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DEVELOPMENTS IN THE ELIMINATION OF
BORON LOSS FROM UO_2 -STAINLESS STEEL
DISPERSION FUEL PLATES FOR THE
ARGONNE ADVANCED RESEARCH REACTOR
MARK I CORE

by

C. Victor Pearson

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Reactor Engineering Division

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DEVELOPMENTS IN THE ELIMINATION OF BORON LOSS FROM UO₂-STAINLESS STEEL DISPERSION FUEL PLATES FOR THE ARGONNE ADVANCED RESEARCH REACTOR MARK I CORE

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I. INTRODUCTION

The Argonne Advanced Research Reactor (AARR) was designed to provide scientists with facilities for conducting basic research in nuclear physics, nuclear chemistry, and solid-state science in thermal-neutron flux environments significantly higher than those afforded by existing research reactors on the Laboratory Site. As completed in fiscal 1966, the Title I design featured a pressurized, light-water-cooled and -moderated, beryllium-reflected, flux-trap-type reactor with a thermal output of 100 MW. Consistent with this power level, the reference Mark I core was being developed to provide, for experimental purposes, unperturbed thermal-neutron fluxes approaching 4×10^{15} n/(cm²)(sec) in the Internal Thermal Column (flux trap), and up to 10^{15} n/(cm²)(sec) in the reflector, where eight horizontal beam tubes were to be located. These tubes, along with proposed dynamic and static vertical irradiation facilities in the ITC and reflector, offered experimenters a wide spectrum of research potentialities. Table I lists the principal design parameters for initial operation of the Mark I core at 100 MW.

Designed for unit replacement, the Mark I core (Fig. 1) consisted of 45 fuel subassemblies, 12 control and safety blades, and supporting structures disposed around the ITC shroud. These structures included the grid plate, core shroud, core holddown, ITC shroud, and lower shroud. Each control and safety blade was guided primarily by the upper end fittings of adjacent subassemblies and the shroud above the core. Within the core, the blades were guided by the subassemblies or the shroud channels. During core loading or unloading operations, the blades were to be locked and supported in the lower shroud guides. Prior to these operations, the ITC facilities were to be removed and replaced with a suitable neutron-absorbing material which served as an additional shutdown device during transport of a new or spent core. The packaged core concept was selected because (1) it significantly foreshortened reactor downtime for refueling; and (2) it provided a high degree of flexibility for unit assembly outside the vessel and partial disassembly within the vessel.

As shown in Fig. 2, each of the 45 fuel subassemblies was rhomboidal in cross section and consisted of Type 347 stainless steel-clad UO₂-SS dispersion-type fuel plates, fabricated by the picture-frame technique. Each

TABLE I. Principal Design Parameters for Initial Operation of AARR Mark I Core

Reactor Power Levels, MW	
Steady-state operation	100
Minimum steady-state burnout	250
Core Life at 100-MW Power Level, days	90
Thermal Neutron Fluxes at 100 MW, $n/(cm^2)(sec)$	
Maximum unperturbed in ITC	3.7×10^{15}
Maximum in typical ITC sample	2.7×10^{15}
Average unperturbed in Be reflector	
Start of fuel cycle	$\geq 1.0 \times 10^{15}$
End of fuel cycle	$\geq 1.0 \times 10^{15}$
Reactor Materials	
Fuel	UO ₂ -SS cermet
Cladding	SS
U ²³⁵ enrichment, %	93.2
Total fuel loading of U ²³⁵ , kg	60 (nom.)
UO ₂ concentration in cermet, wt-%	37 (nom.)
Total B ¹⁰ loading, g/plate	$0.04 \pm 10\%$
Coolant	H ₂ O
ITC moderator	H ₂ O
Radial reflector	Be + H ₂ O
Heat Transfer and Coolant Data	
Normal operating pressure, psi	750
Fuel region	
Geometry	Flat plates in rhomboidal assemblies
Fuel dimensions	
Height of active core, in.	18
Total height of fuel plate, in.	20
Fuel-plate thickness, in.	0.040
Cladding thickness (each surface), in.	0.005
Fuel (cermet) thickness, in.	0.030
Normal coolant-channel thickness, in.	0.040
Hot-channel coolant thickness, in.	0.050
Total number of fuel plates	1167
Total heat-transfer area, ft ²	692
Volume of active core, liters	79.6
Power density, MW/liter	
Average	1.3
Maximum	5
Heat flux, Btu/(hr)(ft ²)	
Average	0.51×10^6
Hot spot	1.94×10^6
Burnout at end of cycle at operating pressure	4.85×10^6
Coolant flowrate, gpm	18,500
Coolant velocity, fps	45
Pressure drop across fuel element, psi	110
Temperature, °F	
Coolant inlet	135
Coolant outlet from core, avg	186
Fuel-plate surface	
Average	205
Maximum	378
Fuel-plate interior, avg	270

Fig. 1. Mark I Core Insert Assembly

Fig. 2. Sectional Views of Fuel Subassembly and Fuel Plates

plate was 20 in. long, 2.546 in. wide, and 0.040 in. thick, with an active fuel region 18 in. long, 2.370 in. wide, and 0.030 in. thick. Physics requirements dictated a minimum of diluent material in the active core region. Therefore, in lieu of side plates, the fuel plates were to be spaced and supported by wires brazed along the edges and centerline of the plates. Brazing was determined to be the only feasible method for securing a complete bond of the center spacer to both adjacent fuel plates. Rhomboidal end fittings, fabricated from Type 347 stainless steel, were to be brazed to plate extensions at the top and bottom. The lower end fitting tapered to a cylindrical cross section for positioning in the core grid plate. Identical upper end fittings were to be installed on all subassemblies to facilitate handling by the same mechanisms.

Five types of subassemblies were to be used, differing only in the number of fuel plates, fuel content and spacing (see Fig. 3 and Table II). A standard fuel plate contained a uniform dispersion of highly enriched (93% U^{235}) spheroidal uranium dioxide particles (37 wt-% max) in a matrix of Type 347 stainless steel. Stainless steel was selected over the originally proposed aluminum core because of its superior strength at reactor operating conditions above 100 MW.* In addition, physics calculations had shown that the UO_2 -SS core: (1) virtually eliminated the shutdown xenon problem posed by the aluminum core, and (2) offered a significantly longer core life. However, a sufficient amount of stable boron compound was required to be uniformly distributed throughout each fuel plate to provide additional reactivity holddown during initial operations. Also, to minimize power peaking at the inner and outer edges of the core, fuel plates in these areas were to contain varied amounts of fuel and boron. Thus the reference Mark I core loading of 60 kg of U^{235} and 250 g of B^{nat} provided a maximum of 9% available excess reactivity during the core lifetime (~90 days at 100 MW and proportionately less at higher power levels).

Design studies in heat transfer, hydraulics, stress analysis, and physics indicated that successful operation at higher power levels (150-180 MW was considered the safe upper limit) was contingent on minimizing variations in specifications affecting flux peaking and generation of local hot spots. Table III lists the tolerances used in the design analysis and those specified for fabrication and inspection of the reference Mark I core. In view of the stringent specifications, all studies relating to fabrication and quality control were focused on maintaining close dimensional tolerances and accurate loading and uniform distribution of fuel and burnable poison in the fuel plates and subassemblies. As can be seen in Table III, the largest variation in quality assurance occurred in the control of the burnable poison.

*AARR was intended to eventually operate at 240 MW.

SUBASSEMBLY TYPE:		A		B		C		D		E	
NUMBER REQUIRED:		6		3		15		18		3	
FUEL PLATES/S'ASSY:		29		29		30		22		20	
DIMENSIONS "H":		2.390		2.390		2.360		1.780		1.750	
FUEL PLATE:	NO.	TYPE	SPACE NO.	TYPE	SPACE NO.	TYPE	SPACE NO.	TYPE	SPACE NO.	TYPE	SPACE NO.
	1	UG-7	0.050	CG-7	0.050	N-1	0.040	N-1	0.040	CG-4	0.050
	2	UG-6		CG-6							
	3	UG-5		CG-5							
	4	UG-4		CG-4							
	5	UG-3		CG-3							
	6	UG-2		CG-2							
	7	UG-1		CG-1							
	8	N-1		N-1							
	9										
	10										
	11		0.050		0.050						
	12		0.040		0.040				0.040		
	13								0.050		
	14										
	15										
	16										
	17										
	18										
	19										
	20										
	21										
	22										
	23										
	24										
	25										
	26										
	27										
	28		0.040		0.040						
	29	N-1		N-1							
	30

NOTE: ALL DIMENSIONS IN INCHES

Fig. 3. Characteristics of Five Types of Fuel Subassemblies Used in Mark I Core

TABLE II. Fuel-plate Loading for Mark I Core

PLATE COMPOSITION													
PLATE TYPE	TOTAL NO.	UO ₂				U ²³⁵				Nb-ZrB ₂		B ¹⁰	
		wt-% (nom.)		g		Enrich, %		g		g		mg	
N-1	990	37.0		65.353		93.15		52.358		1.866		3.953	
UG-1	6	33.3		58.547		93.15		46.901		1.866		3.953	
UG-2	24	27.8		48.484		93.15		38.839		1.866		3.953	
UG-3	24	22.2		38.400		93.15		30.762		1.866		3.953	
UG-4	27	17.4		29.888		93.15		23.943		1.866		3.953	
UG-5	6	13.7		23.408		93.15		18.751		1.866		3.953	
UG-6	6	10.3		17.513		93.15		14.029		1.866		3.953	
UG-7	6	8.1		13.729		93.15		10.998		1.866		3.953	
		A	B	A	B	A	B	A	B	A	B	A	B
CG-1	3	37	37	20.681	44.672	83.84	93.15	14.911	35.786	9.590	1.276	1.250	2.703
CG-2	3	37	37	20.681	44.672	69.98	93.15	12.448	35.786	0.590	1.276	1.250	2.703
CG-3	3	37	37	20.681	44.672	55.89	93.15	9.941	35.786	0.590	1.276	1.250	2.703
CG-4	54	37	37	20.681	44.672	43.81	93.15	7.791	35.786	0.590	1.276	1.250	2.703
CG-5	3	37	37	20.681	44.672	34.49	93.15	6.135	35.786	0.590	1.276	1.250	2.703
CG-6	3	37	37	20.681	44.672	25.93	93.15	4.612	35.786	0.590	1.276	1.250	2.703
CG-7	3	37	37	20.681	44.672	20.39	93.15	3.627	35.786	0.590	1.276	1.250	2.703
IG-1	3	27.8	27.8	15.343	33.141	43.81	93.15	5.781	26.549	0.590	1.276	1.250	2.703
IG-2	3	22.2	22.2	12.152	26.248	43.81	93.15	4.578	21.027	0.590	1.276	1.250	2.703

TOTAL CORE LOADING

PLATES: 1167

U²³⁵, g: 58,017.42 (72,423.10g UO₂ (85% T.D.))

B^{nat}, g: 250 (2,177.51g Nb-coated ZrB₂)

NOTE: ALL DIMENSIONS IN INCHES.

