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INVESTIGATION OF ROLLING PROPERTIES AND CORRELATED MICROSTRUCTURES OF ZIRCONIUM PRODUCED BY THE MATERIALS LABORATORY AT Y-12 AREA

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METALLURGY DIVISION

INVESTIGATION OF ROLLING PROPERTIES AND CORRELATED MICROSTRUCTURES OF ZIRCONIUM PRODUCED BY THE MATERIALS LABORATORY AT Y-12 AREA

by

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ABSTRACT

The Metallurgy Division has carried out vacuum remelting of calcium reduced zirconium prepared by the Materials Laboratory at Y-12. Since zirconium is of interest to the Reactor Technology Division from the standpoint of corrosion resistance, some of the vacuum remelted metal was fabricated by forging and rolling to permit preparation of corrosion test samples.

While these experiments were very preliminary and limited in scope, it may be concluded that calcium reduced zirconium which is substantially free of silicon may be fabricated by hot forging followed by cold rolling. Tests were made using Bureau of Mines zirconium and crystal bar zirconium as control samples indicate that the best calcium reduced zirconium prepared to date is about equivalent in rolling quality to Bureau of Mines zirconium which has been contaminated by repeated remelting in graphite. Hardness data and microstructural analysis of the various samples submitted are included in this report.

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INVESTIGATION OF ROLLING PROPERTIES AND CORRELATED MICROSTRUCTURES OF ZIRCONIUM PRODUCED BY THE MATERIALS LABORATORY AT Y-12 AREA

INTRODUCTION AND SUMMARY

The Metallurgy Division of ORNL was asked to carry out some studies on zirconium metal produced by calcium reduction of zirconium tetrafluoride at the Materials Laboratory of the Y-12 area. The major objective was the preparation of corrosion test samples which was accomplished by melting the zirconium in vacuum and rolling into 1/16 in. strip. Microstructures and relative hardness values were observed before and after melting and after each working operation. All hardness determinations were made with a diamond pyramid indenter in order to allow a variation in load, to permit testing of thin sections and to give a continuous scale of hardness values. Five samples, 3M, 7M, 8M, 10M, and 11M were submitted for this work in the form of as-reduced "buttons." The first four were prepared in a bomb lined with Fluorspar but 11M was prepared using CP grade CaF_2 in order to eliminate the source of an impurity, silicon. Samples of Bureau of Mines and iodide crystal bar Zr were also fabricated as a basis of comparison of rolling quality.

CONCLUSIONS

The preliminary experiments conducted on a limited number of samples indicate that calcium reduced zirconium substantially free of Si may be cold rolled after the cast structure is broken up by hot forging. Control specimens of Bureau of Mines and crystal bar zirconium indicate that the Ca reduced metal does not compare favorably with crystal bar metal in rolling properties but may be comparable to Bureau of Mines material after contamination by repeated melting in graphite. Insufficient work was done to justify a rigorous comparison since all specimens did not receive identical treatment. It was felt that the immediate objective had been attained when the corrosion samples were prepared.

EXPERIMENTAL PROCEDURE AND DISCUSSION OF RESULTS

The samples were melted in graphite crucibles in a high frequency induction vacuum furnace and allowed to freeze in the crucible to form an ingot approximately 1 in. in diameter and 3 in. long. Since the Bureau of Mines and crystal bar zirconium may be cold worked, the first attempt to fabricate the samples was by cold rolling the as cast ingot.

First Button Produced—3M. Metallographic examination of the original button, 3M, showed a general distribution of a second phase with a particularly high concentration at the top surface. Microspectrographic analysis made by Mr. Cyrus Feldman indicated the presence of a phase high in silicon and iron. Silicon and iron were reported to be of the order of three or four times more concentrated at the top of the button than at the bottom. Hardness values ranging from 468 DPH at the top to 233 DPH at the center, may be correlated with this segregation. Photomicrographs of the top surface and center portion are shown in Figs. 1 and 2, respectively.

Sample 3M was melted in graphite and a flat section cut longitudinally from the ingot for cold rolling. It was hard (R_c 38) and brittle and cracked immediately without appreciable reduction. A representative microstructure, presented in Fig. 3, shows that melting has produced a less continuous network and probably has resulted in the formation of a complex zirconium carbide compound. Graphic comparison of the hardness of this compound and the matrix is given in Fig. 4. The matrix hardness is 392-324 DPH and the compound is 1028-1098 DPH. The presence of this compound probably explains the brittleness encountered in rolling.

