magnesium and fluorine. The magnesium content of normal metal billets was from 5 to 25 ppm., but in the XC billets the magnesium content ranged up to 750 ppm. It is interesting to note the definite segregation of ~~these~~ abnormal contents of magnesium toward the top of all of the XC billets and biscuit metal. It is also interesting that the six **Hanford** slugs cover about the same range of magnesium contents as the XC billets, **showing** that the segregation of magnesium is not corrected by the heat treatment and work incidental to the extrusion process. Similarly, fluorine was present in amounts from 370 to 1050 ppm in XC metal. The extruded rod XC-144, which appeared the dirtiest by microscopic examination, also contained the greatest total of magnesium plus fluorine of any of the rods, 970 ppm. The analytical results confirm the evidence of metallographic examination and micro-analysis that "magnesium fluoride" is present in the XC metal. It is not possible to say that all of the magnesium and all of the fluorine are combined as magnesium fluoride. Some fluorine may be combined with other elements, and some of the magnesium may be in solution in the uranium or may be combined with other metallic elements. An additional uncertainty in the interpretation of the analytical data arises from the non-uniform distribution of inclusions, and consequent difficulty of sampling. Different samples were used for the determinations of magnesium

and fluorine.

Effect of Remelting on the Composition of XC and Biscuit Metal

Three remelts in vacuum were made to observe the effect of this operation on the various impurities present in XC or biscuit metal, as compared with normal process metal. The first experiment was a remelt of three slices from the bottom, central, and top sections of billet C1 which, according to microscopic examination, was the "dirtiest" of the lot, i.e., contained the most inclusions. The charge for the second melt consisted of sections from the top portions of billets B2, C1, and C2, representing the highest magnesium contents reported in the analytical results, with correspondingly high fluorine contents. Both of these melts were made in the tilting furnace. Both melts boiled so violently that the sight hole in the cover of the crucible was plugged with splashed metal. Consequently, the temperature and condition of the melt could not be observed directly, and the melt was run on the time-power input schedule previously used for melting comparable amounts of metal to be poured at 1450°C. Both melts were still wild when the metal was poured to form bars 1 1/2" in diameter and about 20" in length. The two bars from the first melt were identified as RA and RB; those from the second melt as RC and RD. Despite the wildness of the melts the cast bars had good surfaces and were sound except for the usual shrinkage cavities at the top.

Analysis of these bars (Table 1) showed that remelting in vacuum produced a substantial decrease in the magnesium, fluorine, and nitrogen contents and an increase in the carbon, the latter representing the usual pickup resulting from melting in graphite. The principal benefits derived from remelting and casting the XC metal appear to be partial elimination of magnesium, fluorine, and nitrogen. Complete elimination of impurities by volatilization or slagging, or their reduction to the amounts occurring in normal process metal, apparently requires a longer melting period or heating to a higher temperature than was obtained in these experimental results. The fact that the metal was wild as it was poured into the bar molds indicates that volatilization was not complete under the conditions of these experiments.

Effect of Dipping XC and Normal Process Metal in Molten Bronze

The presence of copper and tin in the cracks of the failed slugs indicated that failure occurred during the dip in molten bronze in the canning operation, there being no evidence of failure in the uncanned rods. The effect of the bronzing dip was investigated on specimens

DECLASSIFIED

Table 1. Composition of XC and Normal Process Uranium. Results expressed in parts per million.

