The compatibility of stainless-steel cladding materials with uranium carbide fuel*

by W. E. STUMPF†, Pr. Eng., B.Sc. (Eng.) (Pret.), Ph.D. (Sheffield) (Member) and
S. VENTER†, Pr. Eng., B.Sc. (Stell.), B.Sc. Hons. (Pret.), M.Sc. (Imperial Coll.) (Visitor)

SYNOPSIS

Some of the factors that govern the choice of a nuclear fuel are briefly discussed, special reference being made to the introduction of advanced carbide fuels into fast-breeder programmes. One of these factors, i.e. the compatibility of carbide fuels with stainless-steel cladding, is discussed in depth. A very sensitive technique for the study of compatibility interactions between fuel and cladding is described in respect to the effects of particle size, specific surface area and surface oxidation of the fuel, and microstructure of the cladding on the compatibility behaviour of the cladding with the fuels.

Finally, the need for the development of modified or stabilized uranium carbide fuels is discussed, and some results are presented to show the effects of small amounts of sulphur in these fuels on their compatibility with stainless-steel cladding materials.

SAMEVATTING

Sommige faktore wat die keuse van 'n kernbrandstof bepaal word kortliks bespreek met verwysing na die ingebruikneming van die gevorderde karbiedbrandstowwe in die snelkweekreaktore. Een van hierdie faktore, naamlik die samevoegbaarheid van die karbiedbrandstowwe met roesvrystaal-bekledingsmateriaal word breedvoerig bespreek. 'n Baie gevoelige tegniek wat ontwikkel is om die samevoegbaarheidswisselwerking tussen brandstof en bekleding te ondersoek, word beskryf met verwysing na die invloed van deeltjiegrootte, spesifieke oppervlakte en oppervlakoksidasie van die brandstof en die mikrostruktuur van die bekleding op die samevoegbaarheidsgedrag van die bekleding met die brandstof.

Uiteindelik word die behoefte om gewysigde of gestabiliseerde karbiedbrandstowwe te ontwikkel, bespreek en resultate weergegee oor die invloed van klein byvoegings van swael tot uraankarbied-brandstowwe op die samevoegbaarheidsgedrag met roesvrystaal-bekledingsmateriaal.

Introduction

Metallic nuclear fuels have a number of properties that place serious limitations on their serviceability under the stringent conditions encountered in nuclear-power reactors. Consequently, substantial effort has been devoted to the development of ceramic nuclear fuels. The greatest attention has been given to UO_2, with the result that the majority of the commercial nuclear thermal reactors in operation at present are fuelled with this oxide of uranium.

In the past few years, however, the need has arisen for a nuclear fuel capable of operating under the far more stringent conditions encountered in sodium-cooled fast-breeder reactors. The various fast-breeder prototypes that are coming into operation in the world have been fuelled with $(UPu)O_2$, and at least the first generation of commercial fast breeders will also employ the same fuel. However, because of their rather low thermal conductivities and low uranium densities, UO_2 and PuO_2 are not ideally suited to use in fast reactors if all the advantages of the fast flux are to be utilized. Increasing attention is therefore being given to the development of potentially more attractive ceramic fuels for use in fast reactors.

Table I gives a comparison of some of the physical properties of various compounds of uranium and plutonium. The metallic forms have excellent thermal conductivities, and metal densities of 100 per cent (i.e. the reactor core does not have to carry useless atoms), but, owing to their low melting points and their tendency to swell under irradiation, they could not be considered for use in a fast reactor. The oxides have high melting points but rather low metal densities and very low thermal conductivities, especially at the higher temperatures. The carbides manifest considerably more favourable properties, viz high melting points, higher metal densities, and much greater thermal conductivities than the oxides. The nitrides, because of their rather high neutron-absorption cross-sections, and the phosphides and sulphides, because of their low metal densities and also high neutron-absorption cross-sections, are less serious candidates for use in fast-breeder reactors.

The introduction of carbide fuels into fast-breeder reactors could therefore result in much more efficient reactors with lower fuel centreline temperatures, smaller cores, and higher breeding ratios, which would lead to shorter fuel-doubling times — a factor that would become important should the world run into a plutonium shortage.

Unfortunately, carbide fuels also present some disadvantages, one being the much more difficult preparation and handling procedure, which has to be carried out under highly pure inert gas in sealed glove boxes since the carbides are highly susceptible to oxidation (in powder form, uranium carbide is even pyrophoric). A second major disadvantage is the difficulty with which a single-phase material can be prepared, as illustrated by the U–C phase diagram in Fig. 1. At lower temperatures, uranium carbide exhibits no solubility for either uranium or carbon, and, in practice, a two-phase fuel would therefore have to be accepted. Owing to the poor irradiation stability of a (UC+U) fuel, a hyperstoichiometric fuel, which usually consists of the non-equilibrium $(UC+UC_2)$ or, upon slow cooling,

*A paper given at the S.A. Institute of Physics Symposium on 'The Deterioration of Materials in Service', which was held in Cape Town from 5th to 7th December, 1977.

†Atomic Energy Board, Pretoria.

of ($UC+UC_2+U_2C_3$), would be preferred, although this could lead to carburization of the stainless-steel cladding by the higher carbides, as shown by the diagram of free energy of formation in Fig. 2. From this diagram it can be seen that, although uranium carbide would not carburize the main constituents of stainless steel (viz chromium and iron), PuC, and especially all the higher carbides of both uranium and plutonium, would carburize the cladding, causing embrittlement that in turn could lead to premature failure of the cladding tube.

