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COMPATIBILITY OF URANIUM-5 w/o FISSIUM ALLOY WITH TYPES 304L AND 316 STAINLESS STEEL

by

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ABSTRACT

The compatibility of uranium-5 w/o fissium alloy with two types of stainless steel was investigated in diffusion-couple annealing experiments conducted for up to 10^4 hr at temperatures to 650°C. Types 304L and 316 stainless steel are equally compatible with the uranium-fissium alloy. Penetrations of diffusing elements into the steels in 10^4 hr ranged from a maximum of 7 μ at 550°C to a maximum of 30 μ at 650°C. Type 304L stainless steel reacts slowly with the fuel alloy to form a liquid phase at 705 ± 5°C, and Type 316 stainless steel does so at 715 ± 5°C. Higher concentrations of silicon and aluminum in the fissium alloy have no effect on the compatibility of the alloy with Type 304L stainless steel at 650°C, but the temperature at which a liquid slowly forms is increased to 725 ± 5°C.

I. INTRODUCTION

Uranium-5 w/o fissium* alloy and Type 304L stainless steel are, respectively, the driver fuel and jacket (cladding) material currently used in the construction of driver fuel elements in Experimental Breeder Reactor-II (EBR-II). The interdiffusion that may occur between the two materials at reactor operating temperatures has been discussed previously, in connection with the Core I development, by Walter and Kelman.[1,2] The present investigation directed attention to the determination of certain aspects of the out-of-reactor compatibility of the two materials that are of interest in the development of the Mark-II fuel element. These include: (1) the compatibility of the fuel-cladding combination during annealing for times up to 10^4 hr at temperatures to 650°C, (2) the temperature, T_m, at which the materials interact to form a liquid phase, (3) the influence of silicon and aluminum additions to the fuel alloy on the compatibility of the fuel and cladding materials, and (4) the comparative compatibility of Types 304L and 316 stainless steel with the uranium-fissium alloy.

*Fissium (Fs) is an aggregate composed of zirconium, molybdenum, palladium, ruthenium, and rhodium.

II. EXPERIMENTAL PROCEDURE

A. Materials

The uranium-fissium alloy pins were prepared from reactor-grade uranium by injection-casting the homogeneous alloy into Vycor molds.[3] The cast pins were 0.144 in. in diameter and 13.5 in. long. Two batches of pins were prepared and the compositions (listed in Table I) were determined by wet chemical analyses. The compositions of the two batches differ chiefly with respect to concentrations of silicon and aluminum. Batch R-410 was used solely in the investigation of the effects of higher concentrations of these two elements upon compatibility.

TABLE I. Analysis of Uranium-5 w/o Fissium Alloys

Element	Batch R-409	Batch R-410
Mo	2.52 w/o	2.54 w/o
Ru	1.97 w/o	1.97 w/o
Pd	0.186 w/o	0.188 w/o
Rh	0.280 w/o	0.294 w/o
Zr	0.092 w/o	0.084 w/o
Nb	0.01 w/o[a]	0.01 w/o[a]
Si	75 ppm	734 ppm
Al	196 ppm	1406 ppm
C	141 ppm	240 ppm
Fe	100 ppm	100 ppm
Ni	70 ppm	70 ppm
Cr	30 ppm	30 ppm
O	20 ppm	30 ppm
N	17 ppm	10 ppm
H	1 ppm	30 ppm

[a]Percent calculated from charged weight.

Types 304L and 316 stainless steel (cold-rolled rod, 0.25 in. in diameter) were procured from commercial sources. Chemical analyses indicated that the compositions of both types of steel were within AISI specifications.

B. Assembly of Diffusion Couples

Diffusion couples were assembled from specimens, approximately 1/4 in. long, that were saw-cut from the described materials. The uranium-fissium specimens were initially annealed for 18 hr at 500°C to achieve alpha-uranium structures rather than retained gamma-uranium structures, and hence to prevent thermal contraction during annealing of the diffusion couples. Before assembly, the end faces of the specimens were polished flat and parallel through 4/0 emery paper, rinsed in ethyl alcohol, and dried in hot air. One specimen of fissium alloy, 0.144 in. in diameter, was placed between two specimens of steel, 0.25 in. in diameter, providing two interfaces across which interdiffusion could occur. The larger diameter of the steel specimens allowed the initial interface to be identified, upon subsequent microexamination of the annealed couples. A diffusion couple was placed in a molybdenum clamp,[4] which had a significantly smaller linear thermal-expansion coefficient than the specimens, thus restraining the expansion of the specimens during annealing. The clamped couples were placed inside double-walled quartz capsules containing a helium atmosphere, and annealing treatments were conducted in either a

resistance tube furnace or in lead pots at temperatures controlled to ±5°C. Before being annealed at 550°C, all couples were annealed for 20 min at 650°C to ensure the formation of a metallurgical bond (approximately 2 μ total bandwidth).

C. Metallographic Studies

The widths of the diffusion layers formed during annealing were determined from scaler measurements made on etched microstructures. The maximum observed widths for individual couples are listed in Tables II-IV (later) and are precise to ±5%. For duplicate couples annealed for the same time and temperature, measured widths differed by as much as 25%. The widths in certain couples were also determined by means of electron-microprobe analysis and were within 25% of the scaler measurements.