Crystal Bar Zirconium. A sample of crystal bar zirconium was melted in graphite to determine the effect of the carbon pickup on the rolling quality. Photomicrographs of this zirconium before and after melting are shown in Figs. 5 and 6, respectively. An X-ray analysis identified the second phase compound as zirconium carbide. The hardness of the crystal bar metal was increased from 80-105 DPH to 121-137 DPH by the carbide formation. A sample of the crystal bar as deposited was cold rolled to 95% reduction and produced a good strip with negligible edge cracking. The material after melting in graphite was cold rolled for a 93% reduction with much more severe edge cracking. Thus, the presence of the ZrC definitely impairs the rolling quality of the material but still permits rolling satisfactory specimens.

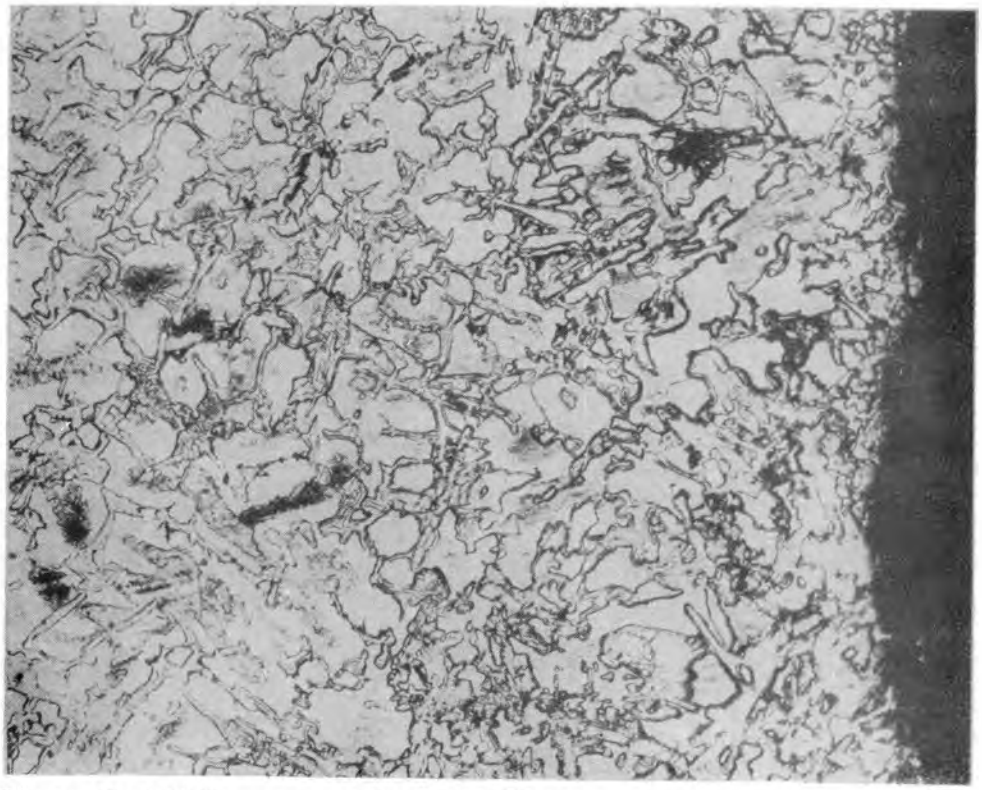


Photo No Y1391 Etch 1% HF 250x

Fig. 1

Top surface of button No. 3M as received. Shows iron-silicon rich phase which is also the area of highest hardness.