TABLE I

SOME PHYSICAL PROPERTIES OF VARIOUS URANIUM AND PLUTONIUM COMPOUNDS

	Metal		Oxide		Carbide		Nitride		Phosphide		Sulphide	
	U	Pu	UO_2	PuO_2	UC	PuC	UN	PuN	UP	PuP	US	PuS
Melting point (°C)	1132	640	2730	2300	2400	1650	2600	2500	2610	2600	2480	2350
Theor. density (g/cm³)	19,05	19,86	10,96	11,46	13,63	13,62	14,32	14,22	10,23	9,87	10,87	10,60
Metal density (g/cm³)	19,05	19,86	9,66	10,11	12,96	12,95	13,51	13,43	9,07	8,74	9,58	9,36
Thermal conductivity (W/m.K) at 500 °C	30		4,7		16		12		≈17		≈14	
Thermal conductivity (W/m.K) at 1500 °C			2,5		17		16					
Neutron-absorption cross-section of non-metallic component: thermal neutrons (b)			2×10^{-4}		$3,4\times10^{-3}$		1,85		0,19		0,52	
fast neutrons (mb)			<< 1		<< 1		90					

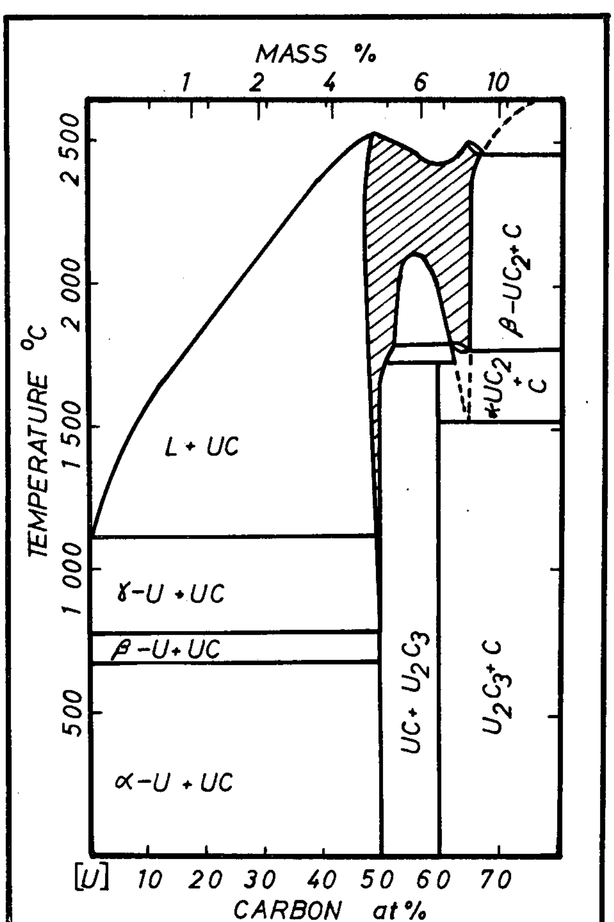

Fig. 1—The U-C phase diagram

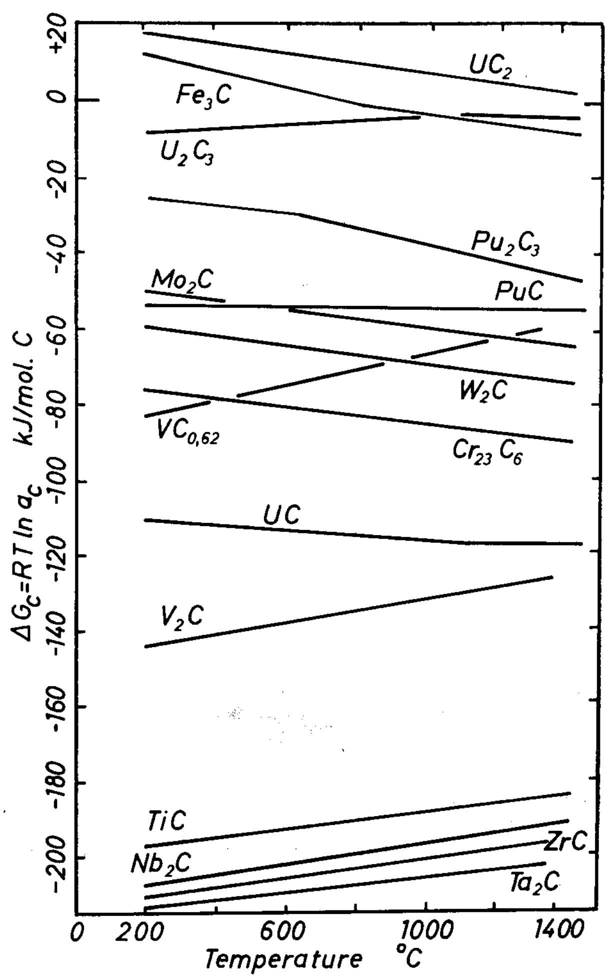

Fig. 2—The free energy of formation of various carbides

This problem of carburization of the cladding by hyperstoichiometric carbide fuel has been studied extensively at the Atomic Energy Board over the past few years.

Experimental Techniques[1-3]

Briefly, the experimental method involves a stainless-steel capsule containing six small tensile specimens of the particular cladding in question, the space between the specimens being filled by a coarse granular uranium carbide fuel of the required composition. The capsule is then either evacuated or filled with purified liquid sodium and sealed off by welding before annealing. An exploded arrangement is shown in Fig. 3. The thickness of the specimens and the annealing temperature are chosen to represent typical conditions in a fast-breeder reactor. The specimens and fuel are subsequently removed for chemical, mechanical, and metallurgical investigation. The combination of these three methods of investigation has proved to be highly sensitive to even very small amounts of carbon pickup by the cladding, which would not have been observed by the traditional diffusion couple alone.

Results

Particle Size of Fuel[3, 4]

Figs. 4 to 6 show, rather unexpectedly, that ball-milled uranium carbide powders with a specific surface area greater than about 200 m^2/kg carburize stainless-steel cladding materials to a much greater extent than do coarser particles of the same fuel obtained by crushing and grinding. In this case, the fuel had a carbon content of 4,83 per cent and consequently consisted of ($UC+UC_2$). The carburization of the specimens wrapped in nickel foil, as shown in Figs. 4 and 5, indicates that transfer of the carbon from the fuel to the cladding occurs via the gas phase rather than by direct contact in a vacuum- or gas-bonded arrangement. The serious extent of embrittlement and carbon pickup that can occur during the carburization of these potential stainless-steel cladding materials is apparent from Figs. 4 and 5, while Fig. 6 shows the marked difference in microhardness and microstructure near the surface between a carburized and an uncarburized steel. In this particular case, shown in Fig. 6(b), the level of carburization was so high that transformation to a pearlitic type of product consisting of ferrite plus M_7C_3 lamella had started on the grain boundaries.