Etching was done electrolytically in a solution containing eight parts phosphoric acid, five parts ethylene glycol, and five parts ethyl alcohol, with a cell potential of 4-100 V. For microexamination, the couples were mounted in epoxy resins. Mounting in bakelite was highly unsatisfactory because of diffusion-bond fracture during application of a load, as required for thermo-setting the plastic.

III. RESULTS AND DISCUSSION

A. Couple of Uranium-5 w/o Fissium (Batch R-409) with Type 304L Stainless Steel

Table II lists the widths of diffusion bands measured for this combination of materials. Included are data reported earlier by Walter[2] for the same combination at annealing times up to 3.0×10^6 sec (840 hr). In general, both sets of data are in good agreement. Figures 1 and 2 are log-log plots of total bandwidth and steel penetration versus the annealing time at temperatures to 650°C. The data closely fit straight-line plots with a slope of 2, giving a general parabolic equation for penetration of $P^2 = Kt$, where P is the penetration in centimeters, K the penetration coefficient, and t the annealing time in seconds. The coefficients determined for each temperature (as mean values for the respective datum point) are indicated in the equations given in Figs. 1 and 2 and are plotted against the reciprocals of absolute temperature (T) of annealing in Figs. 3 and 4. Steel penetration is generally only a small part (average 5%) of the total bandwidth (listed in Table II), and, accordingly, the penetration coefficients for total bandwidth (plotted in Fig. 3) and for fuel-alloy penetration are nearly the same.

At 550°C, interdiffusion between the two materials is extremely limited. With an annealing time of 3.6×10^7 sec (10^4 hr), penetrations into the fuel alloy and the steel are only 95 and 7 μ (0.0037 and 0.0003 in.), respectively.

TABLE II. Interdiffusion Bandwidths for Uranium-5 w/o Fissium (Batch R-409) and Type 304L Stainless Steel

Temp, °C	Annealing Time, sec	Couple No.	Maximum Penetration, 10^{-4} cm		
			Into U-5Fs	Into 304L SS[a]	Total Bandwidth[a]
550	6.0×10^5	No number[2]	18	1.0	19
	1.2×10^6	Ref. 2	25	1.3	26
	3.0×10^6	Ref. 2	40	2	42
	3.6×10^6	25-714	41	2	43
	1.8×10^7	1-712	76	4	80
		1-715	72	4	76
	3.6×10^7	2-716	95	7	102
600	6.0×10^5	Ref. 2	43	2.3	45
	1.2×10^6	Ref. 2	56	3.0	59
	3.0×10^6	Ref. 2	90	4.8	95
	3.6×10^6	26-699	104	6	110
	1.8×10^7	3-708	128	12	140
		3-717	160	10	170
	3.6×10^7	4-700	188	16	204
		4-719	226	14	240
650	6.0×10^5	Ref. 2	94	5.0	99
	1.2×10^6	Ref. 2	133	7.0	140
	3.0×10^6	Ref. 2	209	11.0	220
	3.6×10^6	27-701	288	12	300
	1.8×10^7	5-707	618	22	640
		5-718	608	22	830
	3.6×10^7	6-703	890	30	1220
		6-720	690	30	1020
700	6.0×10^5	665	200	10	190
	3.0×10^6	Ref. 2	503	26.5	530
710	6.0×10^5	741	352[b]	68	420
720	6.0×10^5	737	790[b]	150	940
730	6.0×10^5	673	Gross melting		

[a]For penetration coefficients, see Figs. 1 and 2. From the two data points for 700°C: $P^2_{total} = (7.6 \times 10^{-10}\ cm^2/sec)\ t$, and $P^2_{304L\ SS} = (2.0 \times 10^{-12}\ cm^2/sec)\ t$, where P = penetration in centimeters, and t = annealing time in seconds.
[b]Incipient melting.