Hardness
DPH
233-468

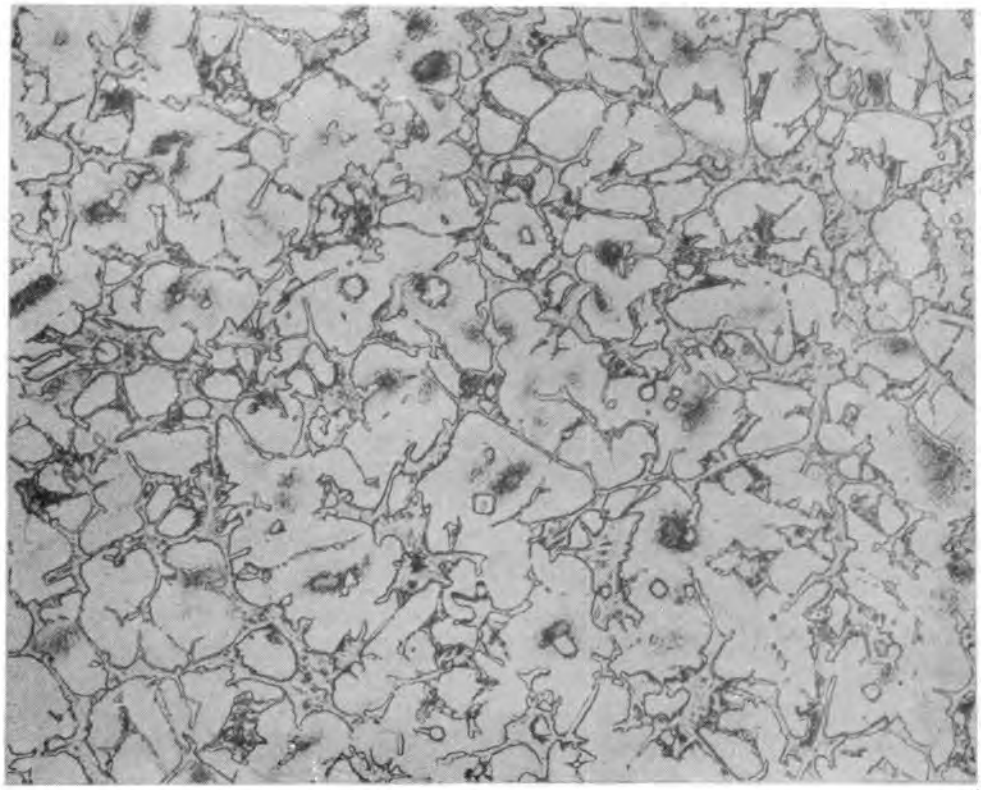


Photo No Y1392 Etch 1% HF 250x

Fig. 2

Center section of button No. 3M as received. Shows less iron-silicon phase than Fig. 1 and area of lowest hardness.

Hardness
DPH
322-430

Photo No Y1378 Etch 1% HF 250x

Fig. 3

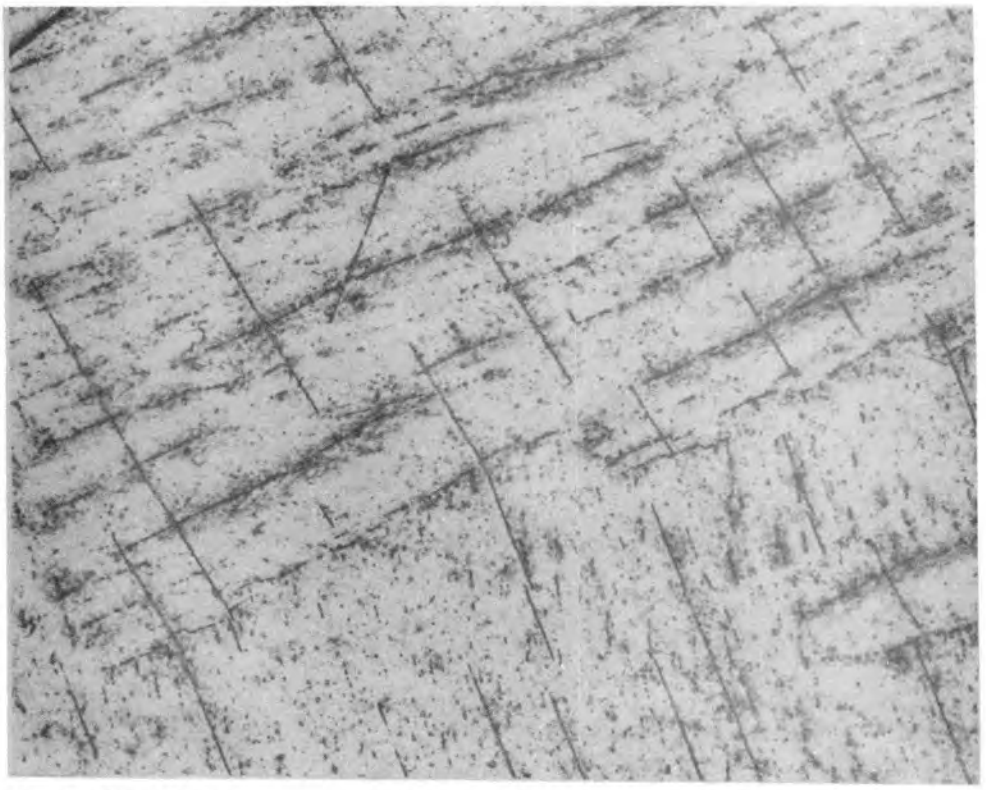
Zirconium button No. 3M melted in graphite crucible. Hardness variation is due to segregation of hard brittle compound.