Effect of Surface Oxidation of Carbide Powder[5]

In some further work it soon appeared that the above particle-size effect could be due to surface oxidation of the powder particles, the finer powders being oxidized to a higher level than the coarser ones. This was followed by an investigation in which the particle size was kept constant but the degree of surface oxidation of the fuel was deliberately varied. Some of these results are shown in Figs. 7 to 10.

From Figs. 7 and 8, it is obvious that surface oxidation of the fuel particles has a direct effect on the carburization of the cladding, but that particle size has only an indirect effect through the surface oxidation. This particular case confirms the thermodynamic data of Fig. 3 that a single-phase uranium carbide of stoichiometric composition (carbon 4,80 per cent) causes no measurable embrittlement or carbon transfer to the cladding, on condition that no surface oxidation is present. However, when surface oxidation of even this type of fuel occurs, carburization of the cladding results. Fig. 9 once again shows the difference in microhardness and microstructure between two cladding specimens annealed in contact with oxidized and unoxidized stoichiometric uranium carbide fuel respectively. The microstructure after tensile

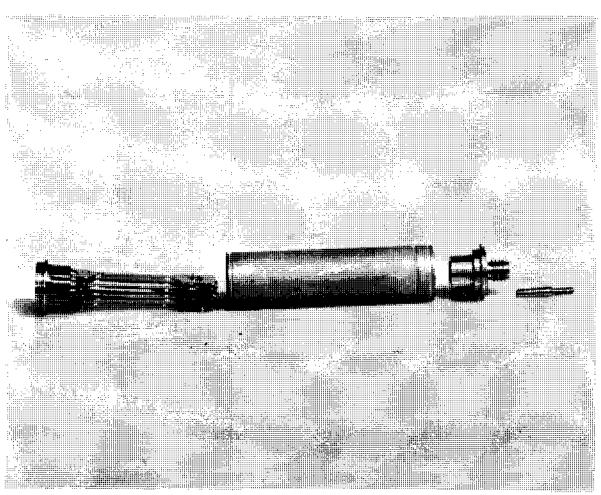

Fig. 3—Arrangement of capsule and specimens

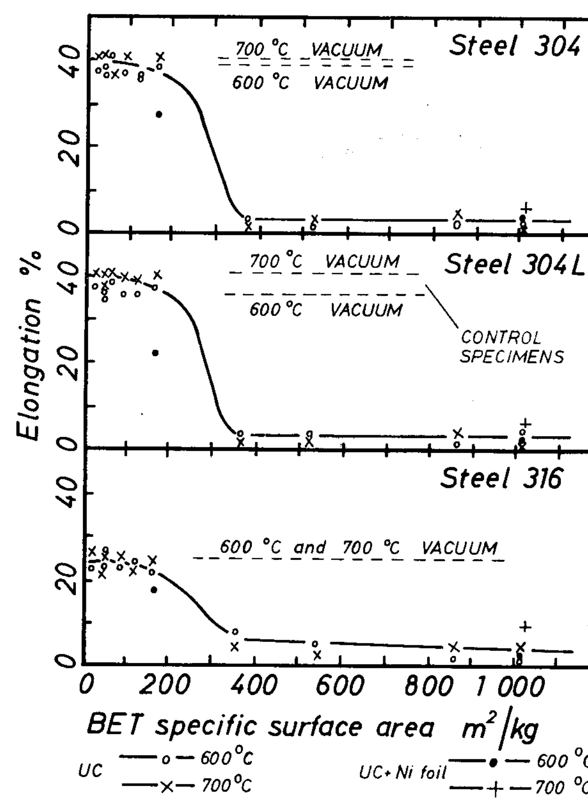

Fig. 4—Room-temperature elongation values for steel specimens after being annealed for 1000 h at 600°C and 700°C in contact with hyperstoichiometric uranium carbide powders (C_{eqw}=4,88 mass per cent) with different BET specific surface areas. Also shown are some results for steel specimens separated from the fuel by a thin nickel foil

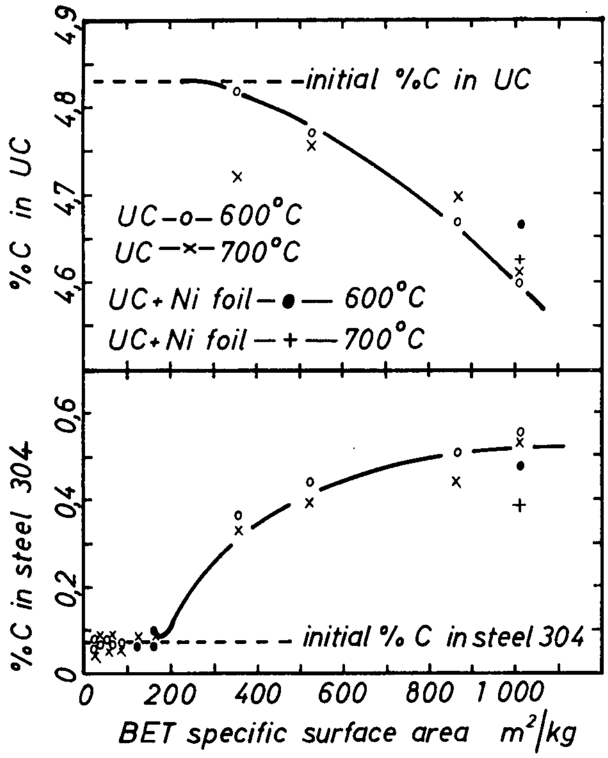

Fig. 5—The total carbon content of steel 304 specimens and the carbon content of the uranium carbide after being annealed for 1000 h at 600 °C and 700 °C in mutual contact, as a function of the BET specific surface area of the hyperstoichiometric uranium carbide powder (C_{eqw}=4,88 mass per cent). Also shown are some results for steel specimens separated from the fuel by a thin nickel foil