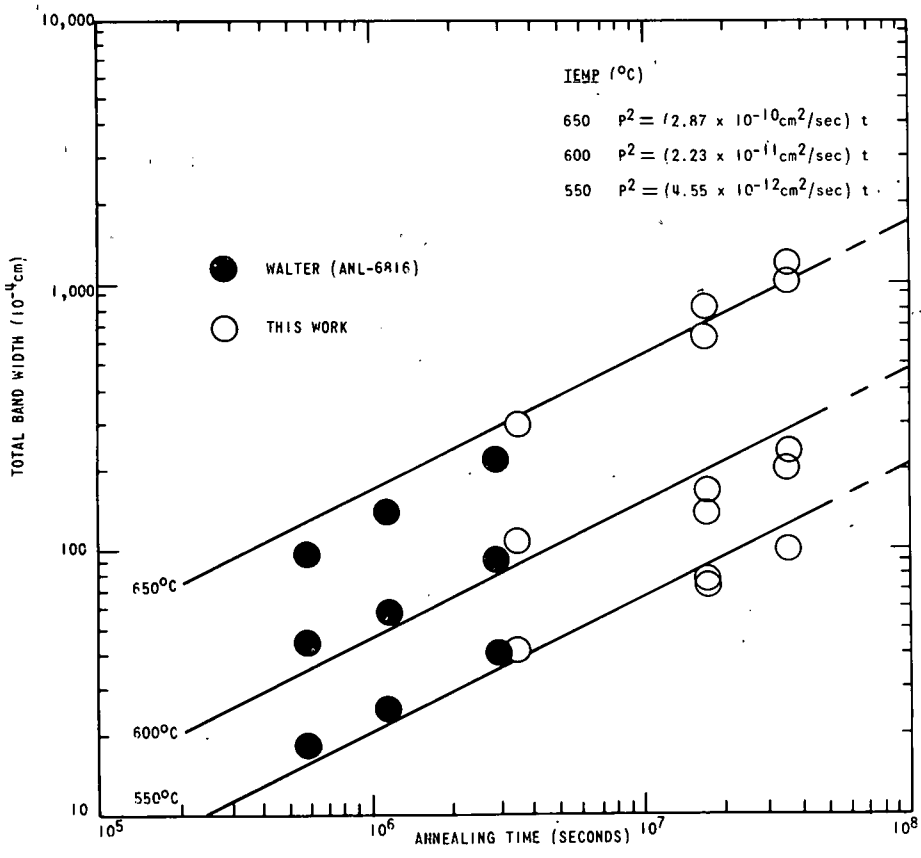

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Fig. 1. Total Bandwidth as a Function of Annealing Time for Uranium-5 w/o Fissium (Batch R-409) with Type 304L Stainless Steel

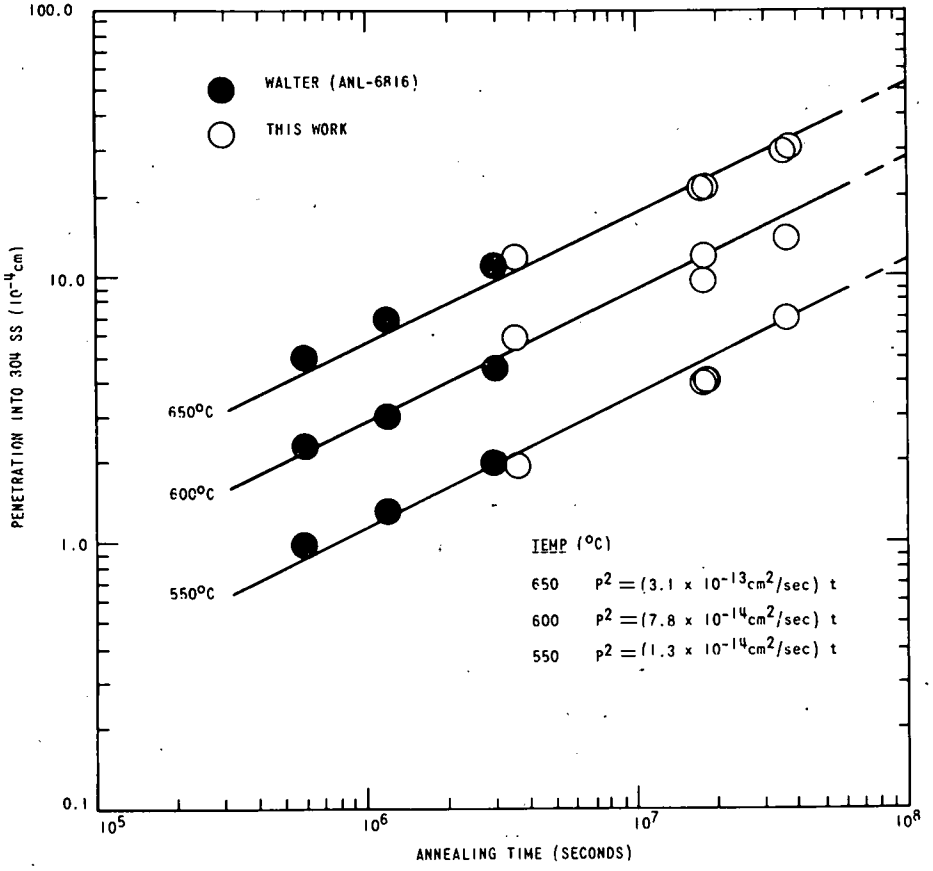

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Fig. 2. Penetration into Type 304L Stainless Steel as a Function of Annealing Time for Uranium-5 w/o Fissium (Batch R-409)