Hardness
DPH
Matrix 324-3
Complex
ZrC 1028-109

Photo No Y1372 Etch 1% HF 500x

Fig. 4

Zirconium button No. 3M melted in graphite crucible. Shows the DPH impression made in various areas of the structure. A Widmanstatten precipitate may be seen in the hard compound.



Hardness
DPH
80-105

Photo No Y1120 Etch 1% HF 250x

Fig. 5

Crystal bar zirconium as received.

Hardness
DPH
121-137

Photo No Y1373 Etch 1% HF 250x

Fig. 6

Crystal bar zirconium as melted in graphite crucible.

Bureau of Mines Zirconium. A sample of Bureau of Mines zirconium was cold rolled and produced a strip suitable for corrosion test samples. However, after melting in a graphite crucible and picking up additional carbon, the metal cracked badly when the as-cast specimen was subjected to cold rolling. Typical microstructures of Bureau of Mines zirconium as received and after melting in graphite are shown in Figs. 7 and 8.

Zirconium Button—7M. Sample 7M was melted in graphite, scalped and cut into two specimens which were jacketed in steel cans for protection at elevated temperatures. Both specimens were heated to 900°C and forged to break up the cast structure. The steel cans were mechanically stripped from the specimens after air cooling and some edge cracking was observed. Subsequent cold rolling resulted in cracking without deformation. The microstructures of 7M before and after melting are similar to those of 3M.

Zirconium Button—8M. Sample 8M was melted, hot forged at 950°C, air cooled and the steel can removed at Y-12 by dissolving in acid. It was reported that the sample had cracked badly and was apparently attacked along the grain boundaries by the acid. No further treatment was given this sample.

Zirconium Button—10M. Sample 10M was melted but was found to have formed a large shrinkage cavity which made it unsuitable for further working. In spite of the fact that the shrinkage cavity offered numerous stress raisers, the specimen was rolled to show that it was brittle and unable to deform plastically. The microstructure did not resemble that of 3M; however, hardness and rolling qualities were comparable.

Zirconium Button—11M. A button, 11M, was prepared using a CP grade of CaF_2 as the liner material in the reduction bomb. As a result, the silicon content was definitely lowered, but the iron content remained high. Microspectrographic analysis showed the iron to be concentrated at the top surface with none detected at the center. Photomicrographs, Figs. 9 and 10, show this concentration variation with an unidentified phase at the center. The aggregate hardness indicates a more uniform structure with values of 210-240 DPH.

The sample 11M was melted in graphite and cut into four specimens. Specimen Nos. 1 and 2 were forged at 900°C to approximately 40% reduction in area and cold rolled approximately 50% to produce 1/16 in. plates. The cracked edges were cropped and a corrosion test sample was cut from one plate. One corrosion sample was annealed at 600°C and another was submitted for corrosion

Hardness
DPH
140-147

Photo No Y1501 Etch 1% HF 250x

Fig. 7

Bureau of Mines zirconium as received.

Hardne:
DPH
319-3

Photo No Y1514 Etch 1% HF 250x

Fig. 8

Bureau of Mines zirconium as melted in 1 in. graphite crucible.