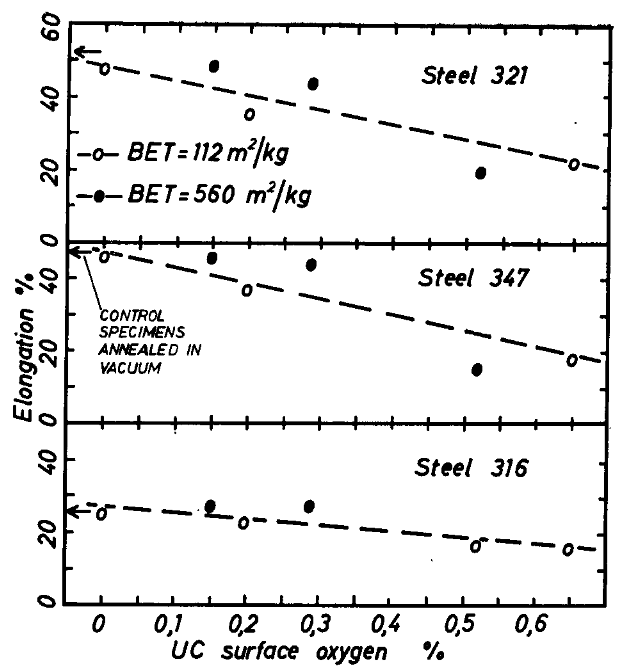

Fig. 7—Room-temperature elongation values of steel specimens after being annealed for 1000 h at 700 °C in vacuum-bonded tests in contact with stoichiometric uranium carbide powders (C_{eqw}=4,79 mass per cent) of different surface oxygen contents

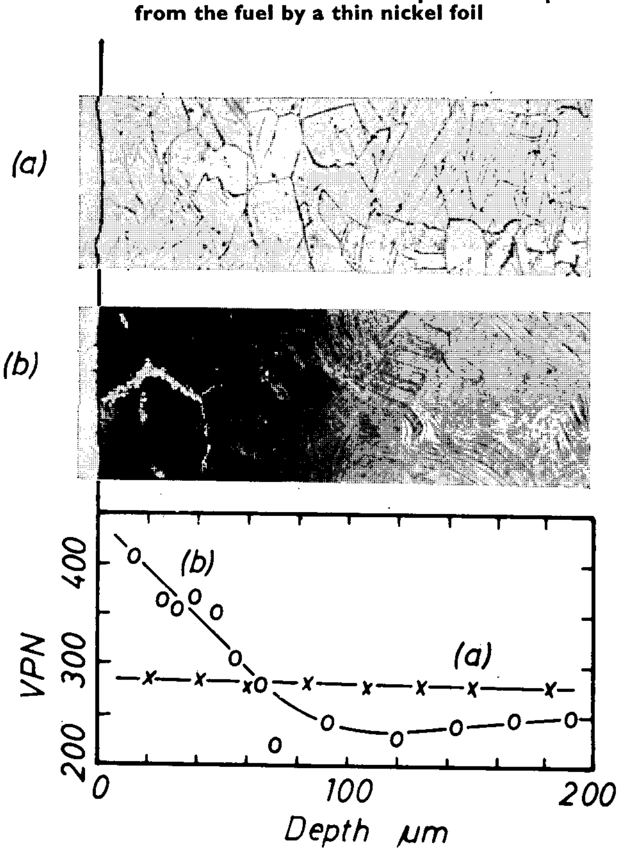

Fig. 6—Steel 316 after being annealed for 1000 h at 700 °C directly in contact with hyperstoichiometric uranium carbide powder (C_{eqw}=4,88 mass per cent) of (a) BET=169 m²/kg and (b) BET=357 m²/kg. The graph shows the corresponding microhardness measurements

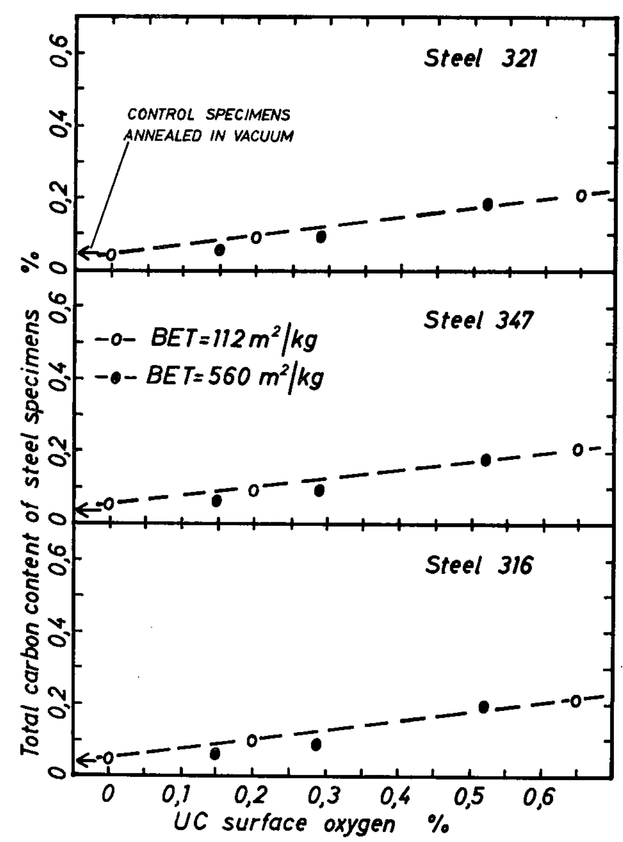

Fig. 8—Total carbon contents of steel specimens after being annealed for 1000 h at 700 °C in vacuum-bonded tests in contact with stoichiometric uranium carbide powders (C_{eqw}=4,79 mass per cent) of different surface oxygen contents

testing — Fig. 9(b) — shows an opened grain-boundary crack, which is typical of grain-boundary embrittlement due to carburization.