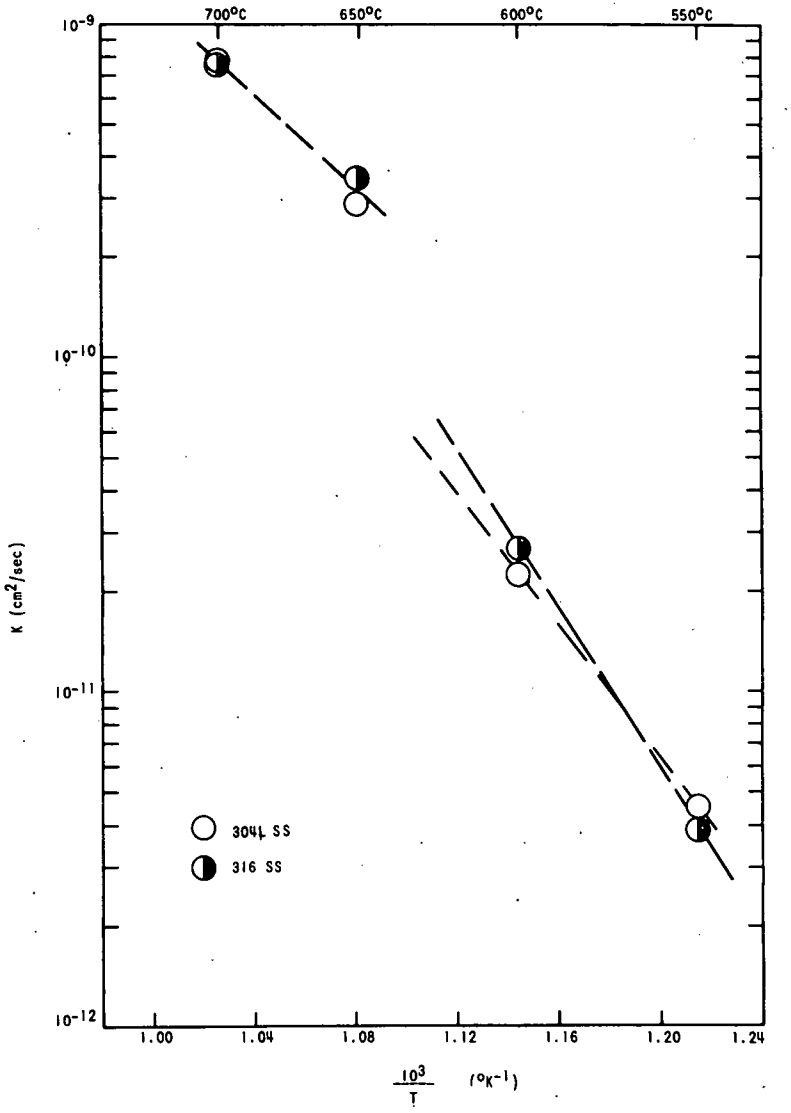

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Fig. 3. Penetration Coefficient K, Based on Total Bandwidth, versus 1/T for Uranium-5 w/o Fissium (Batch R-409) with Types 304L and 316 Stainless Steel

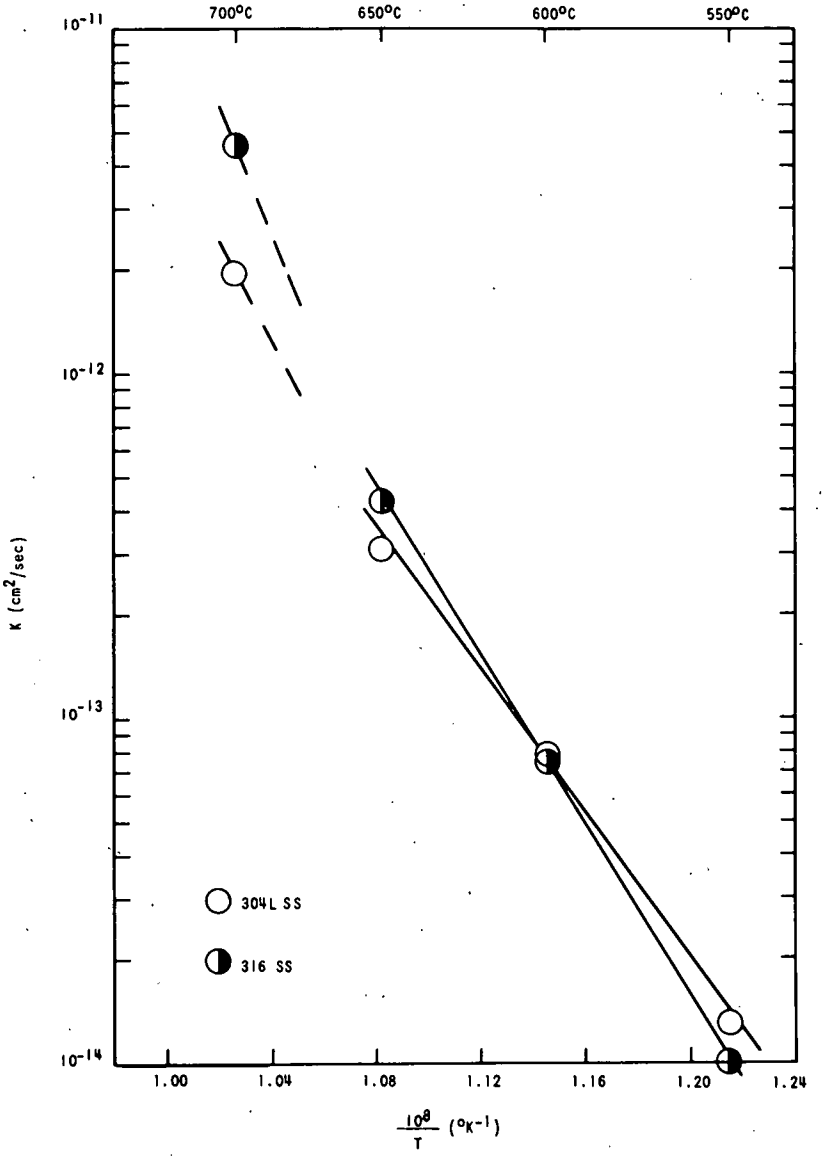

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Fig. 4. Penetration Coefficient K, Based on Steel Penetration, versus 1/T for Uranium-5 w/o Fissium (Batch R-409) with Types 304L and 316 Stainless Steel

At 600°C, the penetration coefficients are nearly one order of magnitude higher than at 550°C and, accordingly, penetrations are at least a factor of two greater for equivalent annealing times. Thus, at 600°C, with an annealing time of 3.6×10^7 sec, fuel-alloy and steel penetrations are 226 and 16 μ (0.0089 and 0.0006 in.), respectively.