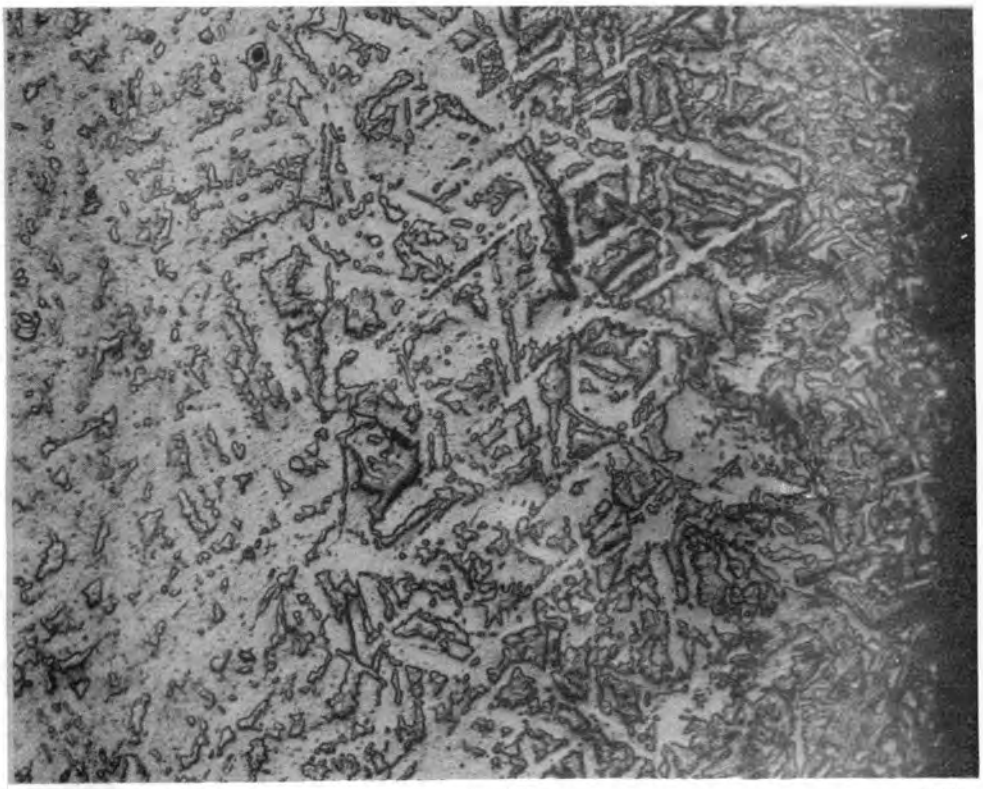


Photo No Y1376 Etch 1% HF 250x

Hardness DPH 210-240

Fig. 9

Top surface of zirconium button No. 11M as received. Shows iron-rich area.

Photo No Y1375 Etch 1% HF 250x

Fig. 10

Center section of zirconium button No. 11M as received. Shows area free of iron-rich phase, second phase not identified.

tests as cold rolled. Specimen No. 3 was forged in the same manner as Nos. 1 and 2. After a 20% reduction by cold rolling a crack developed in the center. This specimen was cut into two sound pieces and numbered 3A and 3B, respectively. Specimen No. 3A was cold rolled to .018 in. thickness for a total reduction of 82%. Specimen No. 3B was annealed at 600°C for 15 minutes and further cold rolled to 24% reduction. Specimen 3B cracked badly indicating that 20% reductions with intermediate anneals show no apparent improvement in rolling quality.

Specimen No. 4 was cold rolled without preliminary forging. Cracks developed after about 10% reduction and progressed rapidly until the entire sample crumbled at 45% reduction. Rolled specimens of 11M, crystal bar and Bureau of Mines zirconium are shown in Fig. 11. The data are tabulated for all samples in Table I in the appendix.

The photomicrograph of 11M, melted in graphite, shown in Fig. 12 reveals an extremely hard dendritic compound (1464-1568 DPH) in a soft matrix (135-177 DPH). The aggregate hardness was 157-203 DPH (R_b 93). A network compound found in the brittle samples was noticeably absent in the samples of 11M as received and after melting in graphite. The hot forged specimens represented by Fig. 13 show that the dendritic structure has been broken up giving a more uniform structure and a smaller range of hardness values (160-166 DPH).

Cold rolling of the forged specimens resulted in a further breakdown of the dendritic structure (Figs. 14 and 15). The cold rolling increased the hardness to 183-194 at 48% reduction and 217-235 at 82% reduction. After annealing at 600°C for 15 minutes the hardness returned to 142-148 DPH for the 48% reduction and to 181-191 DPH for the 82% reduction.

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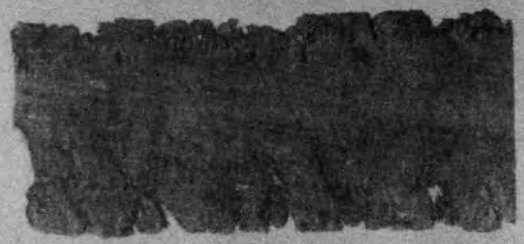
CRYSTAL BAR