A quantitative model was developed for gas-bonded capsules to describe this effect of surface oxidation of the fuel on the carburization behaviour of the cladding. Briefly, the model makes use of the known oxidation behaviour of uranium carbide, which occurs as follows:

$$UC+(2+x)O \rightarrow UO_{2+x}+C,$$

where C is free carbon situated in the surface-oxidized layer of UO_{2+x} on the uranium carbide. The model then predicts the establishment of a suitable CO/CO_2 gas equilibrium in the sealed capsule, which enables the free carbon to be transferred from the fuel to the cladding by the equilibrium reaction

$$C_{fuel}+CO_2 \rightarrow 2CO \rightarrow C_{steel}+CO_2.$$

A comparison between the predicted and observed carbon transfer, according to the model, is shown in Fig. 10. In this diagram the value of x refers to UO_{2+x}, which is formed on the surface of the fuel particles during oxidation. Although the scatter in the observed results is rather large, there is a fair amount of agreement between the model and the observed results, particularly for smaller values of x. Similar results were also found for sodium-bonded capsules, although the transfer of carbon then occurs rather more directly through the liquid sodium.

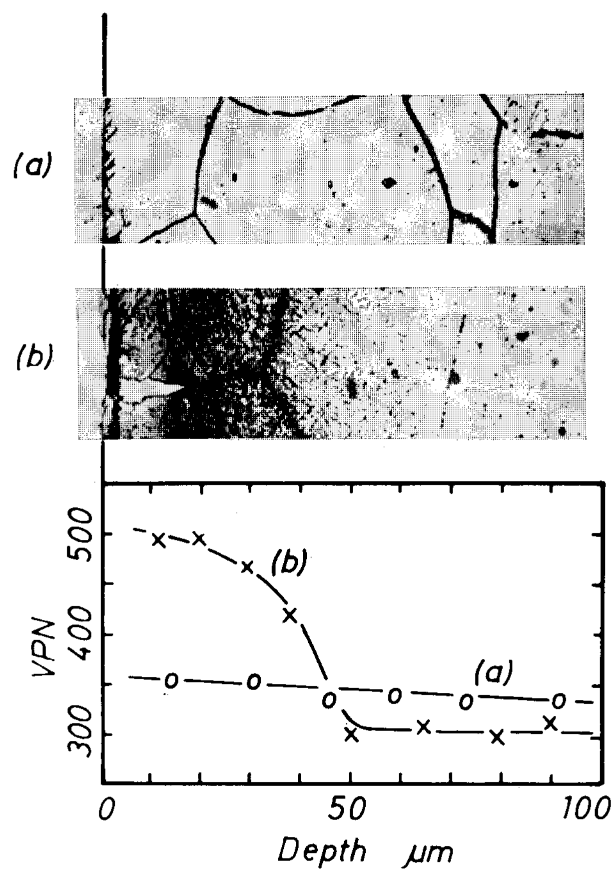

Fig. 9—Steel 321 after being annealed for 1000 h at 700°C in vacuum-bonded tests in contact with near-stoichiometric uranium carbide (C_{eqw}=4,79 mass per cent) and BET= 112 m^2/kg) of (a) no surface oxygen and (b) surface oxygen content=0,65 per cent. The graph shows the corresponding microhardness measurements

Microstructure and Alloy Content of the Cladding[6, 7]

The effect of the microstructure and alloy content of the cladding on its carburization behaviour by a hyperstoichiometric uranium carbide fuel was investigated for the stainless steels 304, 304L, and 316. The heat treatments covered effects of cold-work, solution treatment, and differences in grain size. Although it is known that the thermodynamic and kinetic behaviour of carbon in these steels is affected by the alloy content, and even though the microstructures varied greatly (specimens ranging in grain size from 4 to 40 μm were tested), no significant difference in behaviour between the alloy types and the various microstructures could be observed in the sodium-bonded tests. This points very strongly to the fact that the rate-controlling step in the whole process of carbon transfer from the fuel to the interior of the cladding is not the diffusion of carbon into the steel cladding, but rather the dissolution of the UC_2 phase in the fuel by the sodium.

Modification of Carbide Fuels

Several methods to modify or stabilize carbide fuels by suitable additions of a third constituent have been suggested at various times in the literature. Stabilization is carried out by the addition of, for example, chromium metal powder to the fuel so that carburization of the chromium occurs in the fuel itself rather than in the cladding. Modification of the fuel, on the other hand, usually consists of the addition of a non-metallic constituent to the fuel to alter the phase structure of the fuel. In the latter category, the addition of nitrogen or sulphur to uranium carbide to form solid solutions of UCN or UCS respectively has often been proposed. The purpose of such an addition would be to create a solubility for excess carbon in the uranium carbide, i.e. to displace the solid-solution field in Fig. 1 to lower temperatures. At the Atomic Energy Board, a great deal of attention has been given to all aspects of UCS fuels, and the compatibility behaviour of low-sulphur UCS fuels with stainless steels has been studied in depth[8].

UCS fuels were prepared[9] by the volatile-metal process, which, in brief, consists of reacting purified zinc sulphide with uranium carbide and subsequently driving off the volatile zinc. In general, the sulphur content was kept below about 0,5 mass per cent, which corresponds more or less to the reported limit of solubility of uranium sulphide in uranium carbide.