At 650°C, the coefficient for penetration in the fuel alloy is at least one order of magnitude higher than at 600°C, but the coefficient for the steel at 650°C is higher by a factor of only about four--3.1×10^{-13} cm^2/sec, in contrast to 7.8×10^{-14} cm^2/sec at 600°C. The apparent enhancement of diffusion in the fuel alloy at 650°C is reflected in Fig. 3 by the deviation

from linearity at 650°C in the increase in coefficient with increasing temperature. Note from Fig. 4 that a similar deviation does not occur in the steel-penetration coefficient. The enhanced diffusion in the fuel alloy is also reflected in the fact that at 650°C, steel penetration constitutes only an average of 3% of the total bandwidth, in contrast to 5% at 550, 600, and 700°C (see Table II). The enhanced diffusion at 650°C is probably an induced effect of a phase transformation (alpha to beta uranium).

At 710 and 720°C, steel penetration constitutes about 16% of the total bandwidth, in contrast to 5% at 700°C. The higher proportion at the two higher temperatures is attributed to an enhanced diffusion in the steel as a result of incipient melting at the initial interface. Microstructural evidence for incipient melting (eutectic product) was observed in the couples annealed at 710 and 720°C (see Fig. 5a); gross macroscopic melting was observed in the couple annealed at 730°C.

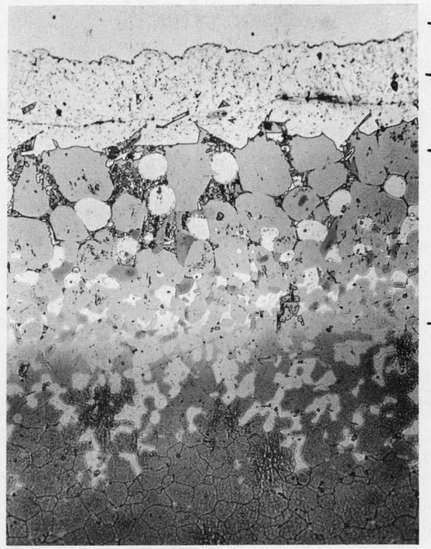
On the basis of a microprobe analysis made of couple 665 (6.0×10^5 sec at 700°C), liquid-phase formation is seen to result from a three-phase interaction of: (1) a phase based on the intermediate binary phase UFe_2, (2) a phase based on the binary phase U_6Fe and containing nickel, and (3) a gamma-uranium solid solution enriched in molybdenum. Uranium, ruthenium, and, to a lesser extent, molybdenum are seen to penetrate the steel; iron and nickel are the major elements diffusing into the fuel alloy. As a consequence of the latter diffusion, two bands, (1) single-phase alpha iron and (2) alpha iron plus sigma (Fe-Cr), are formed in the steel, as shown in Fig. 5b. The diffusion-band formations occurring at lower temperatures are illustrated in Figs. 5c-e.

B. Couple of Uranium-5 w/o Fissium (Batch R-409) with Type 316 Stainless Steel

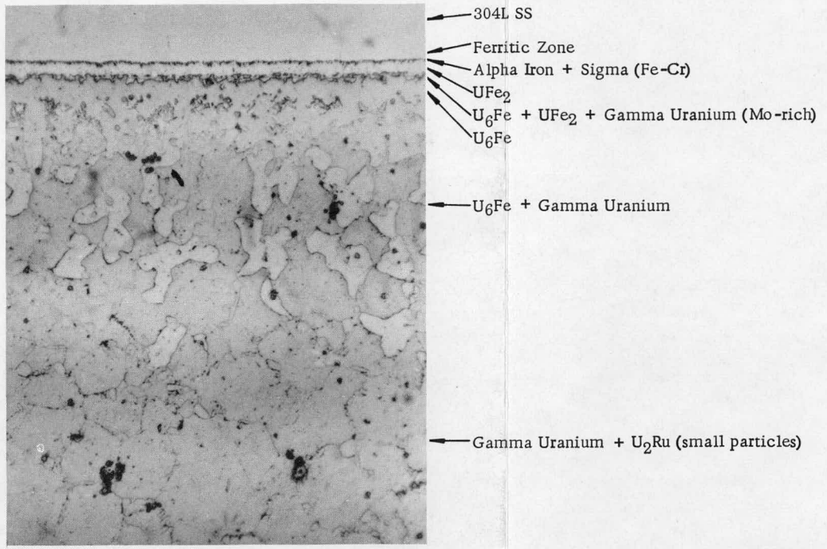
The penetration data obtained for this combination are given in Table III. In general, the penetrations are nearly the same as those measured for Type 304L stainless steel (see Figs. 6 and 7), and, accordingly, so are the penetration coefficients (see Figs. 3 and 4). At 650°C, transformation-induced enhanced diffusion in the fuel alloy is again indicated by the deviation from linearity in the plot of K versus 1/T in Fig. 3. In contrast to Type 304L, for which $T_m = 705 \pm 5$°C, T_m for Type 316 stainless steel is slightly higher, 715 ± 5°C. Incipient melting at 715°C was again observed at the initial interface, rather than in the fuel alloy or steel.