Material	Ag	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Na	Pb	Sn	Si	C	F*	O	N	H
XC Metal																		
Billets																		
B1-1 (Bottom)	0.1	100	0.22	--	--	<2	26	21	6	<5	<1	--	19			14	30	7
B1-8 (Center)	0.1	100	0.25	--	--	2	28	100	7	<5	<1	--	19			50	20	7
B1-14 (Top)	0.1	25	0.26	5	--	<2	43	300	11	<5	--	--	26	60	610	10	40	4
B2-1 (Bottom)	0.1	<10	0.19	--	--	<2	33	42	7	<5	--	--	5			70	9	5
B2-8 (Center)	0.1	50	0.22	--	--	<2	29	100	6	<5	--	--	22			40	17	4
B2-14 (Top)	0.1	50	0.34	<5	--	<2	38	500	8	<5	--	--	31	60	710	360	870	5
C1-1 (Bottom)	0.1	50	0.17	<5	--	<2	18	17	5	<5	--	--	15			10	4	4
C1-8 (Center)	0.1	50	0.31	<5	--	<2	27	300	7	<5	--	--	33			50	10	6
C1-14 (Top)	0.1	50	0.26	--	--	<2	30	300	<5	<5	--	--	3	100	370	20	30	4
C2-1 (Bottom)	0.1	50	0.18	--	--	<2	20	20	5	<5	<1	--	23			20	1	6
C2-8 (Center)	0.1	25	0.23	--	--	<2	15	100	7	<5	1	--	26			60	120	5
C2-14 (Top)	0.1	25	0.31	20	--	<2	25	750	15	<5	1	--	38	90	150	410	1700	-
Slugs (Hanford)																		
1 (a)	0.1	10	0.22	--	--	10	36	100	8	<5	--	--	17		850	20	10	1.0
2	0.1	10	0.27	--	<5	<2	13	25	7	<5	--	--	13	80		10	20	3.0
3	0.1	25	0.23	--	--	<2	34	100	7	<5	1	--	21	60		60	20	1.0
4	0.1	10	0.26	--	--	2	24	100	7	<5	--	15	11			70	25	2.4
5	0.1	25	0.20	<5	--	500	38	300	8	<5	1	10,000	21	60	1050	50	70	1.5
6	0.1	50	0.22	<5	--	100	24	500	7	<5	--	200	25	40		70	40	1.5
Extruded rods																		
XC-72	0.1	25	0.24	<5	--	<2	20	200	5	5	<1	--	14	60	540	430	110	1
XC-105	0.1	25	0.19	--	--	2	20	100	7	<5	--	--	11	80	400	70	30	1
XC-122	0.1	25	0.27	--	--	2	20	100	7	<5	<1	--	20	140	620	70	20	-
XC-128	0.1	25	0.21	<5	--	<2	15	75	5	<5	--	--	14	120	540	30	2	0.4
XC-143	0.1	25	0.26	--	--	2	15	100	10	<5	--	--	17	70	500	130	70	1.
XC-144	0.1	50	0.25	--	--	<2	15	200	10	<5	--	--	14	50	770	10	10	2.
Recast Billets																		
RA (Top)	0.1	50	0.30	<5	<5	<2	35	40	8	<5	--	--	28	570	198	80	10	2
RA (Bottom)	0.1	50	0.28	--	<5	<2	35	5	8	<5	--	--	28	570	162	70	20	2
RB (Top)	0.1	50	0.31	<5	<5	<2	35	50	8	<5	--	--	31	620	175	70	10	1
RB (Bottom)	0.1	50	0.26	<5	<5	<2	35	5	8	<5	--	--	27	590	277	70	20	2
RC (Top)	0.1	50	0.33	5	<5	<2	35	150	8	<5	--	--	34	660		150	100	1
RC (Bottom)	0.1	50	0.33	<5	<5	<2	35	50	8	<5	--	--	38	530		70	30	2
RD (Top)	0.1	50	0.39	<5	<5	<2	35	150	8	<5	<1	--	33	670		180	270	3
RD (Bottom)	0.1	50	0.33	<5	<5	<2	35	10	8	<5	--	--	35	520		60	1	1
Normal Metal																		
Billets																		
D1-1 (Bottom)	0.1	<10	0.18	--	--	<2	25	10	7	10	--	--	18			40	10	2
D1-9 (Center)	0.1	<10	0.20	--	--	<2	15	10	10	<5	--	--	11			40	10	1
D1-16 (Top)(b)	0.1	<10	0.70	5	--	<2	15	25	10	<5	--	--	11			90	20	2
D2-1 (Bottom)	0.1	10	0.18	--	--	2	15	<5	8	<5	--	--	9	570		40	4	1
D2-9 (Center)	0.1	25	0.22	<5	--	<2	15	5	8	5	--	--	12			60	10	2
D2-17 (Top)	0.1	25	0.21	20	--	<2	15	10	8	<5	--	--	8	350		100	30	3
Slugs (Chicago)																		
7	0.1	<10	0.24	--	--	<2	300	<5	11	<5	--	--	24	380		20	--	1.
8	0.1	<10	0.25	--	--	5	111	<5	7	<5	--	--	26			60	10	1.
9 (c)	0.1	10	0.18	--	--	<2	50	<5	10	<5	<1	--	52			20	4	0.2
Biscuit AA 913																		
Top (a)	0.1	25	0.22	5	<2	2	30	1000	10	<5	10	--	30					
Center (a,c)	0.1	25	0.15	5	<2	<2	20	50	10	<5	5	--	15					
Bottom (a)	0.1	25	0.15	--	--	<2	30	10	15	<5	10	--	30					

The following elements were present in all samples in the amounts indicated:- Ni - 2 ppm, Li - 0.2 ppm, Mo - 3 ppm.
None of the following elements were present in any samples:- As, Au, Ba, Be, Bi, Br, Co, Cs, Ge, In, K, La, Rb, Sb, V, Zn.