Figs. 11 and 12 show the post-annealing elongation (at room temperature) and the total carbon content of the tensile specimens after being annealed in sodium-bonded contact with UC and UCS fuels of different non-metal contents. (The impurities oxygen and nitrogen in these fuels generally act as equivalent carbon atoms and should also be added.) From this diagram it is obvious that the carburization of the cladding is a function of only the total non-metal content of the fuel, and that UCS and uranium carbide fuels of the same stoichiometry produce similar amounts of carburization of the cladding specimens, irrespective of the actual sulphur content of the fuel. Absolutely no increase in sulphur content of the steels could be determined after the annealing, indicating that embrittlement is caused

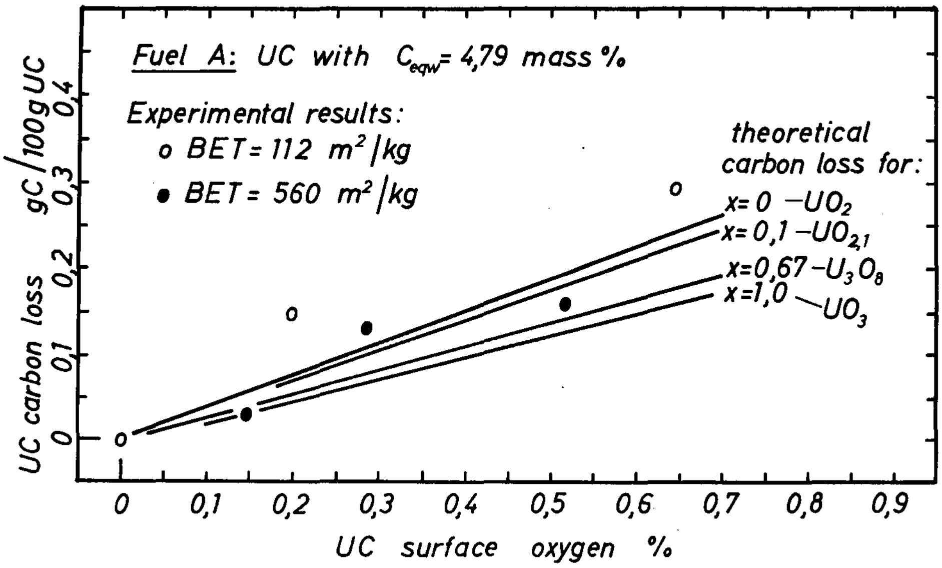

Fig. 10—Experimentally determined carbon losses for near-stoichiometric uranium carbide (C_{eqw}=4,79 mass per cent) after vacuum-bonded compatibility tests with various surface oxygen contents of the fuel powder. Theoretical carbon losses for a stoichiometric fuel as a function of surface oxygen content of the uranium carbide, for various values of *x*, are also shown

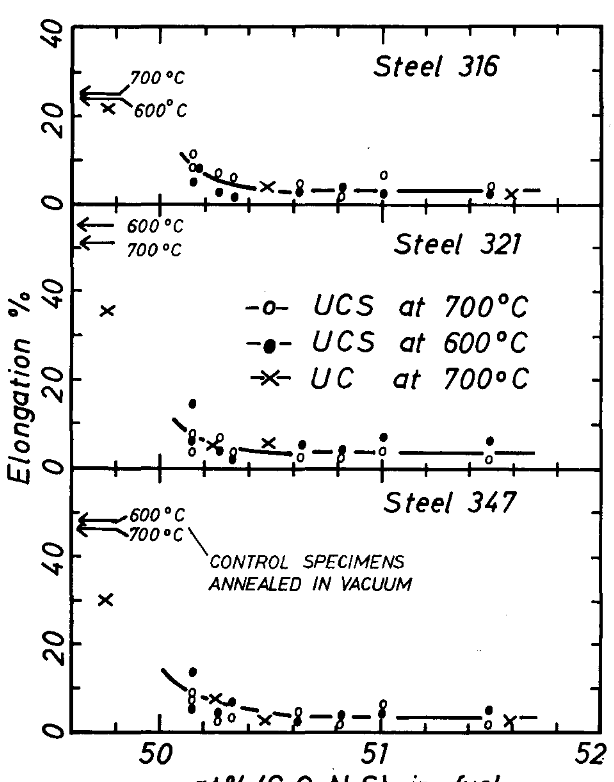

Fig. 11—Room-temperature elongation of steel specimens after being annealed for 1000 h at 600 and 700°C in sodium-bonded contact with UCS and UC fuels of different stoichiometry

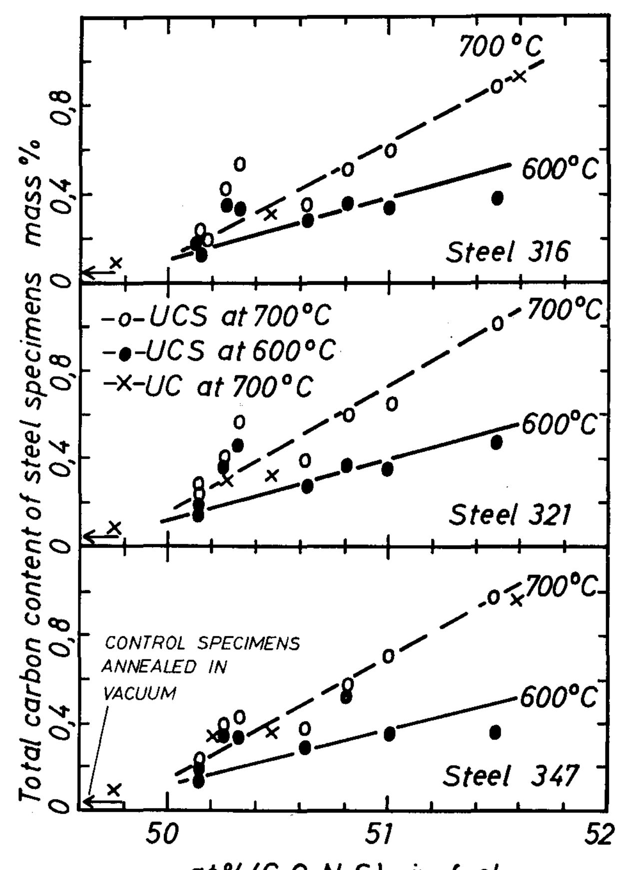

Fig. 12—Total carbon contents of steel specimens after being annealed for 1000 h at 600 and 700°C in sodium-bonded contact with UCS and UC fuels of different stoichiometry

only by carburization due to carbon released by the fuel.