C. Couple of Modified Uranium-5 w/o Fissium (Batch R-410) with Type 304L Stainless Steel

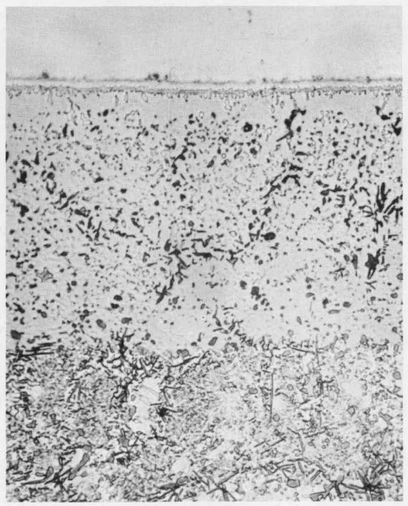
The penetration data for this combination at 650°C are given in Table IV, and are plotted against annealing time in Fig. 8. The plots for uranium-5 w/o fissium alloy (Batch R-409) containing only 75 ppm of



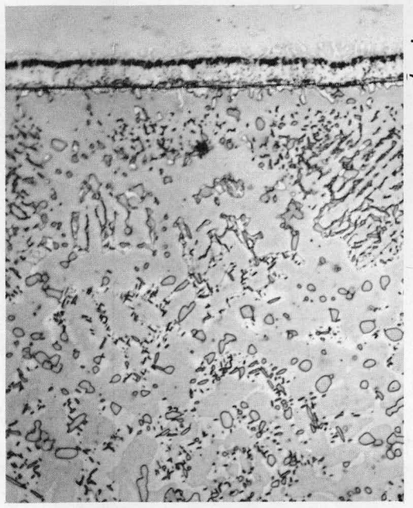
48312 (a)



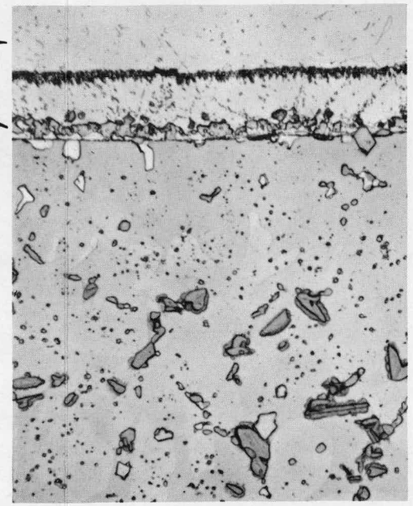
46078 (b)



50504 (c) 500X



49917 (d) 500X



49930 (e) 500X

Fig. 5. Microstructures of Diffusion Couples. (a) Couple 741 (168 hr at 710°C). (b) Couple 665 (168 hr at 700°C). (c) Couple 716 (10^4 hr at 550°C). (d) Couple 700 (10^4 hr at 600°C). (e) Couple 703 (10^4 hr at 650°C).

TABLE III. Interdiffusion Bandwidths for Uranium-5 w/o Fissium (Batch R-409) and Type 316 Stainless Steel

Temp, °C	Annealing Time, sec	Couple No.	Maximum Penetration, 10^{-4} cm		
			Into U-5Fs	Into 316 SS[a]	Total Bandwidth[a]
550	3.6×10^6	785	38	2	40
	1.1×10^7	779	57	3	60
	1.8×10^7	778	66	4	70
600	6.0×10^5	764	48	2	50
	3.6×10^6	781	89	6	95
	1.1×10^7	775	112	8	120
	1.8×10^7	772	165	10	175
650	6.0×10^5	762	126	6	132
	3.6×10^6	803	370	10	380
	1.1×10^7	773	603	17	620
	1.8×10^7	770	920	21	941
700	6.0×10^5	787	172	16	188
710	6.0×10^5	793	180	20	200
715	6.0×10^5	794	220[b]	40	260

[a]For penetration coefficients, see Figs. 6 and 7. From the one datum point for 700°C: $P^2_{total} = (7.5 \times 10^{-10}\ cm^2/sec)\ t$, and $P^2_{316\ SS} = (4.6 \times 10^{-12}\ cm^2/sec)\ t$, where P = penetration in centimeters, and t = annealing time in seconds.

[b]Incipient melting.