TABLE III. Comparison of Design Allowances with Fabrication and Inspection Tolerances for Mark I Core

	Design Allowance, %	Fab. & Insp. Tolerance, %
UO ₂ Distribution in Plate		
Locally (0.5-cm ² areas)	6	6
In any 1-cm ² area (nom max)	5	3
Total UO ₂	5	1
Boron Distribution in Plate		
Locally (0.5-cm ² areas)	~5	<5
In any 1-cm ² area (nom max)	~5	<5
Difference in loading between plates	10	10-20 (nom) ^a
Fuel-plate Dimensions and Mass	3	3
Fuel-plate Spacing (Coolant Channel Variation)		
Locally (1-cm ² areas)	<3	3
Channel spacing (nom avg)	<3	2

^aBased on nominal control of fabrication procedures, as reported by previous investigators. Work reviewed in this report shows that the variation can be reduced to the level of accuracy of measurement (2-3%).

This report treats only the problems encountered in developing techniques for controlling boron loss during fabrication of the fuel plates and brazing of the fuel subassemblies. An attempt to derive a substitute mixture of other high-cross-section elements¹ proved unsuccessful. In the final analysis, boron remained the only practical material to use as the burnable poison.

At the outset, a study was undertaken to assess the qualitative aspects of mechanisms contributing to boron loss. The intent here was to achieve a means for minimizing or even eliminating the problem. A literature review indicated that most of the problem areas had been studied with sufficient thoroughness that further investigation of the deboronization mechanisms under the AARR fuel development program was not warranted.

Therefore, efforts were focused on the effect of certain variables in the UO₂-SS dispersions fabrication process. The objective was to determine where the reference AARR fuel-plate fabrication and assembly processes had to be modified and/or rigidly controlled to minimize or eliminate the boron loss without adversely affecting the fuel quality.

II. PROGRAMMATIC EFFORTS

Problems associated with fabrication of UO₂-SS dispersion-type fuels of general interest to the AARR Mark I fuel development program had received considerable attention in earlier reactor development programs elsewhere. The problem of specific interest, i.e., boron loss in fuel plates, had been investigated by Battelle Memorial Institute (Columbus, Ohio) and

Oak Ridge National Laboratory under the Army Nuclear Power Program. Unfortunately, that program was terminated before a quantitative assessment of the deboronization mechanisms could be achieved. As an alternate to resolving the deboronization problem with the Army SM reactor fuel plates, the core for the PM reactor series was redesigned to accommodate tubular fuel elements having a lumped, rather than a uniform, poison distribution. In this instance, optimum fabrication processes were developed for the UO_2 -SS fuel tubes and the separate inner rods which contained the burnable poison.

Nonetheless, lumped poisoning of the Mark I core was impractical because of the high power densities associated with the AARR. Flux peaking in the tubular fuel configuration would result in excessive heat generation and ultimate burnout. Uniform distribution of a boron-bearing burnable poison was the only practical way to achieve the desired nuclear characteristics in the AARR.

A. Selection of Burnable Poison

Elemental boron could not be used because the AARR fuel-plate fabrication process (see Appendixes A and B) required hydrogen atmospheres at temperatures well into the range where deboronization reportedly²⁻⁸ occurred at a significant and almost predictable rate.

Boron carbide (B_4C) also was reported³⁻⁵ to react in a stainless steel matrix under conditions similar to those employed in the AARR fuel-plate fabrication process. This undesired reaction was compounded further by the questionable behavior and effect of the residual carbon on the fuel plates. On the other hand, Beaver *et al.*⁶ observed no adverse effects from the residual carbon in Type 347 stainless steel. Nevertheless, their observation did not justify the use of the potentially detrimental carbide, particularly since ultimate assembly of the fuel plates by brazing required prolonged exposure of the stainless steel to temperatures in the sensitizing range.

Zirconium diboride (ZrB_2) also was known to behave erratically at high temperatures.^{3,4,7,8} Zirconium diboride had been used in the SM fuel plates with partial success, but no attempt was made to minimize its erratic performance. However, more information was available on this material than on others that might be considered compatible with the AARR fuel fabrication process. Accordingly, ZrB_2 was selected as the reference burnable poison.

More recent studies at BMI had shown that the integrity of the boron compound could be preserved by using a proper barrier material.⁹ In particular, a 4- to 6-micron-thick coating of niobium, with a thin barrier of

chromium carbide between the niobium and ZrB_2 , was shown to markedly inhibit boron loss during fabrication of UO_2 -SS fuel plates. Other barrier materials (e.g., vanadium) also showed promise; however, to warrant serious consideration, any alternate to niobium as a barrier material had to meet certain basic requirements. In addition to a low neutron-absorption cross section, these requirements were:

- (1) Afford a contiguous barrier coating for the irregular-shaped ZrB_2 .
- (2) Possess sufficient ductility, strength, and chemical and metallurgical stability at room temperature and at the fabrication temperatures, to maintain the integrity of the barrier.
- (3) Possess a low permeability to H_2 , O_2 , and H_2O at the fuel-plate fabrication-process temperature.

Vapor disposition of elements or compounds appeared capable of satisfying the first requirement. The second requirement eliminated several potential materials; the third requirement narrowed the field further.

Based on work by Webb,¹⁰ Leitten,¹¹ and others, niobium was selected as the reference barrier material, and behavioral studies were conducted with elemental stainless steel coatings. Stainless steel was reported¹⁰ to have the same permeability to hydrogen as niobium. These studies would also help identify the relative significance of each mechanism contributing to the general problem of boron loss, as postulated by previous investigators.

An alternate activity to the niobium and stainless steel barrier studies was to circumvent the problem of boron loss by fixing a boron compound in a relatively inert material, e.g., borosilicate glasses. Earlier work by Watts,¹² Anderson,¹³ and Leitten¹⁴ on borosilicate glass beads had shown that the higher-boron-content glasses (greater than 20 wt-% B_2O_3) possessed insufficient strength at the plate-fabrication temperatures to be of practical value. Thus it was apparent that, if glass beads were to be used in the AARR fuel plates, the ratio of boron to diluent would of necessity be much lower than would be the case for niobium-coated ZrB_2 . The high-softening-temperature Pyrex glasses, having a nominal 12 wt-% B_2O_3 , yield a net boron content of 3.5 wt-% versus approximately 11.5 wt-% in the niobium-coated ZrB_2 . Thus the borosilicates ultimately would have to contain enriched boron if the net amount of glass beads added to the fuel-plate dispersion was to be kept down to a reasonable level.

B. Work Assignments

Work on burnable poisons for the Mark I core was performed by Martin Marietta Corporation Nuclear Division, BMI, and ORNL in Phase II

of the AARR fuel-development program. Each of these organizations had been active in developing fuels for the Army reactors.

Phase I had established optimum fabrication techniques for the 37 wt-%-SS dispersion fuel plates. Also, the effect of variables in the fabrication process on the overall quality of the dispersion had been assessed on the basis of metallographic and irradiation performance tests of specimen plates. More specifically, BMI and Martin Marietta Corp. had modified the SM and the advanced PM fuel-fabrication techniques, respectively, to adapt them to the AARR requirements. (The SM fuel used conventional powder metallurgy, powder blend, press, and picture-frame assembly techniques; the advanced PM fuels used a stainless steel-encapsulated UO_2 , extrusion press, and hydrostatic compaction process.) Both organizations had evolved an acceptable, flat fuel plate whose physical dimensions, microstructure, and irradiation behavior were considered capable of meeting the Mark I core requirements. The BMI process was selected as the reference, with the Martin process as the backup or alternate method.

The Phase II studies were directed toward: (1) circumventing the deboronization problems encountered during the Army reactor fuel development programs; and (2) establishing a fabrication process that would produce a high-quality UO_2 -SS dispersion fuel containing a closely controlled, uniformly distributed, burnable-boron-bearing material. The studies consisted of two parts: (1) attempt to verify the deboronization mechanisms reported under the Army Nuclear Power Program, and assess the quantitative aspect of these mechanisms as they apply to the AARR fuel-plate fabrication process; and (2) establish parameters for the reference plate fabrication process that will preserve the quality of dispersion obtained in the Phase I studies, yet ensure optimum and uniform retention of the boron. Emphasis was on quality assurance, since nondestructive testing for boron content and distribution in each plate was impractical.

The specific areas of study assigned to the participating organizations were as follows:

BMI: Determine areas of incompatibility of the niobium-barrier-coated ZrB_2 with the AARR Mark I core initial reference fuel-plate fabrication process, and develop a revised fabrication procedure.

ORNL: As a backup to the above studies, evaluate the behavior of various types of borated glass beads using the reference fabrication process.

Martin Corp.: Investigate problems associated with application of a stainless steel barrier coating to ZrB_2 . Also, evaluate the compatibility of the coated poison using their alternate fuel-plate fabrication process for the AARR Mark I core.

C. Procedures and Results

1. Stainless Steel Barrier Coatings on ZrB_2

Most of the work in this area, conducted by J. Monroe and L. Sandquist at Martin Marietta Corp., was concerned with determining to what extent the reactions postulated and assumed by Ward *et al.*,⁸ Cherubini,² Paprocki *et al.*,^{4,15} and others^{3,7,12,16} would be experienced during manufacture of the AARR fuel. This work included attempts to determine what means would be necessary to control these reactions or to eliminate their occurrence. Two coating processes--oxide encapsulation and metal spraying--were investigated, with results as described in the following paragraphs.

a. Oxide-encapsulation Process

Initial efforts were directed toward using the same process for applying a stainless steel barrier to the ZrB_2 particles as was used previously for encapsulating each UO_2 particle. In the latter process, developed for the Advanced Army Reactor Fuel Program¹⁷⁻¹⁹ and modified for the AARR fuel,²⁰ each spherical UO_2 particle (100-150 μ diameter) was coated with a thick layer of Fe_2O_3 , Cr_2O_3 , and NiO_2 in the ratio of 18-8 stainless steel. The coated particle was then spray-flame fired in hydrogen to reduce the oxides and produce a UO_2 -centered stainless steel ball with a reference ratio of 37 wt-% UO_2 and 63 wt-% SS. This process had produced a coated UO_2 particle of very acceptable quality and conceivably could be employed on the ZrB_2 particles, provided the detrimental reactions could be controlled.

To evaluate the magnitude of reaction incurred under conditions required to reduce the oxides to the metallic state, samples of oxide-coated ZrB_2 were exposed for 1 hr in a hydrogen atmosphere at 1150°C. Subsequent metallographic examination revealed (as shown in Fig. 4) that extensive reaction had occurred.

Chemical analysis showed the boron content to be less than 50% of the original value. Deboronization was attributed to the higher negative free-energy reactions postulated by Ward *et al.*⁸ and by the author. Table IV lists these reactions.