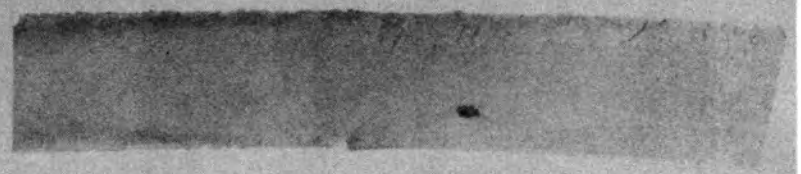
COLD ROLLED-95%

BU. OF MINES

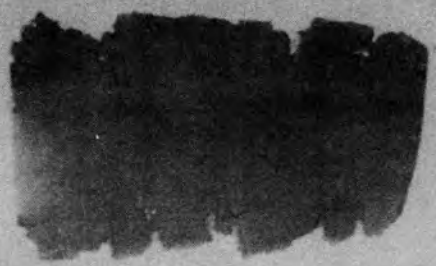


COLD ROLLED-97.4%

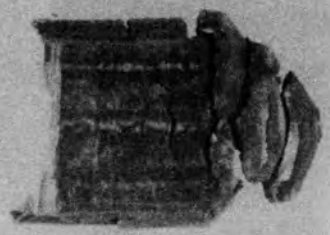
Y-12 NO. 11 M



MELTED IN GRAPHITE
FORGED AT 900°C-50%
COLD ROLLED-82%



MELTED IN GRAPHITE
COLD ROLLED-93.3%

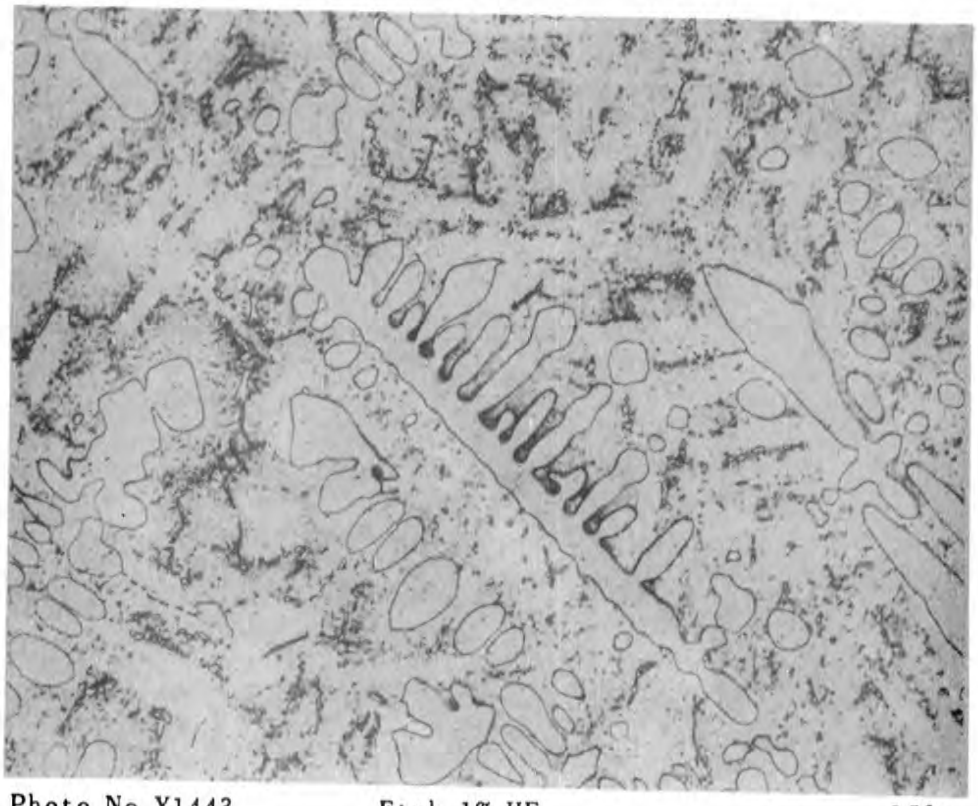


MELTED IN GRAPHITE
COLD ROLLED

MELTED IN GRAPHITE