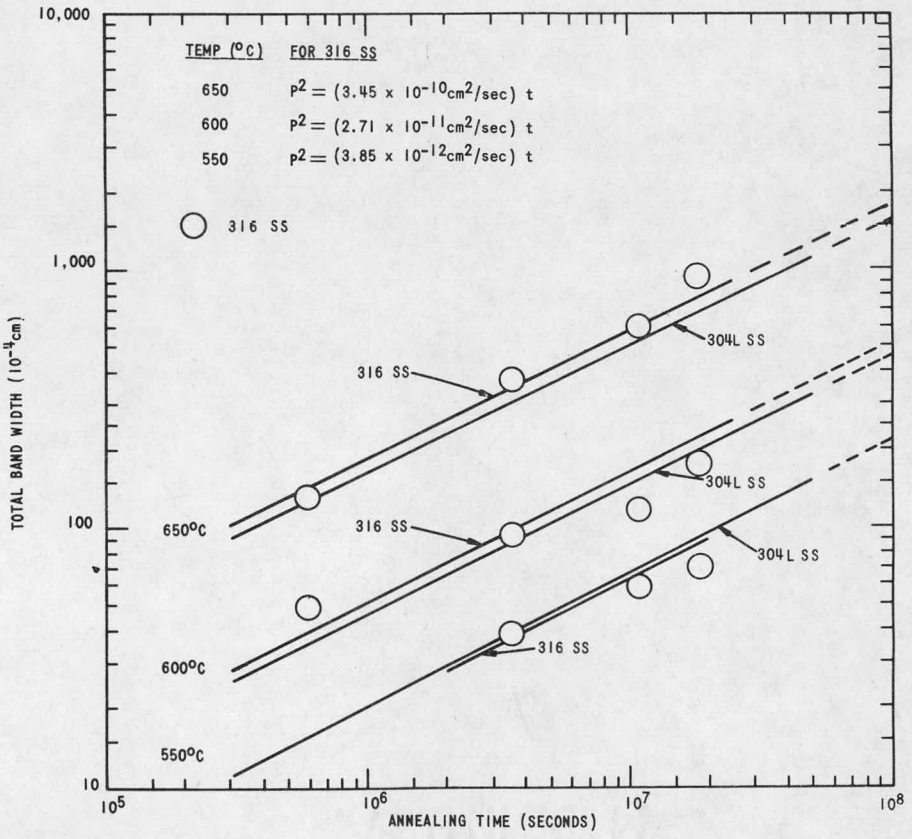


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Fig. 6. Total Bandwidth as a Function of Annealing Time for Uranium-5 w/o Fissium (Batch R-409) with Type 316 Stainless Steel

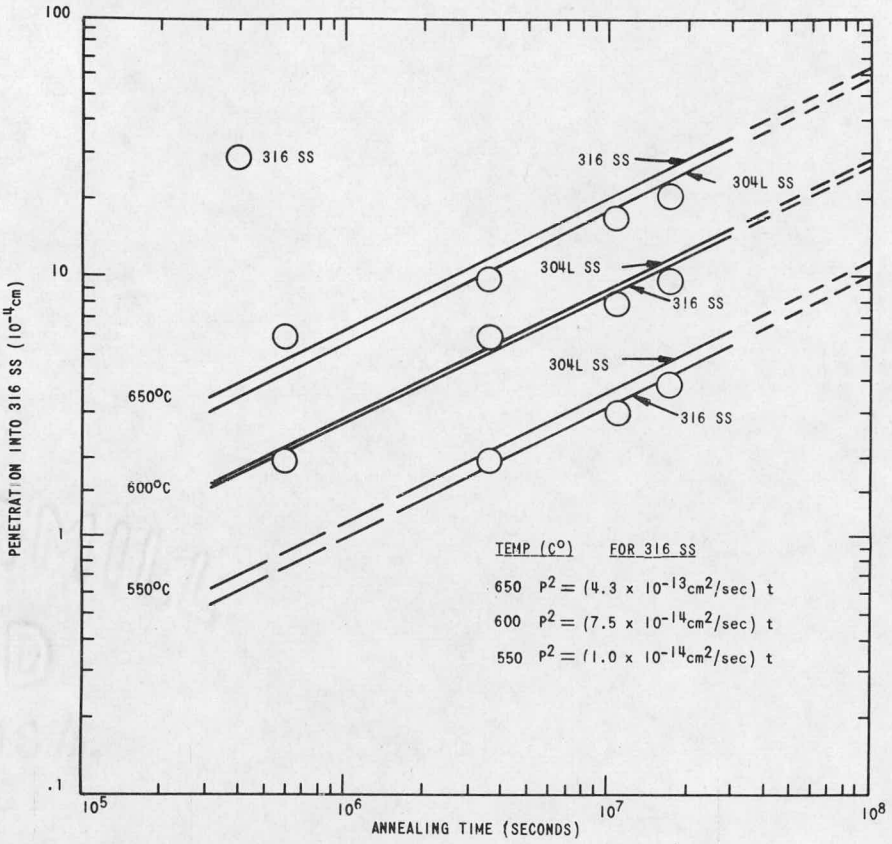

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Fig. 7. Penetration into Type 316 Stainless Steel as a Function of Annealing Time for Uranium-5 w/o Fissium (Batch R-409)

TABLE IV. Interdiffusion Bandwidths for Uranium-5 w/o Fissium (Batch R-410)[a] and Type 304L Stainless Steel

Temp, °C	Annealing Time, sec	Couple No.	Maximum Penetration, 10^{-4} cm		
			Into U-5Fs	Into 304L SS	Total Bandwidth[b]
650	6.0×10^5	7-725	160	7	167
	3.6×10^6	8-722	408	12	420
	6.0×10^6	8-709	450	16	466
	1.8×10^7	9-723	725	25	750
	3.6×10^7	10-724	1050	30	1080
700	6.0×10^5	834	152	8	160
710	6.0×10^5	838	240	12	252
715	6.0×10^5	836	200	14	214
720	6.0×10^5	840	228	16	244
730	6.0×10^5	841	440[c]	~100	>540

[a]Silicon: 734 ppm; aluminum: 1406 ppm.
[b]For penetration coefficients at 650°C, see Fig. 8.
[c]Incipient melting.