Electron-microprobe analysis of a partially reacted specimen provided some insight into the deboronization mechanisms.²¹ With reference to Fig. 5, the reaction zone contained about 25% of the original boron content, whereas none was present in the gray or completely reacted zone. The apparently unreacted ZrB_2 contained 1% iron, whereas the reaction zone contained 16% iron and the gray zone only a trace of iron. Zirconium concentration in the reaction zone was ~50 wt-%, compared with 60 wt-% in the gray zone and ~81 wt-% in stoichiometric ZrB_2 . No boron

As-received ZrB_2

After reduction of oxide coating

Fig. 4. ZrB_2 Particles as Received and after Reduction of Mixed-oxide Coating for 1 hr in Hydrogen at 1150°C (Reduced by 8% photographically)

TABLE IV. Principal Suspect Reactions Involved in
Deboronization of ZrB_2 at 1150°C

	Standard Free Energy of Reaction, kcal
<u>Reduction of Oxides</u>	
(1) $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}(\text{g})$	-11.2
(2) $\text{Cr}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Cr} + 3\text{H}_2\text{O}(\text{g})$	+62.34
(3) $\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O}(\text{g})$	-14.40
(4) $\text{ZrB}_2(\text{c}) + 2\text{Fe}_2\text{O}_3(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + 1/2 \text{B}_2\text{O}_3(1) + \text{FeB}(\text{c}) + 5/2 \text{FeO}(\text{c}) + 1/2 \text{Fe}$	-127.35
(a) $\text{ZrB}_2(\text{c}) + 7/2 \text{FeO}(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + 1/2 \text{B}_2\text{O}_3(1) + \text{FeB}(\text{c}) + 5/2 \text{Fe}$	-99.00
(b) $\text{ZrB}_2(\text{c}) + 2\text{FeO}(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{FeB}(\text{c})$	-52.01
(c) $\text{ZrB}_2(\text{c}) + 2\text{FeO}(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + \text{Fe}_2\text{B}(\text{c}) + \text{B}(\text{c})$	-49.53
(d) $\text{ZrB}_2(\text{c}) + 5/2 \text{FeO}(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + 3/2 \text{FeB}(\text{c}) + 1/2 \text{BO}(\text{g}) + \text{Fe}(\text{c})$	-48.94
<u>Reactions with $\text{O}_2 + \text{H}_2\text{O}$</u>	
(1) $\text{ZrB}_2(\text{c}) + 5/2 \text{O}_2(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + \text{B}_2\text{O}_3(1)$	-352.69
(2) $\text{ZrB}_2(\text{c}) + 5/2 \text{O}_2(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + \text{B}_2\text{O}_3(\text{g})$	-316.89
(3) $\text{ZrB}_2(\text{c}) + 2\text{O}_2(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + \text{B}_2\text{O}_3(\text{g})$	-203.07
(4) $\text{ZrB}_2(\text{c}) + 8\text{H}_2\text{O}(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{H}_3\text{BO}_3(\text{g}) + 5\text{H}_2(\text{g})$	-142.70
(5) $\text{ZrB}_2(\text{c}) + \text{O}_2(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{B}(\text{c})$	-129.09
(a) $\text{ZrB}_2(\text{c}) + \text{O}_2(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{B}(\text{g})$	+51.25
(6) $\text{ZrB}_2(\text{c}) + 6\text{H}_2\text{O}(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{HBO}_2(\text{g}) + 5\text{H}_2(\text{g})$	-128.43
(7) $\text{ZrB}_2(\text{c}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{Zr}(\text{c}) + \text{B}_2\text{O}_3(\text{g})$	-119.56
(8) $\text{ZrB}_2(\text{c}) + 5\text{H}_2\text{O}(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + \text{B}_2\text{O}_3(\text{g}) + 5\text{H}_2(\text{g})$	-105.15
(9) $\text{ZrB}_2(\text{c}) + 4\text{H}_2\text{O}(\text{g}) \rightarrow \text{ZrO}_2(\text{c}) + 2\text{BO}(\text{g}) + 4\text{H}_2(\text{g})$	-41.62
(10) $\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O}(\text{g})$	-40.34

Fig. 5. Cross Section of Partially Reacted ZrB_2 Showing Results of Electron-microprobe Analysis

was detected in the stainless steel barrier, but the iron content was reduced as much as 25% in some areas. Areas low in iron were high in nickel and chromium. Only traces of nickel and chromium were present in the reaction zone. Figure 6 is a highly magnified view of the severely reacted coated ZrB_2 particles in Fig. 5.

The presence of iron in the reaction zone is to be expected since, as shown in Table V,²² the lowest temperature eutectic that can be formed from the materials available contains 84 wt-% Zr and 16 wt-% Fe. Also, the $\text{ZrB}_2 + 2\text{Fe}_2\text{O}_3$ reaction results in formation of FeB as well as Fe, so the driving force for attack on the ZrB_2 is oriented preferentially toward the iron. Figures 7 and 8 show simplified phase diagrams²² of the principal suspect reactants.

b. Metal-spraying Process

Three series of tests were made with ZrB_2 particles sprayed with 0.8- to 1.2-micron-size, stainless steel metal powder to the desired weight-percentages: 37.5 ZrB_2 and 62.5 SS. The submicron-size powders were made by a NASA process, which consisted of ball milling in alcohol with stearic acid additions.²³

In the first series of tests, two groups of coated particles were sintered. The one group was sintered in hydrogen for 1 hr at 1175°C, the other in a vacuum for 1 hr at 1175°C. In both cases, the specimens experienced severe reactions accompanied by indications of internal melting.

No electron-microprobe analysis was made since the same type of reactions postulated for the encapsulated particles was obviously also occurring here. (The source of oxygen was attributed to surface oxides on the stainless steel powder.) The big difference was that the formation of eutectics was more evident, indicating that the chemical reaction had been inhibited and the metallurgical phenomenon had proceeded before the boron and/or the zirconium could form their stable compounds. Regardless of the mechanism postulated, the results had the same net effect: gross degradation of the ZrB_2 .

In the second series of tests, the specimens were sintered for 65 hr in hydrogen at 1000°C. Metallographic examination revealed that the ZrB_2 was severely reacted, but there was no indication of melting. Some of the specimens were then resintered for 1 hr in hydrogen at 1175°C. Again, subsequent examination revealed evidence of a severe reaction, but no sign of melting. It was concluded that the zirconium had formed a stable oxide and that the boron had formed a stable compound, which probably had been driven off, in some volatile form, from the specimen. However, the ZrB_2 was still intolerably degraded.

Fig. 6. High-magnification Photomicrograph Showing Nature of Change in Severely Reacted ZrB_2 Particle

TABLE V. Eutectic Temperatures Associated with ZrB_2 -SS Reactions

Temp, °C	Eutectic, wt-%
934	84 Zr-Fe ^a
961	24 Zr-Ni
985	36.5 Zr-Ni
990	13 B-Ni
1125	10 B-Ni
1140	4 B-Ni
1149	4 B-Fe ^a

^aStrong driving force available for formation of these eutectics if oxygen is present (see Table IV).

NOTE: Where appearing below temperature on face of graph, wt-% in parens, at-% without parens.

Fig. 7. Phase Diagrams of B-Ni and Ni-Zr Alloys

In the third series of tests, two groups of specimens were sintered, one in hydrogen and the other in vacuum, for 30 min at 830°C. Metallographic examination revealed evidence of a slight reaction in specimens sintered in hydrogen, but no signs of reaction in specimens sintered in vacuum. The consensus was that this definitely established the hydrogen reduction of surface oxides to form water vapor, with subsequent reaction between the ZrB_2 and H_2O , as the primary mechanism for boron release.

A vacuum thermogravimetric analysis was made of a stainless steel-coated ZrB_2 specimen to identify the temperature-weight loss relationship. The specimen showed a total weight loss of 8 wt-% up to 1200°C. Approximately 50% of this weight loss (4 wt-%) occurred up to 550°C, and 90% (or 7.2 wt-%) occurred up to 850°C.

c. Stepwise Vacuum Sinter Process

Based on the results of the foregoing tests, the following sinter process was conducted:

- (1) Heat from room temperature to 600°C while maintaining a vacuum of $\leq 5 \times 10^{-5}$ Torr.
- (2) Hold at 600°C for 3 hr while increasing the vacuum to 10^{-6} Torr.
- (3) Raise temperature to 800°C while maintaining a minimum vacuum of 5×10^{-5} Torr.
- (4) Hold at 800°C for 3 hr while increasing the vacuum to 10^{-6} Torr.
- (5) Raise temperature to 1000°C for 16 hr, and decrease the vacuum to 5×10^{-5} Torr.
- (6) Hold at 1000°C for 16 hr, and increase the vacuum to 10^{-6} Torr.
- (7) Furnace cool.

Stainless steel-coated ZrB_2 particles sintered according to this procedure experienced only slight reaction at the SS- ZrB_2 interface. Less than 5% of the particles evidenced any significant reaction. Figure 9 shows cross sections typical of these observations. Chemical analysis indicated a total boron loss of ~2.2%.

2. Stability of Niobium-coated ZrB_2 in AARR Fuel Plates

BMI had developed the niobium and chromium carbide coating technique in a previous program for the express purpose of eliminating the types of reactions described in the preceding subsection. Briefly, the technique involved a process whereby arc-melted and crushed ZrB_2 particles were vapor-coated with a 1-micron-thick layer of chromium carbide followed by a 4-micron-thick layer of niobium. The carbide layer was applied by pyrolysis of dicumene chromium. This layer protected the ZrB_2 from reacting with the halogen-containing atmosphere present during subsequent niobium coating by hydrogen reduction of NbCl_5 . It also acted as a barrier to prevent formation of the 17.5 wt-% Nb - 82.5 wt-% Zr eutectic at 610°C.

Fig. 9. Typical Effects of Stepwise Vacuum Sintering Process on Stainless Steel-coated ZrB_2 Particles. (Left) Slight reaction at SS- ZrB_2 interface of most specimens; (Right) Significant reaction of ZrB_2 in less than 5% of specimens tested. (Reduced by 15% photographically)

Although niobium possessed all the characteristics required for a good reaction barrier, very little was known of its behavior under the optimized AARR fuel fabrication-process conditions. Of particular interest was the extent of formation of the 51.6 wt-% Nb - 48.4 wt-% Ni eutectic (M.P. = 1175°C) during fabrication of the fuel plates and brazing of the sub-assemblies. Earlier Phase I studies had established that fabrication temperatures could not be reduced appreciably below 1175°C if good-quality dispersion, low breakup of the UO_2 , and sound brazed joints with the GE J8100 alloy (brazing temperature = 1150-1160°C) were to be achieved. Also, continuity and integrity of the niobium coating during the fabrication process was essential to prevent chemical reactions and the formation of lower-temperature eutectics between Zr, B, Fe, and Ni.

The studies with niobium-coated ZrB_2 by D. E. Lozier and D. E. Kizer at BMI were concerned more with the metallurgical aspect than with the chemical aspect of eliminating the boron loss. They included the effect of plate rolling temperatures, different types and sizes of matrix feed materials, and reference braze cycle conditions, with the results described in the following paragraphs.

a. Effect of Plate Rolling Temperatures

To determine the relative extent of degradation of the ZrB_2 , dispersion compacts containing uncoated and niobium-coated ZrB_2 particles were rolled into sample fuel plates at 1150, 1175, and 1200°C.