COLD ROLLED-45%

Fig. 11

COLD ROLLED ZIRCONIUM

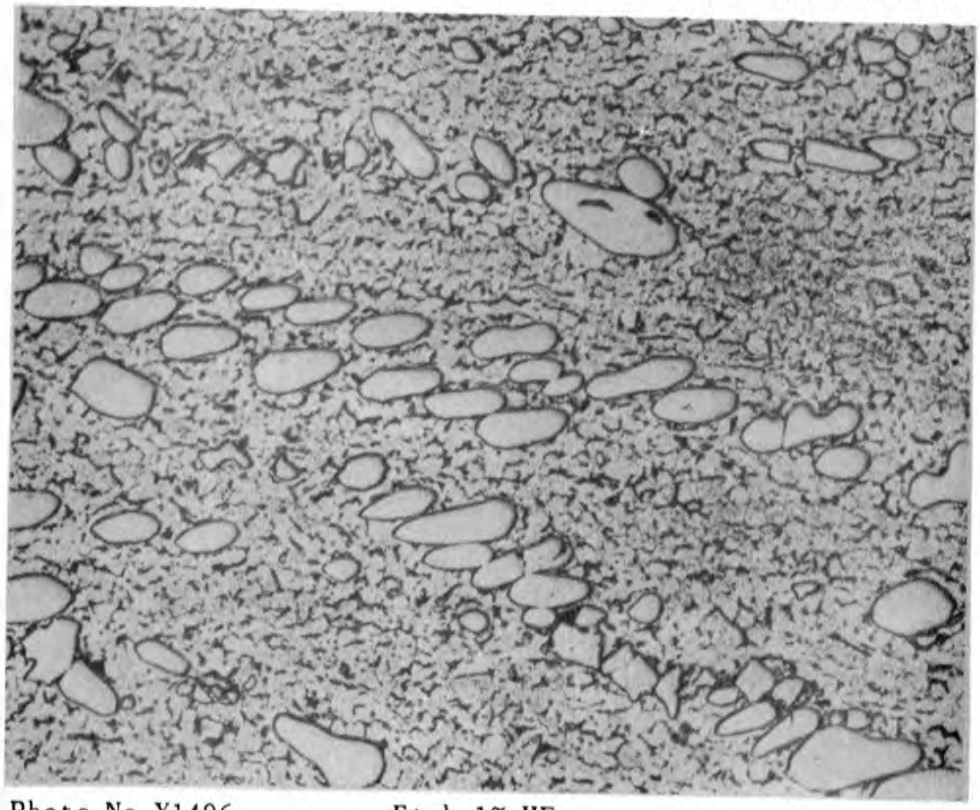


Hardness
DPH
Dendritic
Constituent
1464-1568
Matrix
135-177

Photo No Y1443 Etch 1% HF 250x

Fig. 12

Zirconium button No. 11M melted in graphite crucible. Undoubtedly the absence of the continuous network found in No. 3M melt, Fig. 3, increases the ductility of this metal.