* The fluorine determination is the least reliable of the reported determinations. The method developed for the determination of the fluorine content of ordinary uranium, usually, *less than 100 ppm*, is totally inadequate to determine the amounts of fluorine present in the XC metal. The modified method which was used for these specimens is believed to be reliable for the order of magnitude of the determination, although the numerical values may be questioned. However, there is no question that the fluorine content of the XC metal is definitely greater than that of normal process metal.

DECLASSIFIED

of XC rods and billets, and on remelted XC and normal process metal. Specimens cut from XC rods and normal slugs were about 1" long and 1 1/2" in diameter. Specimens about 3/4" square by 2" long were cut from the top sections of the XC and normal billets. The specimens were cleaned in a 60-40 nitric acid-water mixture, washed and dried quickly, and then immersed for 45 seconds in a bath of 53 per cent tin and 47 per cent copper at 720°C. The bronze was covered with a flux consisting of barium chloride 48 per cent, potassium chloride 31 per cent, and sodium chloride 21 per cent. When cool, the specimens were sand blasted and ground to remove the bronze coating and surface layer of metal, and finally were polished electrolytically.

The results recorded in the fifth column of Table 2 show that specimens of all four XC billets, and four of the six specimens of XC extruded rod developed noticeable cracks as a result of the bronzing dip. In contrast to this, none of the specimens of normal process metal (3 slugs and 2 billets), nor the 2 specimens of remelted XC metal, developed cracks in the bronzing dip.

Attempts to correlate the tendency to crack with the analytical data showed that soundness or failure of specimens after the bronze dip could perhaps be correlated with the sum of the magnesium and fluorine contents, but not with the amount of either element alone. The data in Table 2 show that the sum of the magnesium and fluorine contents is 665 ppm or more for the failed specimens, and 530 ppm or less for the specimens which did not fail. The lack of correlation of failure with the contents of either magnesium or fluorine is illustrated as follows: XC-128 with 75 ppm of magnesium cracked, but XC-105 with 100 ppm did not; Cl-14 with 370 ppm of fluorine cracked, but XC-143 with 420 ppm did not. Complete credence cannot be given to these figures, or to the numerical values for magnesium plus fluorine, because of the uncertainty of sampling this badly segregated material, as has been discussed in previous sections of this report.

To determine whether the cracking that occurred in the bronze dip was simply a matter of thermal shock, depending upon the temperature of the bath and the thermal gradients created in the specimen, or whether the nature of the bath had an effect, specimens of XC and normal process rods were immersed in a fused salt bath of the same composition as the flux used to cover the bronze bath. The time of immersion and the temperature of the bath were the same as in the bronze dip. None of the specimens so tested developed cracks in the salt bath as recorded in column 6 of Table 2 and illustrated in Figure 21 A and B. This showed that cracking is not strictly a thermal effect, but that the bronze bath has a specific action. This was further demonstrated by immersing specimens for 45 seconds in a deep layer of fused salt flux at 720°C. on

DECLASSIFIED

TABLE 2
BRONZING TESTS ON XC AND NORMAL TUBALLOY

XC Metal	Mg (ppm)	F (ppm)	Mg + F (ppm)	In bronze 45 sec.	In salt 45 sec.	In salt - 45 sec. In bronze 45 seconds
Extruded rod XC-72	200	590	790	Cracked slightly	Sound	Cracked slightly
" " XC-105	100	430	530	Sound	Sound	Sound
" " XC-122	100	620	720	Cracked slightly	Sound	Cracked slightly
" " XC-128	75	590	665	Cracked slightly	Sound	Cracked very slightly
" " XC-143	100	420	520	Sound	Sound	Sound
" " XC-144	200	770	970	Cracked badly	Sound	Cracked slightly
Billet B1-14	300	610	910	Cracked slightly		
" B2-14	500	710	1210	Cracked badly		
" C1-14	300	370	670	Cracked slightly		
" C2-14	750	450	1200	Cracked badly		
Remelted XC metal						
RD top	50	175	225	Sound		
RD bottom	10			Sound		
Normal Metal						
Slug 7	5			Sound	Sound	Sound
" 8	5			Sound	Sound	Sound
" 9	5			Sound	Sound	Sound
Billet D1-16	25			Sound		
" D2-17	10			Sound		

DECLASSIFIED

top of the molten bronze, and then lower the specimens into the molten bronze for 45 seconds. In other experiments, the specimens were held in the flux layer for 4 minutes, to bring them completely up to temperature before immersion in the bronze. In all cases the results were similar to those obtained on direct immersion of the cold specimens in the molten bronze; i.e., specimens with high contents of magnesium plus fluorine (665 ppm or more) cracked, whereas the specimens with lower contents of impurities did not crack. The severity of cracking was somewhat less in the duplex dip than it was in direct immersion in the bronze bath, (see Figure 21 C and D) but there was no appreciable difference in the severity of cracking of specimens preheated in the salt bath for 45 seconds or for 4 minutes.