Prior to rolling, all compacts were vacuum-sintered, pressed, and assembled using the initial reference process outlined in Appendix A.

Subsequent metallographic examination of the plates showed that the uncoated and coated ZrB_2 particles performed well at 1150°C . At 1175°C , the uncoated particles evidenced degradation and melting in the surrounding matrix. With respect to the coated particles, the niobium acted as a sacrificial barrier and showed signs of reacting during the relatively short time (<1.5 hr) at temperature. At 1200°C , both the coated and uncoated ZrB_2 particles experienced severe reactions.

Figures 10 and 11 show typical microstructures of the plates rolled at 1175 and 1200°C , respectively. In general, the attack on the ZrB_2 particles was predominantly a surface phenomenon, and particles that were badly fractured and stringered experienced the greatest reaction. As shown in Fig. 10, at 1175°C the smaller fragments of coated ZrB_2 particles reacted more severely than the smaller uncoated particles. (The reaction products were believed to be a niobium-zirconium alloy.) By comparison, the larger fragments experienced less reaction, and this is attributed to the partial protection afforded by the intact coating. Also, unlike the plate specimens with uncoated ZrB_2 particles, there was no evidence of melting and deposition of a binary or ternary eutectic in the matrix grain boundaries.

As shown in Fig. 11, both the uncoated and coated ZrB_2 particles appeared to have experienced severe reactions at 1200°C . However, closer examination of the microstructures revealed that the reaction between the uncoated particles and the matrix left only a type of metallurgical fossil at the original site of the respective particles. In contrast, the coated particles appear to have derived some benefit from the niobium in delaying the onset of reaction during the time period involved. Melting occurred in both types of specimens. Some of the melted material was deposited in open pores in the UO_2 , indicating the mobility of the molten mass during rolling operations.

As a result of these tests, the upper limit on the rolling temperature was established at $1150 \pm 20^\circ\text{C}$, and efforts were directed toward optimizing the fuel-plate fabrication process using this lower temperature.

b. Effect of Matrix Feed Materials

Previous studies had shown that dispersions made by different vendors, using essentially the same fabrication process on their own equipment, resulted in plates that differed in quality. Therefore, the studies at BMI included assessment of the effect that different blends of various types and sizes of Type 347 stainless steel powders had on the quality of the dispersion. Emphasis was on how these blends affected breakup of the UO_2 and ZrB_2 particles.

Figure 12 shows typical dispersions obtained with the different blends and the equipment used by BMI.

As a result of these studies, the initial reference fabrication process was revised to one that produced the least breakup of the UO_2 and the ZrB_2 . Appendix B lists the Revised Reference Materials and Fabrication Process Procedures evolved from the BMI studies.

Fig. 10. Typical Microstructures of Plate Specimens Containing (Left) Uncoated and (Right) Niobium-coated ZrB_2 Particles; Plate Rolling Temperature: 1175°C (Reduced by 15% photographically)

Fig. 11. Typical Microstructures of Plate Specimens Containing (Left) Uncoated and (Right) Niobium-coated ZrB_2 Particles; Plate Rolling Temperature: 1200°C (Reduced by 10% photographically)

Fig. 12. Typical Microstructures of 0.040-in.-thick Plates Made with Different Blends of Type 347 Stainless Steel Matrix Powders and 80% T.D., -100 +140 Mesh, 231-g Crush Strength, Depleted UO_2

c. Effect of Reference Braze Cycle

Developed by Pyromet Co., the reference cycle for brazing 27 fuel plates into a rigid, completely bonded, close-tolerance subassembly required stepwise heating and cooling, with an ultimate hold for 30 min at $1170^{\circ}C$.²⁴ Therefore, the effect of these conditions on the matrix structure and niobium-coated ZrB_2 particles was also evaluated.

Several test plates were rolled at 1150°C and flat-annealed at 1120°C. Some were examined in the as-annealed condition; others were exposed to a simulated braze-cycle heat treatment and then examined. All heat-treated plates showed (see Fig. 13) evidence of coarsening in the matrix grain structure and the onset of reaction between the niobium barrier and the stainless steel. There also was some evidence of widening of the gray reaction zone in the ZrB_2 , on both the outer surfaces and those of the internal cracks.

Fig. 13. Typical Niobium-coated ZrB_2 Particles (Top) Rolled and Flat Annealed at $<1160^\circ\text{C}$; (Bottom) Rolled and Flat Annealed at $<1160^\circ\text{C}$, Then Braze-cycle Heat Treated for 0.5 hr at 1175°C (Reduced by 15% photographically)

Analysis for boron in the core and the cladding of both sets of plates indicated no deboronization in the core or boron migration into the cladding. There was some depletion of boron in the cladding of both sets of plates; i.e., the cladding feed material contained a nominal 17 ppm boron before plate fabrication and 1-14 ppm boron after fabrication. However, there was no significant difference in the net boron content, the pattern, or the distance from the cladding surface in any of the plate specimens. (All specimens were shaved in 0.002-in. increments and analyzed.)

From these studies it was concluded that:

- (1) The braze temperature should be reduced to below 1160°C.
- (2) The time at braze temperature should not exceed 30 min.
- (3) The initial 70-min vacuum sinter at 1170°C should be modified to reduce the temperature to 1150°C as a precaution against possible reactions.

Figure 14 shows the change in the niobium-coated ZrB_2 effected by the modified plate-fabrication process and braze cycle. Net boron loss was within the limits of measurement accuracy.

Fig. 14. Niobium-coated ZrB_2 Particle before and after Exposure to Modified Plate-fabrication Process and Braze-cycle Heat Treatment (Reduced by 15% photographically)

3. Stability of Borosilicate Glass Beads in AARR Fuel Plates

a. Background

Studies of borosilicate burnable poisons for the AARR, at ORNL and BMI, were prompted by results of earlier irradiations of 27 wt-% B_2O_3 -glass beads to a level that achieved 90% depletion of the B^{10} . Postirradiation examinations had shown that no dimensional change occurred in the glass, and that subsequent heat treatment in a vacuum at $540^\circ C$ resulted in 100% release of the helium generated by the $B^{10} + n \rightarrow Li^7 + He^4$ reaction. However, attempts to disperse the beads into a stainless steel plate by standard powder metallurgy techniques (i.e., blending, pressing, and rolling) resulted in complete softening of the beads and the formation of thin glass filaments (stringers) throughout the stainless steel matrix.²⁵ Similar attempts with glass beads containing 4 wt-% B_2O_3 resulted in good dispersion of the beads within the matrix and only occasional cracking of the beads during the plate-fabrication process.

b. Borosilicate Compatibility and Fabrication Performance Studies at ORNL

Using the above-mentioned results as a base, J. M. Jones and W. R. Martin initiated a scoping study of high-temperature borosilicate glass beads having varying amounts of boric oxide or alternate boron-bearing materials fused into the glass. Their work included evaluation of beads containing ~3, 6, 8, 10, and 12.27 wt-% boric oxide in SiO_2 , and a special glass containing 10 wt-% ZrB_2 + 5 wt-% B_2O_3 . The objectives were to identify the general problem of compatibility of the borosilicates and the stainless steel matrix, and to determine the parameters for fabricating the borosilicates into good-dispersion-quality materials.

Unfortunately, because of the untimely termination of the AARR Mark I Core Development Program, this work was interrupted before a complete study could be made. The following subsections summarize the nature of the work and the observations made up to the time of termination. A more detailed account is to be published in an ORNL report.

(1) Selection of Glass Beads

The glass beads used in the study were selected on the basis of softening temperatures as predicted by the manufacturer (Corning Glass Co.). It was anticipated that glass beads containing 12 wt-% B_2O_3 - SiO_2 could be made that would have a softening temperature in the range 1200 - $1300^\circ C$. It was also anticipated that a special glass containing 10 wt-% ZrB_2 + 5 wt-% B_2O_3 would have a slightly lower softening temperature range. Figure 15 shows the general range of softening temperatures projected for the borosilicates that were studied.

Fig. 15. Relationship between B_2O_3 Content and Softening of Borosilicates Studied at ORNL

were exposed to a simulated braze cycle consisting of an 8- to 10-hr heat treatment in hydrogen at 1100-1200°C.

In all instances, posttest examination revealed no evidence of deterioration or distortion of the glass beads. Chemical analysis indicated that, for all practical purposes, there was no boron loss.

(3) Fabrication of Test Coupons

Their compatibility having been demonstrated under simulated process temperatures and atmospheres, the glass beads were fabricated into small UO_2 -SS dispersion coupons. The fuel material consisted of depleted UO_2 having a nominal theoretical density of 78%. The matrix feed material comprised a mixture of 12% irregularly shaped, -200 +325 mesh, and 88% spherical, -100 +325 mesh, Type 347 stainless steel powders. With one variation, these materials were blended, compacted, and rolled according to the revised reference process described in Appendix B. The only variation was that the coupons were rolled at 1100, 1150, and 1175°C.

All the starting compacts displayed a good dispersion of the glass beads after sintering. However, the quality of the final rolled dispersion was significantly lowered as a result of breakage and fragmentation of the beads. In some cases, many beads were reduced to submicron-size powder, which was stringered throughout the matrix. Of the borosilicates evaluated, beads with the highest boric oxide content (12.27 wt-%) experienced the least fragmentation, but did show some evidence of softening at the 1175°C rolling temperature. The ZrB_2 -bearing borosilicate beads, though having a lower softening temperature than the 12.27 wt-% B_2O_3 -bearing beads, suffered considerably more breakage and fragmentation. Figure 16 shows typical cross sections of coupons rolled at 1175°C.

(2) Boron Retention in Beads

Two types of tests were conducted to evaluate the boron-retention capabilities of the glass beads (-100 +425 mesh) under simulated Mark I core fabrication-process temperatures and atmospheres. First, the beads were exposed to a heat-treatment cycle which simulated the 1170°C-sinter, the 1100°C-anneal, the 1150°C-roll heat cycle, and the 3-hr postroll anneal at 1150°C. Next, a series of thermal-stability tests was performed during which the beads

3 wt-% B_2O_3 - SiO_2

10 wt-% ZrB_2 + 5 wt-% B_2O_3 - SiO_2

12.27 wt-% B_2O_3 - SiO_2

Fig. 16. Typical Longitudinal Cross Sections of Borosilicate-bearing Coupons Rolled at $1175^{\circ}C$ (Reduced by 10% photographically)

The boron-retention capabilities of the glass beads were also evaluated. Boron analyses were conducted on the coupons after rolling at 1100, 1150, and 1175°C, and then after a simulated braze cycle consisting of a 4-hr heat treatment in hydrogen at 1175°C. This final heat treatment was slightly more severe than the braze cycle.

In general, the higher boron loss occurred in coupons containing glass beads having the lower softening temperature. The nominal 3 wt-% B_2O_3 (Vycor 7900) glass, with a softening temperature of ~1500°C, showed the least loss, whereas the special glass with the lowest softening temperature (10 wt-% ZrB_2 - 5 wt-% B_2O_3) showed the greatest loss. Boron loss increased as the rolling temperature increased, a marked increase occurring during the postroll heat treatment. Table VI lists the respective losses in the two highest boron-bearing coupons.

