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LUCAS HEIGHTS

GRAPHITE FUEL STUDIES

PART 3

COMPACTION OF GRAPHITE AND MIXTURES OF GRAPHITE AND FISSILE AND FERTILE MATERIALS

by

J. R. MAY

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ABSTRACT

Sound high density cylinders of graphite have been made by cold compacting finely ground artificial graphite at pressures of 60 t.s.i. Cylinders could be made only if the graphite used was 50 per cent. finer than 10 microns and freshly ground. Storage of the powder in moist atmospheres or heating of the powder reduced its compacting properties.

Uranium and thorium metal powders and uranium and thorium oxide up to 60 weight per cent. equivalent metals have been added to the graphite and sound cylinders made from the mixtures. The compacts have been heated to high temperatures (up to 2800°C) to convert the metals or oxides to carbides which rapidly hydrolyse in moist air. Measurements of compressive strength and density changes and investigation of the properties of the compacts on thermal cycling have been made. Compacts made from metal powders are considered satisfactory for use as fuel for a High Temperature Gas Cooled reactor system provided their irradiation stability is satisfactory. Recommendations for further work are made.

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1. INTRODUCTION

Dispersion fuels are of interest in the Australian High Temperature Gas Cooled (HTGC) reactor project, since they have the advantage of limiting damage by fission fragments, while giving a high heat rating. As graphite has good strength at high temperatures, high thermal conductivity, low neutron absorption cross-section and can be fabricated readily, it is a very attractive matrix material. By choice of suitable fissile particle size, it should be possible to limit the damage by fission fragments to the fuel particles and a small area of the matrix around each of them.

One method of fabricating such fuel elements is by compaction of ground graphite with metal powders to give a cylinder or sleeve of the required composition and dimensions, followed by firing to form the carbides of the metals. In earlier work on the compaction of ground graphite binders were used to produce high density strong bodies. Thus Lock, Slyh and Duckworth (1954), Nathans (1954) and Hay et al. (1956) all used binders of various types to produce sound graphite bodies. However, once a binder is used a baking step is needed to carbonize the binder. Therefore, Nathans and Hay et al. both attempted to produce sound bodies without the use of binders. Nathans found that natural graphite compacted satisfactorily but once the graphite was purified, no sound compacts could be made. Hay et al. found that they could compact minus 200 mesh artificial graphite by pressing at 80,000 p.s.i. only after a preliminary wet oxidation.

Following earlier success in compacting graphite with the aid of binders, Schofield, Slyh and Lock (1950) and Lock, Slyh and Duckworth (1954) made detailed studies of the preparation of uranium-bearing graphite, by hot pressing graphite powder, UO_2 nodules and a phenolic resin binder. However, Livey et al. (1958) showed that finely ground artificial graphite could be compacted, without binders, to give sound bodies. They also showed that uranium and thorium could be added to the graphite and cylinders or sleeves made from the mixture which, after heating, could be suitable for use as a dispersion fuel.

This report discusses the preparation of graphite bodies by compaction of finely ground artificial graphite. The effect of the initial condition of the powder used on its compacting properties is shown and the properties of compacts made from such powders are given. Compacts were also made from mixtures of graphite and fertile and fissile materials such as thorium and uranium as metals and oxides. The properties of the resultant compacts are discussed.

2. EXPERIMENTAL

2.1 Equipment

A 60 ton hand operated Archer press was used throughout this work. The dies were made from K9 steel, (an oil hardening tool steel having a nominal composition of 1.00% C; 0.85% Mn; 0.75% Cr; 0.40% W) and designed to take 90 t.s.i. A nitrogen blanketed glove box was used to prepare mixtures containing fertile and fissile materials and to load the dies. An Amsler mercury displacement volume meter was used in the early stages to measure compact volumes, but it was found simpler and just as accurate to calculate the volume from the measurements of diameter and length. The graphite resistance tube furnace and the thermal cycling furnace used in the programme are discussed in Appendix 1. A Hounsfield tensometer was used for compressive strength determinations. Identification of the phases present in some of the compacts was carried out by x-ray diffraction on powder samples using a Guinier camera.

2.2 Materials

Details of the size, origin and chemical analysis of the materials used in this investigation are given in Appendix 2. All particle sizes quoted have been obtained using a Sharples Micromerograph.

2.3 Procedure

Using graphite powder, the effects of compacting pressure, pitch binder additions and the die size used on the compact properties were investigated. Measurements of the expansion of the resulting compacts on ejection from the die were made. The behaviour of the compacts on thermal cycling to 800° C was noted and the removal of iron at high temperatures measured. The effect of particle size and pretreatment of the graphite powder on its compacting properties was studied. This was done by measuring the compressed height of the powder under load and the expansion taking place on removing the load.

Single ended pressing has been used throughout. Initially, a suspension of colloidal graphite in acetone was used as lubricant on the plungers of the dies. However, this was found unnecessary and its use was discontinued. Care had to be taken in loading the dies, as tamping left a plane of weakness in the compact and, in many cases, resulted in fracture of the compact on ejection from the die.