This conclusion is confirmed by Fig. 13, which shows that the carburized microstructure and the microhardness gradients are very similar for both a UCS and a UC fuel of the same stoichiometry. These results, in addition to some X-ray work, prove that sulphur atoms, just like oxygen and nitrogen, act as carbon equivalents in that they dissolve in the uranium carbide lattice but thereby replace carbon atoms, which are then free to form higher carbides. This is also shown by the three microstructures of three different UCS fuels in Fig. 14. In both cases, with a non-metal content of more than 50 atom per cent, the needle-like UC_2 phase is still present and a solubility for excess carbon apparently does not exist.

The conclusion is therefore drawn that the addition of small amounts of sulphur to UC fuels has no direct advantage as far as the compatibility behaviour of the fuel towards the cladding is concerned.

Conclusions

To reduce the risk of cladding rupture due to carburization by the fuel, the following aspects should be kept in mind in the design of a sodium-bonded carbide fuel element for use in a fast breeder.

(a) Use highly dense fuel with little open porosity or, in the case of a granular fuel, use granules as coarse and as dense as possible.

(b) Avoid any surface oxidation of fuel pellets or granules.

(c) Keep the carbon content of hyperstoichiometric fuel as low as would be practically possible without producing a hypostoichiometric fuel.

(d) Deliberate additions of sulphur to a hyperstoichiometric uranium carbide fuel serve no useful purpose.

(e) Sulphur impurities in a uranium carbide fuel should be added as a carbon equivalent in the determination of the stoichiometry of the fuel.

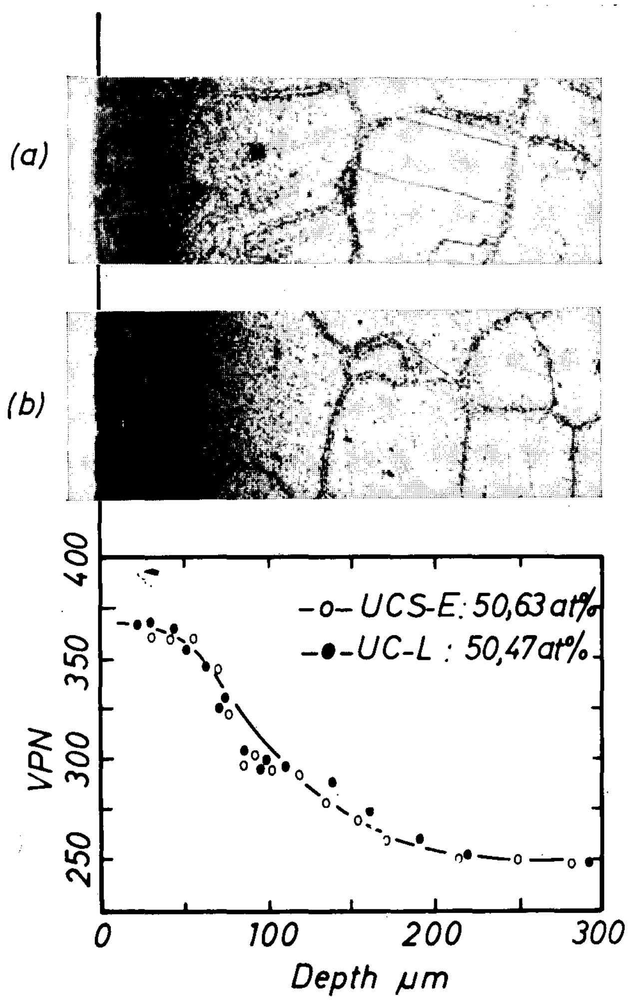

Fig. 13—Optical microstructures and microhardness gradients in steel 347 annealed for 1000 h at 700°C in sodium-bonded contact with (a) UCS and (b) UC fuels of similar stoichiometry