TABLE VI. Comparison of Boron Losses in High-boron-bearing Coupons

Coupon, wt-%	Roll Temp, °C	Boron Loss, %	
		After Rolling	After Heat Treatment
12.27 B_2O_3	1100	4.0	20.3
	1150	13.3	23.0
	1175	17.6	26.0
10 ZrB_2 + 5 B_2O_3	1100	44.4	71.6
	1150	56.4	65.2
	1175	48.0	79.2

Boron loss appeared to be highest in coupons that displayed considerable breakage and fragmentation of the beads. But since a large amount of breakage was observed in all but the Code 7230 (12.27 wt-% B_2O_3) beads, any attempt to establish a correlation based on the limited test data was considered more a matter of conjecture than of fact.

Attempts were also made to evaluate the significance of these tests and to postulate on mechanisms that could contribute to the behavior observed. However, the very nature of the glasses, their manufacture, and, more specifically, the proprietary nature of manufacture of the special borosilicate glasses, virtually eliminated any conclusion of scientific significance. The special glasses had a softening temperature much higher than that of the commercially available Vycor, Pyrex, and the borosilicate low-expansion glasses. (The commercial glasses have softening temperatures ranging from 1500°C for the Vycor, to 454°C for the Pyrex and other low-expansion glasses.²⁶)

Regardless of the mechanisms, boron losses were excessive in all coupons and were acceptable only in those containing the lowest boron-bearing glasses (3 wt-% B_2O_3 , Vycor 7900) and fabricated at temperatures limited to 1150°C.

c. Fabrication of Irradiation Test Fuel Plates at BMI

This work by D. Kizer and D. Lozier consisted primarily of fabricating specimen fuel plates containing niobium-coated ZrB_2 particles or borosilicate glass beads, using essentially the processes and techniques described in Appendix B. The glass beads, which contained 3.8 wt-% B_2O_3 , were part of an inventory furnished by the 3M Company for an earlier activity at ORNL.¹⁶ They were made available for the purpose of evaluating their behavior during fabrication and irradiation under AARR conditions.

Figure 17 shows microstructures of a typical as-pressed compact and a final-annealed plate, both containing 33 vol-% UO_2 and 6 vol-% borosilicate glass beads. Metallographic examination revealed no reaction zones in either the UO_2 or the stainless steel matrix. (Analysis for boron loss was deemed unnecessary.) The high glass content in the fuel-plate core appeared to have no detrimental effect on the quality or properties of the dispersion. A few of the glass beads were broken, and some of the fragments evidenced an appreciable amount of softening. In general, the dispersion was adjudged satisfactory for irradiation tests.

d. Discussion

Unfortunately the AARR Mark I Core Development Program was terminated before the merits of using borosilicate glass beads as a burnable poison could be thoroughly investigated. Conceivably, such an investigation would have identified the loss mechanism(s) and provided possible solutions to the problem of deboronization. This is supported by a review of the observations and the limited data reported during the studies.

First of all, these studies showed that the types of borosilicate glass beads used in these tests exhibited excellent boron retention when exposed to simulated fabrication-process conditions, but only moderate to poor boron retention during actual fabrication into fuel plates. Boron loss from the glass appeared to be affected, in some measure, by the presence of stainless steel; yet metallographic examinations revealed no evidence of a reaction between the matrix material and the glass or with the boron, as was the case in the studies with ZrB_2 . This leads to speculation that the deboronization mechanism involved loss of a stable compound of boron rather than reaction of elemental boron, as was observed during the ZrB_2 studies.

Secondly, high-magnification examination of the glass beads showed them to be amorphous solutions, with no evidence of colloidal suspensions, dispersions, large open-lattice porosity, or variations in density

that might indicate the presence of a high-density, impervious outer shell. Although the beads were badly fragmented in some plates, there was no definite pattern of behavior whereby the amount of bead breakup could be correlated directly to the amount of boron loss.

Fig. 17. Typical Longitudinal Cross Section of (Top) As-pressed Compact and (Bottom) Final-annealed Irradiation Test Plate Containing 33 vol-% UO_2 and 6 vol-% Borosilicate Glass Beads (smaller, darker, spheres)

ORNL made a general diffusion plot of the different plates in an attempt to determine the effect of increased surface-to-volume ratios on boron loss in the fragmental beads. (Note: At the fabrication temperatures of interest, the permeability of H_2O in glass is quite high. Also, there is sufficient water vapor in the dry hydrogen (-40 to $-80^\circ F$ dew point) used in the furnace to facilitate completion of the boron-water reaction, especially if the surface-to-volume ratio is high.) However, in all cases, the calculated boron losses were less than the measured values. This observation was significant because it indicated that the prime suspect mechanism (i.e., diffusion of H_2O into the glass, thus providing the driving force for removal of the B_2O_3) was not the dominant mechanism of deboronization.

The best correlation between any known single property or characteristic of the glass and the observed boron losses was the softening temperature of the various borosilicates evaluated. In general, the boron losses increased as the temperature difference between the plate fabrication temperature and the reported softening temperature of the glass decreased. Admittedly, this correlation applies only to the bead behavior during actual fabrication into plates; it offers no insight as to why the beads behaved in one manner in the plate and in a different manner when tested alone under simulated process conditions.

The plates fabricated by BMI and ORNL also provided an excellent example of the wide range in dispersion quality that can result from supposedly "identical control conditions." With reference to Fig. 18, the BMI plates contained 3.8 wt-% B_2O_3 glass beads made by the 3M Company. The ORNL plates contained the same type of beads (3 wt-% B_2O_3 , Vycor 7900) made by Corning Glass Company. Both laboratories used the same stainless steel powders, but slightly different UO_2 powders. BMI used 75% theoretically dense (T.D.) UO_2 with ~ 0.3 wt-% CaO and 0.7 wt-% TiO_2 additions, made by Martin Marietta Corp. Nuclear Division; ORNL used 74% T.D. UO_2 with no additives, made by Numec Corp. Finally, the plates were fabricated using the basic process developed by BMI. However, this process was optimized for the 8-in.-diam rolling mill at BMI, whereas the limited program at ORNL did not permit revision and optimization of the rolling schedules for their 19.25-in.-diam mill. As shown in Fig. 18, the Corning glass beads are not as uniformly spherical as the 3M beads, the UO_2 fuels have different microstructures, and there is a marked difference in the amount of bead fragmentation incurred during plate fabrication.

This type of variation in quality is consistent with previous experience with fuel-plate fabricators who were restricted to a process specification rather than a good-product specification. It re-emphasizes the need for proper allowance for optimization of materials and techniques before any comparison-evaluation of product for either research or production.

As-pressed compact (BMI)

As-pressed compact (ORNL)

Final-annealed plate (BMI)

Final-annealed plate (ORNL)

Fig. 18. Comparison of Dispersion Fuel Plates Fabricated by BMI and ORNL, Both Using Basic Process Developed by BMI (Reduced by 10% photographically)

4. Irradiation Tests

a. Nature of Irradiations

All irradiation tests in support of the AARR Mark I Core Fuel Development Program were conducted in the G-12 water loop of the Engineering Test Reactor at NRTS, Idaho. Reference 27 gives a detailed

description of the specimen fuel plates and subassemblies that were irradiated up to the time of program termination. This subsection summarizes the results of irradiation tests performed on six plates of the type shown in Fig. 19, but containing burnable poison additions in the form of niobium-coated ZrB_2 particles or B_2O_3 borosilicate glass beads.

NOTE: All dimensions in inches

Fig. 19. Composition and Dimensional Characteristics of AARR Irradiation Test Plate

Because of uncertainties in the (AARR) design, two niobium-coated $\text{ZrB}_2/\text{U}^{235}$ loading ratios were investigated. Calculations had shown that 4.2 mg $\text{B}^{\text{nat}}/\text{g U}^{235}$ probably would be the reference design ratio, but that increased boron loadings might be required. A value of 6.6 mg $\text{B}^{\text{nat}}/\text{g U}^{235}$ represented the highest ratio anticipated.

While some of these higher-boron-content plates were being made early in the fabrication studies, a faulty temperature sensor in the power control unit allowed the furnace to overheat. Best estimates indicated that the temperature increased to 1300-1400°C. (The overheating was first detected when molten material was observed in the trailing edge of the fuel core as it passed through the rolls.) At the time of furnace malfunction, the dispersion compacts had been sintered in vacuum at 1200°C, and were being heated in a hydrogen furnace at 1200°C prior to rolling. Subsequent

metallographic examination revealed (see Fig. 20) that extensive Nb-ZrB₂-SS reaction had occurred and that the open pores in the UO₂ were filled with the resultant eutectic.

Normal fuel plate

Overheated fuel plate

Fig. 20. Comparison between Normal and Overheated Fuel-plate Cores, Both Containing 37 wt-% UO₂ and Niobium-coated Particles in the Ratio 6.6 mg B^{nat}/g U²³⁵

This type of incident could occur during manufacture of the fuel core and not be detected by conventional nondestructive testing techniques. Therefore, one of the plates with an overheated core (Plate No. 938/23) was also irradiated to determine the effect of the consequent reaction on overall plate performance.

Table VII lists the specimen plates and their irradiation environments.

TABLE VII. Irradiation Test Conditions for Burnable-poison-bearing AARR Mark I Core Fuel Plates in the ETR-G12 Water Loop

Plate No.	Poison	Ratio, mg B ^{nat} /g U ²³⁵	Burnup, % U ²³⁵ Fission		Heat Flux, Btu/(hr)(ft ²) x 10 ⁶		Avg Temp, °F		Max Temp, °F
			Avg	Peak	Avg	Peak	Plate Surface	Plate Centerline	
927/48	Nb-ZrB ₂	4.2	19.6	21.8	0.93	1.05	262	379	430
928/49	Nb-ZrB ₂	4.2	18.0	19.6	0.86	0.94	257	365	400
929/50	Nb-ZrB ₂	4.2	20.2	22.5	0.98	1.09	266	390	445
936/77	Nb-ZrB ₂	6.6	17.0	22.3	0.82	1.07	254	357	409
938/23	Nb-ZrB ₂	6.6 ^a	18.4	23.5	0.88	1.12	240	352	419
939/68	B ₂ O ₃ -SiO ₂	0.76	17.8	22.8	0.80	1.02	253	354	400

^aOverheated during fabrication; ZrB₂ badly reacted with SS; actual amount of boron was probably less than 10% of this value.

b. Postirradiation Examination

Figure 21 shows typical, highly magnified microstructures of fuel plates containing 4.2 mg B^{nat}/g U²³⁵ in a 37 wt-% UO₂-SS dispersion before and after irradiation to approximately 20% fission of the U²³⁵ (~24% U²³⁵ depletion). There are ample voids in the irradiated ZrB₂ particles (i.e., fabrication cracks and spaces between the ZrB₂ and coating materials) to accommodate the helium generated. In addition, it was expected that irradiation at the low temperature (<450°F) would inhibit agglomeration of the gases, which, in turn, would inhibit swelling in the particles.