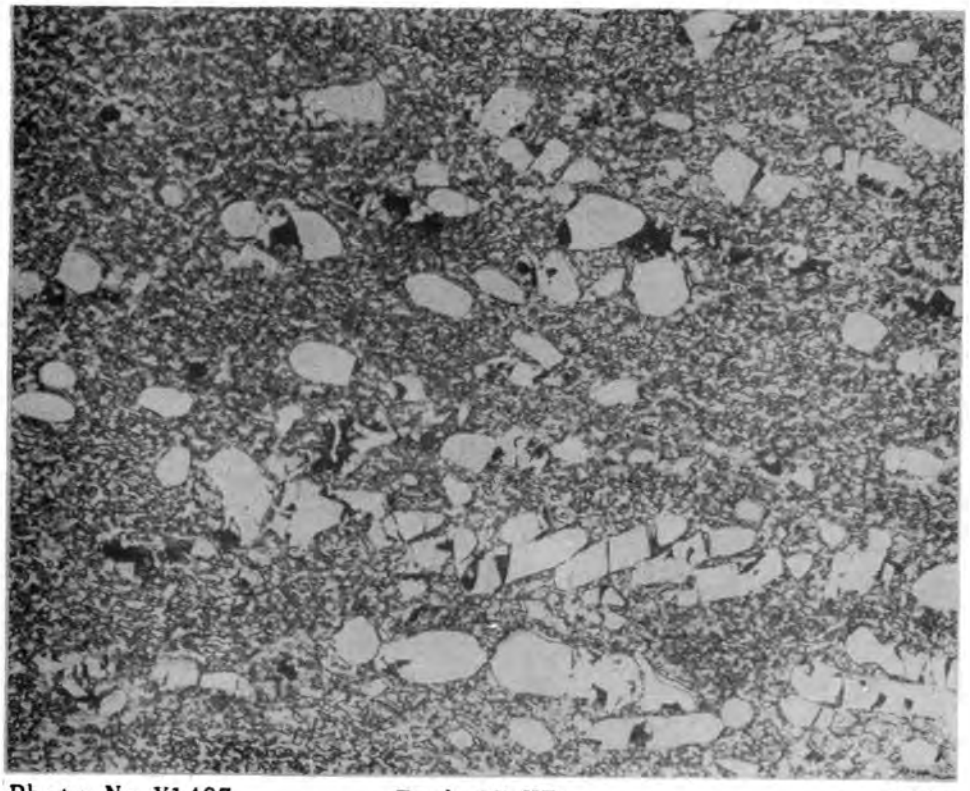


Hardness
DPH
160-166

Photo No Y1496 Etch 1% HF 250x

Fig. 13

Zirconium button No. 11M melted in graphite crucible and hot forged at 900°C. Shows some break up of the dendritic coring and a fine grained recrystallized matrix.



Hardness
DPH
183-194

Photo No Y1497 Etch 1% HF 250x

Fig. 14

Zirconium button No. 11M melted in graphite crucible, followed by hot forging at 900°C and cold rolling to 48% reduction. Shows further break up of the dendritic structure.

Hardness
DPH
217-235

Photo No Y1495 Etch 1% HF 250x

Fig. 15

Zirconium button No. 11M melted in graphite crucible, followed by hot forging at 900°C and cold rolling to 82% reduction. Complete break up of the dendritic structure. The presence of the very hard dendritic compound does not seem to inhibit rolling of this material.

APPENDIX

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TABLE I

SAMPLE NO.		ANALYSIS	ORIGINAL DIMENSIONS BEFORE WORKING	FORGED			COLD ROLLED		HARDNESS, DPH	REMARKS
				TEMP. (°C)	FINAL DIMENSIONS	PERCENT RED.	FINAL DIM. (in.)	T. RED. (%)		
3M		Fe 1.1 Al 1.3 Ca 0.36 Mg 0.07 Ti 0.10	...	...	...	...	...	0	Original button 217-468 Melted in C 322-430 (R_c 38)	Cracked without plastic deformation.
7M	No. 1		0.439"thick x 0.941"dia.	900	0.125"thick x 2"dia.	40.0	...	0	Original button 332-448 Melted in C R_c 26	Considerable edge cracking occurred during hot forging.
	No. 2		0.414"thick x 0.94"dia.	900	0.150"thick x 1-5/8"dia.	37.5	...	0		Cracked without deformation when rolled.
8M			0.25"thick x 0.835"dia.	900	.04"thick x 1-7/8"dia.	64.0	...	...	Melted in C R_c 26-30 Remelted in C R_c 38-50	Cracked badly when hot forged. Can removed with acid.
10M			...	...	...	...	...	...	Melted in C R_c 38	Ingot of poor quality. Cracked when rolled.
11M	No. 1	original button Fe 0.35 Al 2.00 Ca 0.60	0.400"thick x 0.95"dia.	950	.118"thick x .2"dia.	38.0	.0615	48	Original button 210-240(R_b 93) No. 1 melted C 157-203 No. 1 hot forged 160-166 No. 1 CR 48% 183-194 No. 1 annealed 142-148	No. 1, 2, and 3 rolled with slight edge cracking. No. 4 which had not been forged, did not roll well but cracked after 10% reduction and crumbled after 45% reduction.
	No. 2	Mg 0.10 Ti 0.11 Hf ..	0.403"thick x 0.95"dia.	900	.095"thick x 2"dia.	50.0	.034	60		
	No. 3	C 0.04 N_2 0.023 melted in graphite	0.381"thick x 0.95"dia.	900	.100"thick x 1-7/8"dia.	45.5	a).018 b).060	82 40	No. 3 CR 82% 217-235 No. 3 annealed 181-191	
	No. 4	Rolled sample C 1.37 N_2 0.023	0.363"thick x 1"dia.	...	...	...	.200	45		
Iodide Crystal Bar Zr	No. 1 orig. Bar		0.300"thick	...	...	...	.015	95	Original bar 80-103 (R_b 30)	Original bar rolled very well. Sample melted in graphite rolled with some edge cracking.
	Bar melted in C		0.297"thick	...	...	...	.020	93.3	Melted in C 116-137 CR 95%	
Bureau of Mines Zr	Orig. BM Sample		0.600"thick	...	...	...	.016	97.4	Original Zr (R_b 80)	Original sample rolled with fairly severe edge cracking. Sample melted in graphite did not roll but cracked.
	BM sample melted in C		0.600"thick	...	...	...	...	0	Melted in C (R_b 110) CR 97.4%	

[redacted]