Uranium, thorium UO_2 and ThO_2 were added to the graphite and the effect of these on the compacting properties of the powder measured. The changes in properties of compacts containing metal or oxide powders following high temperature heating in argon were noted. The removal of iron in this operation was followed by chemical analyses. A preliminary investigation by metallographic techniques, was made of the size and shape of the carbide particles resulting from high temperature treatment. The effect of thermal cycling on both sintered and unsintered compacts was studied.

It was found difficult to ensure a homogeneous dispersion of heavy metals in the graphite. Hand mixing in a glass container was satisfactory in most cases but at uranium concentrations above 30% w/w some segregation occurred giving a wider scatter to the density measurements.

3. EXPERIMENTAL RESULTS

3.1 Graphite

Using graphite ground to 50% minus 10μ and all finer than 25μ, a series of cylinders 1 cm in diameter were made by cold compacting the graphite at pressures up to 80 t.s.i. The cylinders, although weak in tension and shear, had remarkably good handling properties and showed no signs of chipping on the edges. The relationships between density, compressive strength and compacting pressure are shown in Figure 1. Ten compacts were tested at each condition and Table 1 shows the average results and standard deviations for these tests. The improvement at 80 t.s.i. operation over that at 60 t.s.i. was not considered sufficiently great to warrant higher pressure operation which would stress the dies close to their upper limit. Thus for all subsequent work 60 t.s.i. operation was used.

Due to the success of earlier workers using binders, some tests were made with pitch additions to the ground graphite. Up to 5% pitch added to the fine graphite gave no improvement over powder compacted without the use of a binder. The pitch, dissolved in small quantities of a solvent such as benzene, was mixed with the graphite powder and dried in an air oven. The powder was then either cold or warm (120°C) compacted. The pitch was also added as a fine powder and mixed at 120° C with the graphite powder in a Winkworth mixer. The density of compacts made using 5% pitch decreased by 2 to 5% on baking to 800°C. The slow baking cycle of 5° C rise/hour also added complications to an otherwise simple fabrication process and hence no binder additions were made in subsequent work.

Compacts were made using different dies of diameter up to 2.0 cm. Table 2 shows the relationship between compact density and diameter and indicates that increasing diameter had no effect on density. Compressive strength measurements did not produce useful comparative results, due to the difference in length to diameter ratios. It was found difficult to produce 1 cm diameter compacts of greater length than 1.5 cm due to capping (cracking off of layers near the top of the compact.) However, up to 1.5 cm, there was no decrease in density on increasing the length of compact.

On measuring the dimensions of 1 cm diameter compacts over a period of 20 hours following removal from the die it was found that considerable expansion, and hence reduction in density, took place. There was virtually no change in diameter but a length change of about 1% was observed. Nearly two-thirds of this expansion took place in the first hour after removal from the die.

Compacts, heated to 800° C at 5° per hour showed no density change but compressive strengths decreased from 1530 to 1120 p.s.i. On cycling to 800°C in a nitrogen atmosphere, the density and compressive strength of the compacts decreased, at first quite rapidly, with increase in the number of cycles. Graphs of density and compressive strength against the number of cycles up to 200 cycles are shown in Figure 2.

Because " pick-up" of iron during grinding is undesirable in nuclear grade graphite, attempts have been made to remove it. Earlier work (May and Warner, 1959) showed it could be reduced to less than 20 p.p.m. by hot leaching with concentrated HCl. It has also been found feasible to reduce the iron content in both powder and compacts to less than 20 p.p.m. by heating them to 2400° C for 1 hour in argon.

The compressive strengths of the compacts were particularly sensitive to the original graphite particle size and this accounts for some of the differences in strengths from batch to batch. Neither graphite ground 50% minus 18μ not 50% minus 12.6μ could be compacted to give coherent cylinders up to pressures of 60 t.s.i. This is in agreement with the earlier work done by Frechette (1952).

The high densities of the compacts obtained as above can only be achieved using freshly ground graphite. If the ground graphite is left to stand in air or nitrogen or over water for several weeks, the resulting densities are lower by some 5%. The compacting properties of the graphite powder are also reduced (shown by a density decrease of 5%) by heating in an air oven for several days at 120° C. Table 3 shows typical results of this work. The differences shown in these results are statistically significant.

With higher temperature heating (2400°C) in argon, the compacting properties are completely destroyed and no compacts of any sort could be made. In earlier work on contamination removal May and Warner, 1959, found that leaching with 2N HCl, washing and oven drying decreased the compacting properties of the graphite as shown by a decrease of 7% in the density of the compacts. The BET nitrogen adsorption surface area measurements showed a decrease of 40% on acid leaching and 50% on high temperature treatment.

On measuring the compressed height of the graphite powders under load and their expansion when the 60 t.s.i. load was removed, it was shown that the powder heated to 2400°C in argon expanded more than double the amount of the unheated powder. Table 4 shows these results for the powder 50% minus 10μ as-ground and after heating and also for the powder ground 50% minus 12.6μ.