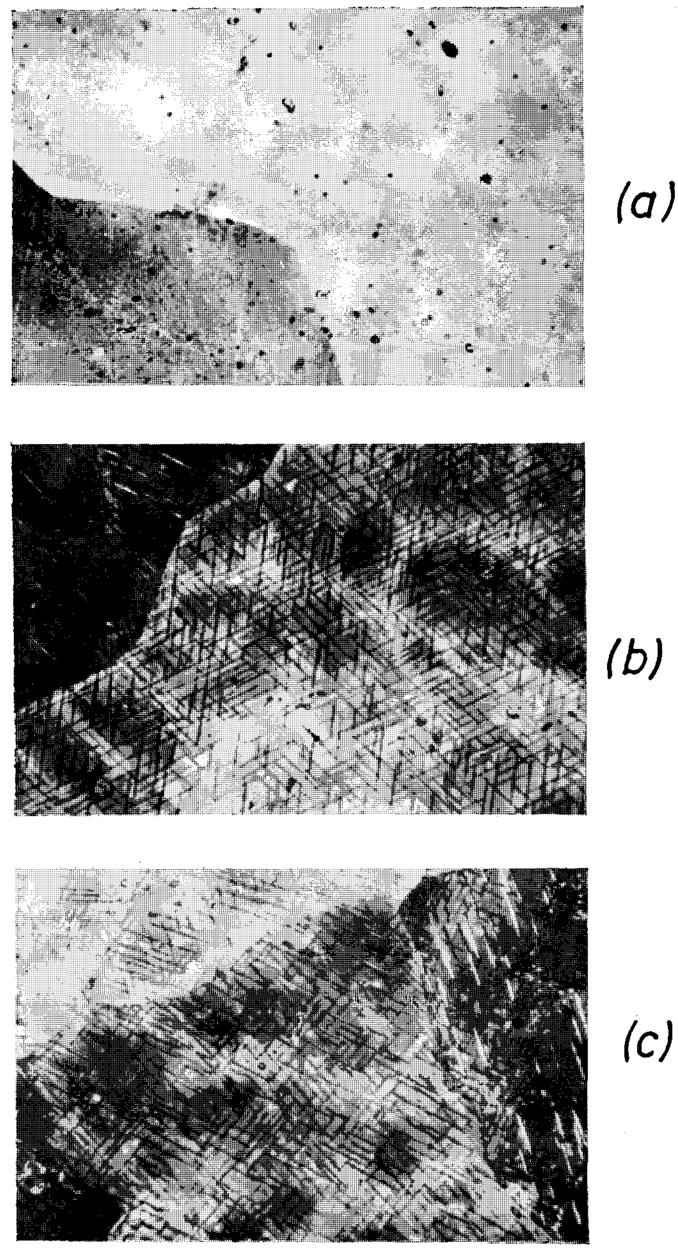

Fig. 14—Optical microstructures of arc-melted UCS specimens with total non-metal contents of (a) 49,20 atom per cent, (b) 50,17 atom per cent, and (c) 50,42 atom per cent. Magnification 500 X

(f) The choice of alloy type and/or microstructure of stainless-steel cladding is not critical as regards its compatibility with carbide fuel.

Acknowledgements

The authors thank their colleagues for their assistance in all aspects of the work reported here, and also the Atomic Energy Board for permission to publish these results.

References

1. Stumpf, W. E., and Götzmann, O. *Karlsruhe report* KFK 1385. 1971.
2. Stumpf, W. E. *Prakt Metallographie*, vol. 9. 1972. p. 166.
3. Stumpf, W. E., and Venter, S. *J. Nucl. Mater.*, vol. 58. 1975. p. 211.
4. Stumpf, W. E., and Venter, S. Pelindaba, Atomic Energy Board, *Report PEL-243*. 1975.
5. Venter, S., and Stumpf, W. E. *J. Nucl. Mater.*, vol. 59. 1976. p. 221.
6. Stumpf, W. E., and Venter, S. Pelindaba, Atomic Energy Board, *Report PEL-242*. 1975.
7. Venter, S., and Stumpf, W. E. To be published.
8. Stumpf, W. E., and Venter, S. *J. Nucl. Mater.*, vol. 60. 1976. p. 195.
9. Lovell, G. H. B., van Tets, A., and Britz, E. J. *J. Nucl. Mater.*, vol. 48. 1973. p. 74.

Company Affiliates

The following members have been admitted to the Institute as Company Affiliates.

AECI Limited.
Afrox/Dowson and Dobson Limited.
Amalgamated Collieries of S.A. Limited.
Apex Mines Limited.
Associated Manganese Mines of S.A. Limited.
Billiton Exploration S.A. (Pty) Limited.
Blackwood Hodge (S.A.) Limited.
Blyvooruitzicht G.M. Co. Ltd.
Boart International Limited.
Bracken Mines Limited.
Buffelsfontein G.M. Co. Limited.
Cape Asbestos South Africa (Pty) Ltd.
Compair S.A. (Pty) Limited.
Consolidated Murchison (Tvl) Goldfields & Development Co. Limited.
Deelkraal Gold Mining Co. Ltd.
Delfos & Atlas Copco (Pty) Limited.
Doornfontein G.M. Co. Limited.
Durban Roodepoort Deep Limited.
East Driefontein G.M. Co. Limited.
East Rand Prop. Mines Limited.
Engineering Management Services (Pty) Ltd.
Envirotech (Pty) Ltd.
Free State Saaiplaas G.M. Co. Limited.
Fraser & Chalmers S.A. (Pty) Limited.
Gardner-Denver Co. Africa (Pty) Ltd.
Goldfields of S.A. Limited.
The Grootvlei (Pty) Mines Limited.
Harmony Gold Mining Co. Limited.
Hartebeesfontein G.M. Co. Limited.
Highveld Steel and Vanadium Corporation Limited.
Hubert Davies Heavy Equipment (Pty) Ltd.
Impala Platinum Limited.
Ingersoll Rand Co. S.A. (Pty) Ltd.
Johannesburg Consolidated Investment Corp. Ltd.
Kinross Mines Limited.
Kloof Gold Mining Co. Limited.
Lennings Holdings Limited.
Leslie G.M. Limited.
Libanon G.M. Co. Limited.
Lonrho S.A. Limited.
Loraine Gold Mines Limited.
Marievale Consolidated Mines Limited.
Matte Smelters (Pty) Limited.
Natal Cambrian Collieries Limited.
Northern Lime Co. Limited.
O'okiep Copper Company Limited.
Otjihase Mining Co. (Pty) Limited.
Palabora Mining Co. Limited.
Photometric Sorters.
President Steyn G.M. Co. Limited.
Pretoria Portland Cement Co. Limited.
Prieska Copper Mines (Pty) Limited.
Rand Mines Limited.
R. J. Spargo Limited.
Rooiberg Minerals Development Co. Limited.
Rustenburg Platinum Mines Limited (Union Section).
Rustenburg Platinum Mines Limited (Rustenburg Section).
St. Helena Gold Mines Limited.
Shaft Sinkers (Pty) Limited.
S.A. Land Exploration Co. Limited.
Stilfontein G.M. Co. Limited.
The Griqualand Exploration and Finance Co. Limited.
The Messina (Transvaal) Development Co. Limited.
The Randfontein Estates Gold Mining Co. Witwatersrand Ltd.
The Robbins Co. (Africa) (Pty) Ltd.
The Steel Engineering Co. Ltd.
Trans-Natal Coal Corporation Limited.
Tvl Cons. Land & Exploration Co.
Tsumeb Corporation Limited.
Union Corporation Limited.
Vaal Reefs Exploration & Mining Co. Limited.
Venterspost G.M. Co. Limited.
Vergenoeg Mining Co. (Pty) Limited.
Vlakfontein G.M. Co. Limited.
Welkom Gold Mining Co. Limited.
West Driefontein G.M. Co. Limited.
Western Areas Gold Mining Co. Ltd.
Western Deep Levels Limited.
Western Holdings Limited.
Winkelhaak Mines Limited.