Summary and Discussion

Experimental results have shown: (1) that the XC metal contains more magnesium and fluorine than the normal process metal; (2) that the XC metal contains numerous inclusions some of which form longitudinal striations when the metal is extruded; (3) that the XC metal is more apt to crack when dipped in molten bronze, (4) that failures produced in the laboratory were similar in character, but were less severe than the failures of the full-sized slugs at Hanford. The size of specimens and perhaps the conditions of dipping were different in the two cases.

These results indicate that the ~~Hanford~~ failures occurred in the bronze dip operation, and show that other specimens of XC metal were subject to similar failures under similar conditions. The question of why XC metal is more subject than normal process metal to failure by cracking may be answered as follows:

The fact that cracking of XC metal occurs in the bronze dip, and not in an equivalent dip in a fused salt bath, suggests that the cracking is a stress-corrosion phenomenon, i.e., a combination of stress and corrosion which together cause failure of the specimen. The evil effects of such a combination of stress and corrosive action has been generally established for many other metals, for example, to explain the rapid failure of stressed brass in contact with molten solder. The susceptibility of uranium to stress-corrosion was proposed to explain the failure of normal process slugs which were dipped in molten magnesium in early experiments at Battelle in the development of the canning process, as described in report CT-1163. For the successful operation of the canning process, it was desired to find a bath which would wet the uranium surface without cracking it as violently as did the magnesium. Evidently the molten magnesium is corrosive to normal process metal; molten bronze is not too corrosive to normal process metal, but acts on XC metal as magnesium does on normal process metal.

DECLASSIFIED

The stresses which enter into this stress-corrosion picture presumably result from a combination of temperature gradients set up in the immersed specimen, and the changes in volume that accompany the transformation of alpha to beta, or beta to alpha uranium. The beta-alpha transformation, i.e., the transformation on cooling, is accompanied by a contraction in volume. Thus, on cooling, the surface layers would be under tension as the transformation began, and a crack once started by corrosion of the stressed surface layer would progress readily into the underlying layers of metal which were still in the brittle beta condition. Thus the contraction on cooling from beta to alpha appears to be more apt to cause cracking than would the expansion that occurs on heating. The film of bronze would still be molten at the transformation temperature of about 660°C. and, consequently, molten bronze would be sucked into the crack as it formed.

To see whether the tendency to crack was affected by the rate of cooling through the beta-alpha range, a specimen was held in the flux bath for 4 minutes, lowered into the bronze for 45 seconds, and then returned to the flux bath, while the latter was cooled at slightly less than 2°C. per minute until the temperature dropped below 600°C. In this specimen the cracks were minute, but were visible at 4 diameters magnification. Slow cooling through the transformation range therefore decreases the amount of cracking, but cooling rates as slow as 2°C. per minute do not entirely eliminate the cracks.

The greater susceptibility to cracking shown by the XC metal as compared with the normal metal is probably only a difference of degree. The difference between XC and normal process metal in the bronze dip is similar to the difference in behavior of normal metal in the magnesium and bronze dips. Anything in the XC metal which increases even slightly the corrosive action of the bronze, or the brittleness of the metal, might be enough to initiate cracking. It is highly probable that the presence of magnesium and fluorine, both of which have high vapor pressures regardless of their state of combination, would stimulate the corrosive attack of the bronze bath to produce cracks in the surface of the specimen; and that the presence of non-metallic inclusions, and of impurities such as magnesium and fluorine, would facilitate the progress of the cracks inward from the surface, particularly along the striated lines of very fine inclusions which were observed in many of the specimens of extruded XC metal.

Indirect support for these theories of the susceptibility of uranium to cracking is found in the cracking and splitting of high-iron rods, reported to have occurred during cooling after extrusion. Here the iron-uranium compounds present constituted points of weakness, where cracks occurred under the stresses developed during cooling; in the case

DECLASSIFIED

of the X-C metal similar points of weakness are created by the action of the bronze bath on inclusions, or on magnesium- and fluorine-rich areas.