Fig. 21. Typical Microstructures of Plates Containing 4.2 mg B^{nat}/g U²³⁵ in a 37 wt-% UO₂-SS Dispersion before and after Irradiation to ~20% Fission of the U²³⁵ (Reduced by 15% photographically)

Table VIII lists the calculated and measured swelling incurred in all plates during irradiation. All the ZrB_2 -bearing plates evidenced increased swelling, which was attributed to lithium and helium formations in the particles. The actual incremental volume increase in the plates, after irradiation to approximately twice the AARR Mark I Core design burnup, amounted to only $4 \pm 3\%$ of the total measured swelling (i.e., fission products + helium). Calculations indicated complete depletion of the B^{10} at about one-fifth to one-sixth of the total exposure sustained by the plates. Extrapolation of data from these and prior irradiations of AARR-type, 37 wt-% UO_2 -SS dispersions without burnable poison additions, indicated that although the theoretical volume increase in the fuel plate at the time of B^{10} depletion yielded a net volumetric increase of $\sim 3\text{--}4\%$, the measured swelling was equivalent to only 5-50% of this amount (i.e., zero to 2% total $\Delta V/V$).

TABLE VIII. Swelling Characteristics of Burnable-poison-bearing Plates Irradiated in the ETR

Plate No.	Avg Burnup % U^{235} Fission	Initial Void Fraction in Fuel Core, %	Total Swelling			% Measured Swelling Attributed to:	
			Calculated ^a T.D. UO_2 , %	Measured, %	% of Calculated	Li + He	Fission Products
927/48	19.6	6.25	7.54	3.27	43.4	0.33	2.93
928/49	18.0	5.63	6.97	2.92	41.9	0.35	2.58
929/50	20.0	5.83	7.85	3.40	43.3	0.35	3.05
936/77	17.0	5.4	6.59	3.25	49.3	0.55	2.71
938/23	18.4	4.31	7.34	5.18	70.4	0.06-0.55	5.12-4.63
939/68	17.8	5.33	6.59	2.90	44.0	0.06	2.84

^aBased on 1.6% $\Delta V/V$ per at.-% U^{235} fissioned.

With respect to the overheated plate (No. 938/23), post-irradiation examination revealed (see Fig. 22) that despite the extensive reaction and consequent filling of porosity in the UO_2 with the eutectic, the plate suffered little more than a moderate, but acceptable, increase in swelling. The extent of the reaction and depletion of boron is best illustrated by the microstructures of the irradiated ZrB_2 -bearing plates in Fig. 22. Although both plates initially contained a comparable amount of ZrB_2 particles, only an occasional isolated intact particle or trace of gray residue (probably unreacted Zr or ZrO_2) could be found in the overheated plate. Because of the untimely termination of the program, no tensile or bend tests were made on the plate to determine the effect of the eutectic on the matrix.

Finally, metallographic examination of the 6 vol-% borosilicate-bearing plate revealed (see Fig. 22) negligible change in the 4 wt-% $\text{B}_2^{\text{nat}}\text{O}_3\text{-SiO}_2$. This was expected because of the small B^{10} content (i.e., ~ 0.8 wt-%) in the glass beads. There was no evidence of gas bubbles in the beads. This was concluded to mean that (1) no appreciable agglomeration of helium atoms occurred at the irradiation temperature; and (2) for all practical purposes, the helium atoms were retained in the atomic lattice where they were formed.

UNIRRADIATED

IRRADIATED

(A)

(B)

(C)

Fig. 22. Microstructure of (A) Overheated and (B) Normal Plates Containing Niobium-coated ZrB_2 Particles; and (C) Borosilicate Bead-bearing Plates before and after Irradiation in the ETR ($\sim \text{X}200$)

III. CONCLUSIONS

Although not exhaustive in researching the problem of boron loss in AARR fuel plates, the foregoing programmatic efforts of knowledgeable people from several organizations did establish a measure of confidence in the capabilities of certain burnable, boron-bearing poisons of interest to fuel designers. Based on the observations made during these studies, as well as information derived from the earlier referenced activities, the following conclusions can be drawn regarding their application to the AARR Mark I Core:

1. The temperature-atmosphere-time-dependent reactions that promote boron depletion during fabrication of AARR fuel plates can assume significant proportions.
2. At conventional fabrication temperatures for UO_2 -SS dispersions, the forces available for deboronization are sufficient to render most of the barrier and fixing materials examined ineffective for achieving boron retention within the limits ($\pm 5\%$) specified for the AARR Mark I Core.
3. The use of stainless steel barrier coatings on ZrB_2 particles is not an effective method for controlling boron loss to less than $\pm 5\%$ during fabrication of the fuel plates and their subsequent brazing into fuel subassemblies.
4. Under certain conditions, a niobium-chromium carbide barrier coating is effective in preserving the chemical constituency of the ZrB_2 . These conditions are:
 - a. The ZrB_2 must be carefully prepared and coated.
 - b. Initial sintering and annealing of the UO_2 -SS, niobium-coated ZrB_2 -bearing core compact must be performed in a high-vacuum furnace (10^{-5} to 10^{-6} Torr).
 - c. The hydrogen atmosphere in the furnace during rolling, flat annealing, and brazing must have a low water content (-40°F dew point, or better).
 - d. No heat-treatment temperature should exceed 1160°C , and time at temperatures above 1150°C should be kept to a practical minimum.
 - e. The rolling schedule and the temperature at which the plate is actually rolled should be designed to maintain integrity of the barrier-coating materials around the ZrB_2 particles. If the plate is allowed to cool to a temperature at which the stainless steel matrix becomes too hard, the ZrB_2 particles will be crushed, with consequent rupture of the barrier coatings.

5. The borosilicate glass beads are less dependable in quality and performance than the niobium-coated ZrB_2 particles at temperatures required for fabricating good-quality UO_2 -SS dispersion fuel plates for the AARR Mark I Core. They can be fabricated into plates of acceptable quality (i.e., negligible damage to the beads), provided the fabricators are not restricted to a reference process specification, but rather to a good-product specification. The latter should afford sufficient latitude for optimization of materials and techniques consistent with the equipment and capabilities of personnel employed by the respective fabricators. However, even with a good dispersion and negligible breakage of beads in the fuel plate, the boron losses at temperatures above 1150°C in all but the low B_2O_3 -bearing silicates exceeded 5% and are unacceptable for the AARR. The mechanism of deboronization in the borosilicates at these temperatures is highly speculative, as is most information on their behavior above 1000°C .

6. In general, the following temperature-atmosphere-dependent characteristics of the component materials were observed during these studies:

a. At 1200°C and Above

Uncoated ZrB_2 , niobium-coated ZrB_2 , and the borosilicate beads, when in contact with austenitic stainless steel and exposed to H_2 , H_2O , and/or O_2 , experience boron losses that render them completely ineffective as reliable burnable poisons.

b. Between 1200 and 1175°C

(1) Uncoated ZrB_2 and niobium-coated ZrB_2 in contact with stainless steel react and form low-temperature eutectics or volatile forms of boron (if exposed to H_2O or O_2). The rates at which these reactions occur result in appreciable boron loss from the ZrB_2 (and ultimately through the matrix and cladding) during fabrication of the fuel plates and subassembly.

(2) During fabrication of fuel plates, the rate of deboronization of borosilicates in contact with austenitic stainless steel in a hydrogen atmosphere results in boron losses varying from 20 to 80%, depending on the time at temperature.

c. Below 1175°C

Below the niobium-nickel eutectic liquidus temperature, the niobium barrier coating used is stable and can preserve the chemical constituency of the ZrB_2 particles to a high degree, provided the integrity of the coatings is not breached during plate fabrication.

d. Between 1175 and 1150°C

(1) The rate of reaction between ZrB_2 and iron and/or nickel, and the reaction rate between oxygen and water vapor and the ZrB_2 , results in a moderate rate of degradation of the ZrB_2 , which ultimately may yield significant loss of boron from the plate.

(2) Above 1150°C, there is pronounced deboronization of the borosilicates, the highest rate of reaction occurring in the 12 wt-% B_2O_3 -bearing beads and the special glasses containing 10 wt-% ZrB_2 + 5 wt-% B_2O_3 .

e. Between 1160 and 1145°C

Within the temperature range specified for brazing AARR fuel plates into subassemblies using GE J8100 braze alloy (Ni, 19% Cr, 10% Si):

(1) Uncoated ZrB_2 experiences gross reaction if appreciable quantities of O_2 or H_2O are present; if not, a reaction of lesser degree occurs between the ZrB_2 and the stainless steel.

(2) Niobium suffers negligible reactions.

(3) Borosilicates containing less than 8 wt-% B_2O_3 experiences boron losses ranging from 2 to 10%; those with higher B_2O_3 loadings show losses in excess of 10%.

f. Between 1150 and 1125°C

(1) If protected from O_2 and H_2O , uncoated ZrB_2 evidences moderate degradation during rolling into dispersion fuel plates. This protection can be afforded only by vacuum-sintering the dispersion compact and vacuum-sealing the fuel-plate core in the frame and cladding prior to rolling operations.

(2) Degradation of ZrB_2 in the niobium-coated ZrB_2 is negligible.

(3) Boron losses are less than 10% in borosilicate beads containing 6-8 wt-% B_2O_3 , and 3-5% in materials of low boric oxide content (3 wt-% B_2O_3).

g. Below 1125°C

(1) Uncoated ZrB_2 evidences a slight reaction with the stainless steel matrix, but a marked reaction with O_2 or H_2O .

(2) With the exception of the special $\text{ZrB}_2\text{-B}_2\text{O}_3$ glass, boron loss in the borosilicates is tolerable ($<5\%$).

(3) Restricting the sintering and annealing temperatures to below 1125°C results in a more porous compact. Considerable breakage of the UO_2 and the burnable poison-bearing particles will occur if the compact is then rolled in the conventional manner at roll-furnace temperatures below 1125°C . However, fracturing and stringing of the dispersion materials can be minimized by using roll-furnace equipment that maintains plate temperatures within the range $1100\text{-}1125^\circ\text{C}$ during rolling operations.