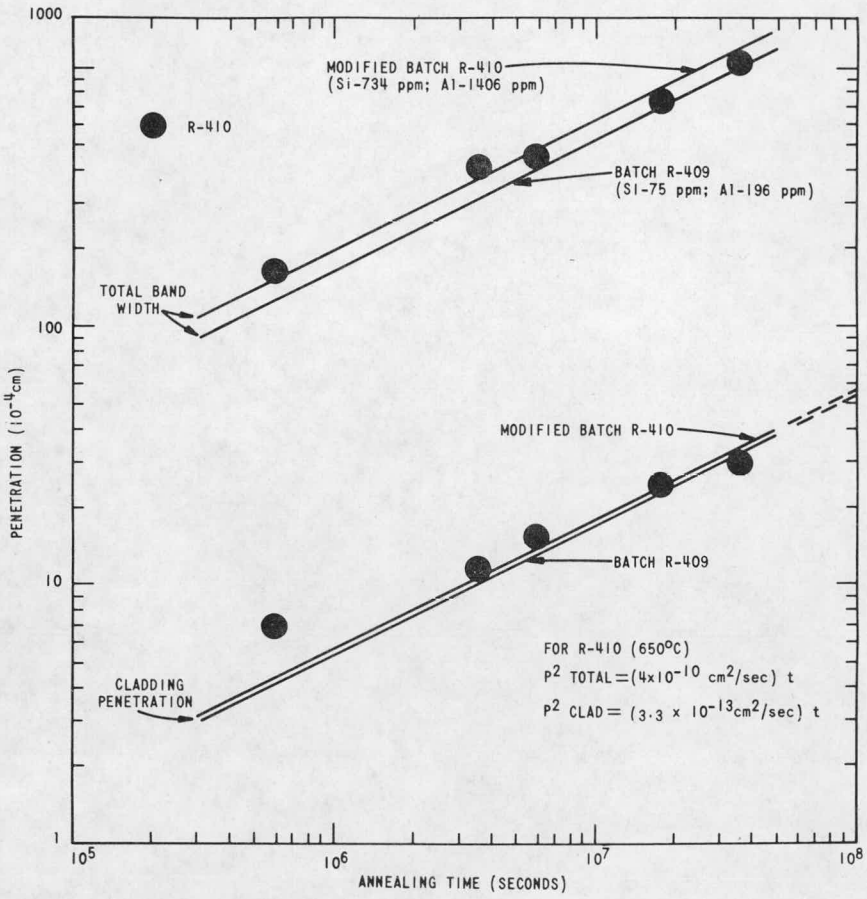

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Fig. 8. Penetration as a Function of Annealing Time at 650°C for Modified Uranium-5 w/o Fissium (Batch R-410) with Type 304L Stainless Steel

silicon and 196 ppm of aluminum are included in Fig. 8 for comparison. By comparison, compatibility at 650°C is unaffected by the presence of the larger concentrations of silicon and aluminum (734 and 1406 ppm, respectively) in the fissium alloy. The higher concentrations seem to be beneficial in increasing the temperature at which liquid-phase formation occurs upon reaction with the stainless steel. For Batch R-410, T_m is 725 ± 5°C, in contrast with 705 ± 5°C for Batch R-409.

IV. CONCLUSIONS

The experimental data indicate that at temperatures up to 650°C and for times to 10^4 hr, uranium-5 w/o fissium alloy is equally compatible with Types 304L and 316 stainless steel. With both steels, the compatibility is characterized by much more penetration of diffusing elements into the fuel alloy than into the steels. When the steels were annealed for 10^4 hr at 650°C, penetration was only about 30 μ (0.0011 in.), which is highly encouraging for the selection of either steel as a jacket material. The relatively larger fuel-alloy penetrations and the occurrence in the steels of diffusion

bands containing the brittle UFe_2 and sigma (Fe-Cr) phases are second-order effects, but should be considered.

Type 316 stainless steel reacts with the fuel alloy to form a liquid phase at a slightly higher temperature than Type 304L stainless steel, a factor favoring the former alloy. With Type 304L, however, a similarly high T_m can be attained by adding large concentrations of silicon and aluminum to the fissium alloy.

The penetration data for Batch R-410 indicate that high silicon and aluminum contents have no effect on the compatibility of the fuel material with Type 304L stainless steel at temperatures to 650°C.

ACKNOWLEDGMENT

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REFERENCES

1. C. M. Walter and L. R. Kelman, Penetration Rate Studies of Stainless Steel by Molten Uranium and Uranium-Fissium Alloy, J. Nucl. Mat. 6(3), 281-290 (Aug 1962).
2. C. M. Walter, Interdiffusion between Uranium-5 w/o Fissium Alloy and Type 304 Stainless Steel, ANL-6816 (March 1964).
3. Annual Report for 1961, Metallurgy Division, ANL-6516, p. 374 (1962).
4. C. M. Walter and J. A. Lahti, Compatibility of U-Pu-Fz Fuel Alloys with Potential Cladding Materials, Nucl. Appl. 2, 308-319 (Aug 1966).