Some consideration was also given to the possibility that hydrogen might contribute to the tendency of the XC metal to crack. Work at Battelle indicated that hydrogen contents of 8 or 10 ppm had an embrittling action whereas metal with 2 or 3 ppm was not brittle. Although the hydrogen content of the XC billet metal was higher than that of any other class of metal examined, the XC extruded rods had very low hydrogen contents, fully as low as the normal process metal and slugs, and yet they were as susceptible to cracking as the high-hydrogen XC billet metal. A high hydrogen content perhaps would promote cracking, but cracking also occurs when the hydrogen content is negligible. Consequently hydrogen is not considered to be a primary cause of the cracking of XC metal.

Conclusions

1. The cracking of one-step process XC slugs during the canning operation apparently is the result of a stress-corrosion condition in which the stresses result from differential contraction during cooling and the corrosion results from the action of the bronze dip on the uranium.

2. The susceptibility of XC metal to cracking, in comparison with normal process metal, is a difference in degree only. Evidence has been cited to show that normal process metal also is subject to cracking under somewhat different conditions. The presence of magnesium, fluorine, and inclusions is associated with the susceptibility of XC metal to stress-corrosion cracking.

3. Modification of the one-step process to reduce the content of magnesium, fluorine, and occluded gross should reduce the susceptibility to cracking, and eliminate it when the impurity content is reduced to that of normal process metal. If these objectionable impurities are present in the solid metal, variation in the rate of cooling and other details of the canning process reduce, but have not been found to eliminate, the tendency of XC metal to crack.

DECLASSIFIED

1

2

3

4

5

6

Figure 1
Defective XC slugs as received. x 1 (approx.).

DECLASSIFIED

1 2 3 4 5 6

Figure 2
Defective XC slugs after pickling in nitric acid and cleaning
electrolytically. x 1 (approx.).

DECLASSIFIED

Figure 3
Sections of slugs 4, 5 and 6, showing radial cracks filled
with copper-tin bronze. x 1.

0049105070

Figure 5
Coarse structure of XC billet C1-1. Polished electrolytically,
photographed with polarized light. x 50.

Figure 6
Section of XC billet C1-1 electrolytically etched. Structure similar
to that revealed by polarized light on polished section. x 50.

691010691111

Figure 7
Coarse structure of normal billet D1-1. Polarized light. x 50.

Figure 8
Structure of extruded rod XC-105. Inclusions appear white with polarized light. x 50.

6 910102010

Figure 9
Structure characteristic of the XC slugs. Slug No. 2 photographed with polarized light. x 50.

Figure 10
Fine structure of slug 7, normal process metal, polarized light. x 50.

Figure 11

A crack passes through a dark grain near the center but the usual path of the cracks is intercrystalline. A section of a large crack, filled with bronze, is visible in the upper left hand corner. Polarized light. x 75.

691 DECLASSIFIED

Figure 12

Inclusions in normal process metal are mostly carbides and are uniformly distributed. Billet D1-1, electrolytically polished. x 500.

69103210

Figure 13
Circular inclusion, prevalent in XC metal, in slug No. 3. x 250.

Figure 14
Trapped metal inside a non-metallic inclusion in XC billet B1. x 500.

691
DECLASSIFIED

Figure 15
Elongated inclusions with clustered carbides in billet C1. x 500.

651
DECLASSIFIED

Figure 16
Group of elongated inclusions in extruded rod XG-144. x 500.

DECLASSIFIED

Figure 17

Another type of inclusion occurring in XC metal but less frequently than types seen in Figures 13 to 16. XC slug No. 3, polished electrolytically. $\times 500$.

A

B

Figure 18

Striations exist in longitudinal sections of extruded XC metal (B) but are not observed in normal metal (A). $\times 11\frac{1}{2}$.

DECLASSIFIED

A

B

Figure 19

Longitudinal sections of normal slug 7 (A) and extruded rod XC-72 (B).
Striations in XC metal are bands of small inclusions. x 500.

691
DECLASSIFIED

A-2914

28

A

B

Figure 20

In biscuit metal AA913, inclusions are concentrated near the top (A). Occasional carbide inclusions in the body of the biscuit are surrounded by gray material (B). x 500.

69/1
DECLASSIFIED

UNCLASSIFIED

CONFIDENTIAL

A-2914
29

A

B

C

D

Figure 21

Specimens of extruded rod XC-144 used in bronzing tests. The surfaces shown are parallel to the cut surface which was in contact with the hot bath.

- A. Specimen as cut from rod and polished electrolytically contained inclusion but no cracks.
- B. Specimen dipped in salt bath at 720°C. remained sound.
- C. Specimen held 4 minutes in salt bath then 45 seconds in bronze, both at 720°C., cracked slightly.
- D. Specimen immersed directly in bronze for 45 seconds at 720°C. cracked badly. All figures x 1.

CONFIDENTIAL

UNCLASSIFIED