APPENDIX A

Initial Reference Fabrication Procedures for
UO₂-Stainless Steel Dispersion Fuel Plate1. Preparation of Fuel Core Compactsa. Materials

- (1) Uranium dioxide powder
 - (a) Shape: Spherical.
 - (b) Size: Minus 100 plus 140 mesh (105-149 μ).
 - (c) Density: Shall not exceed 92% by mercury pycnometer or metallographic point count measurement.
 - (d) O/U ratio: Between 2.00 and 2.02.
 - (e) Average crush strength: Should exceed 200 g.
- (2) Stainless steel powder
 - (a) Type: 347 with 2% silicon addition.
 - (b) Shape: Irregular.
 - (c) Size: Minus 325 mesh (minus 44 μ).

b. Screening of UO₂ and Stainless Steel Powders

- (1) Screen the dry stainless steel powder through a 325-mesh screen.
- (2) Screen UO₂ powder through a 100-mesh screen, collect on a 140-mesh screen, and wash with CCl₄.

c. Weighing of UO₂ and Stainless Steel Powders

- (1) Weigh to ± 0.02 g.

d. Blending of UO₂-Stainless Steel Powders

- (1) Coat UO₂ powder with 1½ wt-% paraffin binder, using CCl₄ as the solvent.
- (2) Chill coated UO₂ powder to approximately minus 10°C.
- (3) Screen chilled coated UO₂ powder through a 60-mesh screen onto stainless steel powder.
- (4) Blend powders in a rotating glass jar so that the stainless steel powder will adhere to the UO₂.

e. Consolidation of Blended Powders

- (1) Distribute blended mixture in the die cavity.
- (2) Green press at 50 tsi in a double-acting steel die.

f. Sintering of Compacts

- (1) Sinter in a hydrogen furnace equipped with a cooling chamber.
- (2) Place compacts in an austenitic stainless steel boat, with approximately 1/4-in. spacing between compacts. Use

molybdenum sheets to separate cores from themselves and the boat.

- (3) Insert boat into an intermediate heat zone of the furnace for 1/2 hr to drive off the paraffin binder.
- (4) Sinter compacts at 1200°C for 75 min in hydrogen (dew point to be minus 60°F).
- (5) Cool sintered compacts in cold zone of the furnace.

g. Weighing and Measuring of Compacts

- (1) Weigh each compact to nearest 0.02 g, and measure to nearest 0.5 mil.

h. Coining of Compacts in Double-acting Die at 50 tsi

i. Inspection of Coined Compacts

- (1) Measure thickness of core at each corner and at the center. If thickness variations are extensive, compact is to be rejected.
- (2) Reject extensively oxidized cores or cores with nicked corners.

2. Preparation of Fuel Assembly

a. Fabricate frames

- (1) Material: Type 347 stainless steel (ASTM Designation A167-61T).
- (2) Design: Machine frame from rolled stainless steel plate to dimensions shown in Fig. A.1.

All dimensions in inches

Fig. A.1
Dimensions of Type 347 Stainless
Steel Frame for Fuel-plate Core

b. Fabricate cover plates

- (1) Material: Type 347 stainless steel
- (2) Roll to 0.040-in. thickness and shear to size 0.125 in. smaller in length and width than the frame.

c. Clean frames and cover plates

- (1) Degrease in acetone.
- (2) Scrub in hot Alconox solution.
- (3) Rinse first in hot water, then in cold water. Final rinse in 200-proof ethyl alcohol (or hot water) and dry with lint-free towels.

d. Clean all cores by wiping with 600-grit paper.

e. Weigh and measure cores prior to insertion into frame.

f. Insert cores into frames and clamp top and bottom cover plates.

g. Weld cover plates to frame by tungsten-heliarc welding in an inert atmosphere dry-box, leaving a 1-in.-long unwelded area on one end of the fuel assembly. Complete welding of plates by vacuum-electron-beam welding.

h. Spot-weld cover plates to the frame across a line $1/8$ in. in front of the leading edge of the core.

3. Fabrication of Assembled Component

a. Preheating Prior to Rolling

- (1) Preheat in an Inconel muffle purged with hydrogen for 30 min at 1200°C.

b. Hot-rolling

- (1) Equipment: Eight-inch-diameter (or larger) two-high mill.
- (2) Reductions in thickness to be 25% per pass after the initial two passes at 30% reductions.
 - (a) Roll to 0.048 in.; then roll at constant roll settings to 0.045 in.
 - (b) Preheat plates 5 min between passes.
 - (c) Rotate plates about their longitudinal and transverse axes between passes.
 - (d) Anneal plates 5 min after final pass.

c. Removal of Surface Oxide

- (1) Measure as-rolled thickness.
- (2) Remove all traces of oxide by immersing and agitating plates in a hot aqueous solution of 15% HNO_3 and 5% HF .

d. Shearing of Hot-rolled Plates

- (1) Shear or saw excess stock from ends of rolled plates, taking precautions not to scratch or clamp over the core.

e. Cold-rolling

- (1) Equipment: Eight-inch-diameter (or larger) rolls with good surface.
- (2) Reductions should be less than 1% per pass.
- (3) Rotate about longitudinal and transverse axes after each pass when rolling to final dimensions of 0.039 to 0.041 in.

f. Flat-annealing Cold-rolled Plates

- (1) Coat top and bottom surfaces of the plates with a 10% levigated alumina suspension.
- (2) Stack plates between two 3/4-in.-thick stainless steel platens.
- (3) Bolt platens together, using stainless steel bolts.
- (4) Insert platens into the cold zone of the furnace, and allow hydrogen to purge them of any contaminating gases.
- (5) Slowly push plates into the hot zone of the furnace and heat for 2 hr at 1175°C.
- (6) Remove plates from the hot zone to the cold zone and allow to cool.
- (7) Remove plates from the platens and scrub alumina off with water.
- (8) Rinse plates in hot water and dry.

4. Inspection of Cold-rolled Plates

- a. Measure depth of pits with Zeiss Light Section Microscope.
- b. Radiograph to determine fuel-section dimensions and homogeneity of UO_2 dispersion.

5. Plate Machining

- a. Machine plates to size individually or collectively in a jig, using radiograph(s) as a guide.

6. Inspection of Fuel Plates

- a. Radiograph fuel plates to determine fuel-section dimensions and homogeneity of UO_2 .
 - b. Determine surface roughness with rms number.
 - c. Make final dimensional measurements.
- ✓

APPENDIX B

Revised Reference Materials and Fabrication Process Procedures for AARR Mark I Core Fuel Plates

1.0. Materials

1.1. Enriched Uranium Dioxide Powder

1.1.1. Scope

This specification is for the fully-enriched UO_2 spherical powder to be used as the active material in the fuel plate core.

1.1.2. Reference Standards

(1) ASTM B 214-56: Method of Test for Sieve Analysis of Granular Metal Powders

(2) ASTM E 112-61: Estimating the Average Grain Size of Metals

1.1.3. Property Requirements

(1) Physical Characteristics

(a) Particle Size. The particle size of the UO_2 powder shall be 104 to 149 μ (minus 100 plus 140 mesh).

(b) Grain Size. The average grain size shall be less than 10 μ in diameter. The maximum grain size shall not exceed 30 μ in diameter.

(c) Shape. Ninety-five percent of the UO_2 particles shall be spheroidal. The ratio of the major to the minor axis for each particle shall not exceed 2 to 1. A maximum of 1% of agglomerate particles shall be allowed. (An agglomerate particle is one consisting of two or more sub-particles mechanically or chemically bonded.)

(d) Structure. Uranium dioxide shall be the only phase present. The ratio of oxygen to uranium shall be between 1.998 and 2.01.

(e) Density. Density of the UO_2 particles shall be in the range of 9.30 to 9.85 g/cm³.

(f) Crush Strength. Average crush strength of the UO_2 particles shall exceed 200 g.

(2) Chemical characteristics (Composition)

The uranium content of the UO_2 shall exceed 85.6 wt-%. Impurities in the UO_2 powder shall not exceed the following levels:

<u>Impurity</u>	<u>Maximum Level, ppm</u>	<u>Impurity</u>	<u>Maximum Level, ppm</u>
Boron	1.0	Cadmium	10.0
Beryllium	0.5	Gadolinium	10.0
Lithium	5.0	Aluminum	200.0
Cobalt	10.0		

Other metallic impurities, except for the additives, shall not exceed 100 ppm each. The total of other metallic impurities shall not exceed 500 ppm.

(3) Additives

Additives to increase strength and ductility of the UO_2 spheroids shall not exceed 2 wt-% of the total particle weight. Additives shall be limited to ZrO_2 , CaO , and/or TiO_2 .

1.1.4. Test and Inspection Requirements

(1) Physical Characteristics

(a) Particle Size. Particle size shall be determined on samples of each lot of UO_2 powder in accordance with ASTM B 214-56.

(b) Grain Size. Grain size shall be determined on samples of each lot of UO_2 by extrapolation of methods in accordance with ASTM E 112-61.

(c) Shape. Shape and agglomeration shall be determined on samples of each lot of UO_2 powder by microscopic examination of three slides each of 100 particles minimum.

(d) Structure. Structure shall be determined on representative samples of each lot of UO_2 powder by X-ray diffraction. The ratio of oxygen to uranium shall be determined by the polarographic method.

(e) Density. Density shall be determined on samples of each lot of UO_2 powder by metallographic point count, plastic impregnation, or an equivalent process acceptable to the purchaser.

(2) Chemical Characteristics (Composition)

A minimum of three samples shall be taken from each lot of UO_2 powder and analyzed individually to ascertain the chemical elements and contaminants.

1.2. Prealloyed Spheroidal Type 347 Stainless Steel Powder

1.2.1. Scope

This specification is for the AISI Type 347 (modified) prealloyed stainless steel powder used in the matrix of the fuel core.

1.2.2. Reference Standards

(1) ASTM B 214-56: Method of Test for Sieve Analysis of Granular Metal Powders

1.2.3. Property Requirements

(1) Physical Characteristics

(a) Particle Size. Particle size of the stainless steel powder shall be minus 270 plus 500 mesh.

(b) Shape. The powder shall be spheroidal as obtained by atomizing the melt charge in an inert or reducing atmosphere.

(c) Density. There shall be no internal porosity in the spheroidal particles.

(2) Chemical Characteristics (Composition)

The chemical composition of the stainless steel powder shall be as follows:

<u>Element</u>	<u>wt-%</u>	<u>Element</u>	<u>wt-%</u>
Carbon	0.06	Columbium	10x carbon min; 1.00 max
Nickel	9.0-11.0	Manganese	0.40 max
Chromium	17.0-19.0	Cobalt	0.025 max
Silicon	1.0-1.25	Tantalum	0.010 max
Phosphorous	0.010 max	Oxygen	0.10 max
Sulfur	0.010 max	Iron	Balance

1.2.4. Test and Inspection Requirements

(1) Chemical Characteristics

A minimum of three samples shall be taken from each lot of stainless steel powder and analyzed individually to ascertain the chemical elements and contaminants.

1.3. Prealloyed Irregularly Shaped Type 347 Stainless Steel Powder

1.3.1. Scope

This specification is for the AISI Type 347 (modified) prealloyed stainless steel powder used in the matrix of the fuel core.

1.3.2. Reference Standards

(1) ASTM B 214-56: Method of Test for Sieve Analysis of Granular Metal Powders

1.3.3. Property Requirements

(1) Physical Characteristics

(a) Particle Size. The particle size of the stainless steel powder shall be minus 100 plus 325 mesh.

(b) Shape. The powder shall be irregular or spiny in shape as obtained by producing the powder electrolytically.

(2) Chemical Characteristics (Composition)

The chemical composition of the stainless steel powder shall be as follows:

<u>Element</u>	<u>wt-%</u>	<u>Element</u>	<u>wt-%</u>
Carbon	0.06	Columbium	10x carbon min; 1.00 max
Nickel	9.0-11.0	Manganese	0.40 max
Chromium	17.0-19.0	Cobalt	0.025 max
Silicon	2.0-2.25	Tantalum	0.010 max
Phosphorous	0.010 max	Oxygen	0.3 max
Sulfur	0.010 max	Iron	Balance

1.3.4. Test and Inspection Requirements

(1) Chemical Characteristics (Composition)

A minimum of three samples shall be taken from each lot of stainless steel powder and analyzed individually to ascertain the chemical elements and contaminants.

1.4. Type 347 (Modified) Stainless Steel Plate

1.4.1. Scope

This specification is for the AISI Type 347 stainless steel plate and sheet with controlled cobalt and tantalum contents used for roll bonding frames and cover plates.

1.4.2. Reference Standards

(1) Technical Society Standards

(a) ASTM A 240-61T: Corrosion-resisting Chromium and Chromium-Nickel Steel Plate, Sheet and Strip for Fusion-welded Unfired Pressure Vessels

(b) ASTM E 45-62T: Determining Inclusion Content of Steel

(2) Purchaser Standards

(a) CMRS-1: Revised Section of Schaeffler Constitution Diagram

1.4.3. Property Requirements

(1) General

The plates shall comply with all requirements of ASTM A 240-61T, including the additions and modifications herein.

(2) Chemical Characteristics

(a) Composition. The material shall conform to the chemical requirements of ASTM A 240-61T for AISI Type 347 stainless steel, with the additions and modifications as specified below:

<u>Element</u>	<u>wt-%</u>
Molybdenum	0.50
Nitrogen	0.05
Copper	0.50
Cobalt	0.025
Tantalum	0.01

(b) Delta Ferrite. The delta ferrite content of the plate material shall be a minimum of 2% and a maximum of 10%.

(c) Inclusions. Inclusions rating of a 1-in.-thick sheet bar as determined by Method "A" of ASTM E 45-62T shall be comparable to the following:

<u>Inclusion Type</u>	<u>Thin Series</u>	<u>Heavy Series</u>
Sulfide	2	1½
Alumina	2½	2
Silicate	3	3½
Globular Oxide	3	2

The thickness of each inclusion found in a 1-in.-thick sheet bar shall not be greater than that specified in the inclusion chart of ASTM E 45-62T.

1.4.4. Test and Inspection Requirements

(1) General

The requirements of this specification shall be met by performing all applicable tests described in ASTM A 240-61T and additions herein.

(2) Chemical Characteristics

(a) Composition. A minimum of three samples shall be taken from each lot of plates and analyzed individually to ascertain the chemical elements and contaminants.

(b) Delta Ferrite. The delta ferrite content of the plate material shall be determined on samples from each lot of plates by calculations using the Revised Schaeffler Constitution Diagram of CRMS-1.

(c) Inclusions. Inclusions shall be determined on samples from each lot of plates using procedures and techniques for Method "A" as outlined in ASTM E 45-62T.

1.5. Zirconium Diboride Powder

1.5.1. Scope

This specification is for zirconium diboride (ZrB_2) powder, prepared from double-arc-melted stock, for use as burnable poison in the fuel plate core.

1.5.2. Reference Standards

(1) ASTM B 214-56: Method of Test for Sieve Analysis of Granular Metal Powders

1.5.3. Property Requirements

(1) Physical Characteristics

(a) Particle Size. The particle size of the ZrB_2 powder shall be 74 to 149 μ (minus 100 plus 200 mesh).

(b) Density. The density of the double-arc-melted ZrB_2 button or skull shall be a minimum of 5.95 g/cm³.

(2) Chemical Characteristics (Composition)

The chemical composition of the ZrB_2 powder shall be as follows:

<u>Element</u>	<u>wt-%</u>	<u>Element</u>	<u>wt-%</u>
Boron	18.8 $\pm$ 0.2	Tungsten	1.0 max
Carbon	0.1 max	Copper	0.02 max
Iron	0.3 max	Zirconium	78.0 min
Chromium	0.1 max	Boron-10	18.5 $\pm$ 0.2
Hafnium	2.0 max		

1.5.4. Test and Inspection Requirements

(1) Physical Characteristics

(a) Particle Size. Particle size shall be determined on a sample from each lot of ZrB_2 powder in accordance with ASTM B 214-56.

(b) Density. The density shall be determined on each button or skull using the Archimedes Method.

(2) Chemical Characteristics (Composition)

A minimum of three samples shall be taken from each lot of ZrB_2 powder and analyzed individually to ascertain the chemical elements and contaminants.

1.5.5. Vapor Coating of Zirconium Diboride Powder

(1) Precoating Heat Treatment

The powder shall be heat treated in a vacuum of $<10^{-5}$ Torr for 1 hr at 1200°C. The vacuum furnace shall have a leak rate not exceeding 1×10^{-3} Torr/hr.

(2) Protective Coating of Powder

The ZrB_2 powder shall be coated with a $1\text{-}\mu$ layer of chromium carbide by pyrolysis of dicumene chromium.

(3) Coating of Protected Powder with Refractory Metal

The ZrB_2 powder coated with a $1\text{-}\mu$ layer of chromium carbide shall be coated with the desired thickness of refractory metal by vapor deposition in a fluidized bed or by vacuum deposition. The coated powder shall be outgassed for 1 hr at 1200°C in a vacuum of 10^{-5} Torr. The vacuum furnace shall have a leak rate not exceeding 1×10^{-3} Torr/hr.

(4) Chemical Characteristics (Composition)

A minimum of three samples shall be taken from each lot of coated ZrB_2 powder and analyzed individually to ascertain the boron content in relation to the coatings applied.

2.0. Fabrication Guide for 37 wt-% UO_2 -Stainless Steel Dispersion Fuel Plates

2.1. Preparation of Fuel Cores

2.1.1. Blending

(1) Coat the UO_2 and ZrB_2 (separately) with a solution of 2 wt-% (of the UO_2 or ZrB_2 weight) paraffin in CCl_4 . Continually stir the UO_2 and ZrB_2 until dry while slowly blowing heated air over the evaporating disk to promote evaporation. Do not heat disk on hot plate.

(2) Place the coated UO_2 and ZrB_2 in a dry-atmosphere cooling chamber, and cool to approximately 0°C .

(3) With the aid of a brass screen brush, screen powders through a chilled 60-mesh screen onto a chilled pan and return to the cooling chamber. (The paraffin is reduced to $1\frac{1}{2}$ wt-% by this screening.)

(4) Place the stainless steel matrix powder in a pan below a clean 80-mesh screen, and cool to approximately 0°C in the dry cooling chamber. The matrix powder is a blend of 12 wt-% irregularly shaped particles of minus 100 plus 325 mesh and 88 wt-% spheroidal particles of minus 270 plus 500 mesh.

(5) Rescreen the UO_2 onto the stainless steel powder while revolving the pan and screen to coat the UO_2 particles as they fall through the screen.

(6) Rescreen the ZrB_2 particles onto the blend while revolving the pan and screen.

(7) Transfer the blend to a 6-oz wide-mouth glass jar and revolve at 30 rpm at a 20-deg angle on a set of rolls until the paraffin coating on the UO_2 particles becomes tacky and the stainless steel matrix powder thoroughly adheres to the particles.

2.1.2. Dispersion Core Pressing

(1) Pour the blended powders gently into the cavity of a double-acting die having a $3/32$ -in. radius at the four corners, and level with the minimum disturbance.

(2) Press at 30-tsi pressure (77% of theoretical density).

(3) Degas the binder, and sinter the dispersion core in a vacuum furnace for 70 min at 1150°C and approximately 10^{-5} Torr.

(4) Repress the dispersion core at 50 tsi (84% of theoretical density).

(5) Anneal the dispersion core in a vacuum for 2 hr at 1120°C and approximately 10^{-6} Torr.

(6) Coin the dispersion core at 70 tsi (89% of theoretical density).

(a) Core thickness: 0.186 to 0.190 in.

(b) Core width: 2.525 in.

(c) Core length: 3.00 in.

2.2. Roll Bonding

2.2.1. Compact Assembly Preparation

(1) Clean cores by rubbing lightly with 600-grit paper. Record weight and dimensions of core.

(2) Frame dimensions.

(a) Thickness: 0.180 in.

(b) Side width: 1.00 in.

(c) Leading edge: 1.50 in.

(d) Trailing edge: 1.00 in.

(e) Overall dimensions: 4.565 by 5.500 in.

(3) Cover-plate dimensions

(a) Thickness: 0.043 in.

(b) Length and width: 1/8 in. less than frame (4.400 by 5.375 in.)

(4) Cleaning

(a) Degrease chemically or clean ultrasonically with a degreasing agent.

(b) Clean with hot Alconox solution and a stiff-bristled brush; thoroughly rinse first in hot, then in cold water, and dry with lint-free towels.

(5) Insert core into cladding frame using lint-free gloves, and clamp cover plates in place.

(6) Heliarc-weld three sides of assembly in a vacuum-inert atmosphere dry box. Seal final side of assembly by vacuum electron-beam welding (10^{-4} Torr).

(7) Spot- or seal-weld cover plates to the frame 1/8 in. from the core on the leading end.

2.2.2. Rolling

(1) Equipment

(a) The rolls shall be 8 in. in diameter or larger.

(b) Furnace shall be equipped with a muffle to contain flowing hydrogen and have a uniform hot zone at least 22 in. long.

(c) Furnace design and temperature control system shall maintain a heating-zone temperature in the range 1130-1150°C.

(2) Preheat compact for 20 min to allow temperature throughout compact to be in the range 1130-1150°C.

(3) Roll to a 6:1 reduction in thickness.

(a) Reductions shall be 25% per roll pass.

(b) Rotate plates about their longitudinal and transverse axes between each roll pass.

(c) Reheat plates after each roll pass for ~10 min to assure that entire plate temperature is in the range 1130-1150°C.

(d) Hot-roll to a final thickness of 0.043 to 0.044 in.

2.3. Removal of Surface Oxides

Pickle in a hot aqueous solution of 15 vol-% HNO_3 and 5 vol-% HF. Scale removal will reduce plate thickness to 0.041 to 0.042 in.

2.4. Cold Rolling

Cold-roll plates 1-2% in thickness to improve surface condition and obtain final plate thickness of 0.040 ± 0.002 in.

2.5. Flat Annealing

(1) Spray plate surfaces with a parting compound of levigated alumina.

(2) Clamp plates between stainless steel flattening platens.

(3) Anneal for 2 hr in a hydrogen-atmosphere furnace at 1120°C.

2.6. Machining

(1) Mark reference point for core centerline and plate end on each plate from a radiograph template.

(2) Machine to dimensions.

3.0. Inspection

Each plate shall be radiographed to determine the core dimensions, camber, end effects, and any gross inhomogeneity in the rolled dispersion. The plate surfaces shall be free of all scratches, pits, or defects in excess of 0.001 in. deep.

Each plate shall be ultrasonically tested for nonbond of cladding.

Each plate shall be gamma-scanned, using a Co^{57} source, to ascertain distribution of the uranium.

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