3.2 Graphite and Uranium and Thorium Metals

The effect of metal content on the compacting properties was investigated. The results are given in Table 5 and Figure 3. Minus 300 mesh uranium was used and the Th:U ratio was 30:1 atoms. As with the graphite compacts, it was possible to make larger diameter compacts up to the limiting loading of the press. Provided the length to diameter ratio was not too great, the compacts had consistent bulk densities.

The effect of sintering such compacts in argon to 2500°C for 30 minutes is also shown in Table 5 and Figure 3. The theoretical densities after heating have been calculated assuming complete conversion of the U and Th to UC_2 and ThC_2, these being the stable phases at the sintering temperatures used. The effect of sintering temperature on the properties of compacts containing 60% w/w metals in a 30:1 atom ratio of Th:U, is shown in Figure 4. The heating time was half an hour. Qualitative x-ray diffraction studies of these compacts showed conversion of the metals to the dicarbides at temperatures

of 1600°C or greater. No monocarbide was detected. Traces of UO_2 and ThO_2 detected were no doubt due to hydrolysis of the carbides and some residual oxide impurities remaining from the metal powders. Unfortunately, the high atomic ratio of Th:U masked the uranium carbide patterns in most instances. However, there is little doubt that the dicarbides were the major product of the sintering operations.

The sintered specimens were analysed for iron to determine the iron impurity removal at high temperatures. These results are plotted in Figure 5 and show that, unlike compacts containing no metal, the iron content is only reduced from 270 p.p.m. to 150 p.p.m. after heating for 40 minutes in argon at 2600° C.

If the sintered compacts are left to stand in air at room temperature, they rapidly decompose due to hydrolysis (Figure 6). A study of the rate of breakdown of these compacts in argon atmospheres containing various quantities of moisture is incomplete at the date of this report. The argon and moisture are passed over the compact and the weight gain of the compact is used as the measure of decomposition. At an early stage, it was found that compacts containing only uranium carbide showed negligible weight gain in a moist atmosphere at room temperature. Therefore it was the thorium carbide that was the unstable compound under these conditions. The very rapid decomposition of the sintered compacts due to hydrolysis leads to many handling and storage difficulties. Once sintered, the compacts containing ThC_2 need to be stored in a desiccator over P_2O_5. Any operations on the sintered compacts in the laboratory atmosphere lead to some conversion of the carbides to oxides with resulting deterioration of the surface of the compacts.

Some interesting results were found when the compacts were thermally cycled to 800°C in nitrogen and argon. The nitrogen used had 30 to 40 p.p.m. of oxygen in it and the argon up to 100 p.p.m. oxygen. Both gases were passed through a bed of Linde molecular sieves to remove moisture. The compacts containing unsintered metal were unstable and with only 6 cycles showed marked signs of crumbling with a 12% length increase. X–ray diffraction studies on these cycled compacts showed marked oxidation of the thorium and uranium showing that some back–diffusion and leakage of oxygen into the furnace occurred. On the assumption that the chemical reactions due to the impure furnace atmosphere were responsible for the breakdown of the compacts, unsintered compacts were sealed under pure helium in stainless steel capsules and cycled for 250 cycles. The length showed an increase of 2% and there was no change in diameter. These results contrast markedly with the previous results from unsealed compacts.

Following removal from the stainless steel container there was a slow weight increase and signs of hydrolysis on standing in the laboratory for several weeks. Thus the carbide forming reactions, although slow at 800°C, must have commenced.

The outside surface of the cycled compact and the inside surface of the capsule showed no signs of reaction between the compact and stainless steel after the cycling operation. However, no metallographic examination of the surfaces was made and the compacts were only a loose fit in the capsules.

3.3 Graphite and Uranium

A preliminary investigation into the compacting behaviour and properties of uranium metal–graphite mixtures has been carried out using minus 300 mesh uranium. A range of uranium contents up to 60% w/w have been looked at both before and after sintering (Figure 7). The effect of temperature of sintering on the compact properties has also been determined and compressive strength and density as a function of temperature up to 2600°C are shown in Figure 8.

On thermal cycling some of these compacts, it was found that 10 cycles to 800°C in nitrogen completely broke up the unsintered compacts to a powder. The sintered compacts showed signs of cracking after 60 cycles. The cycle times used were the same as described in Section 3.1. X–ray diffraction indicated marked oxidation of the uranium in the unsintered compacts after cycling. This result is in keeping with those of Section 3.2.

3.4 Graphite and Uranium and Thorium Oxides

A similar investigation has been made using uranium and thorium oxides instead of the metals. Figure 9 shows the compacting properties as a function of oxide content up to an oxide content of 60% w/w equivalent metal. Thorium oxide calcined at 1100°C was used since some difficulty was experienced in making satisfactory compacts from the coarser 300°C material. On sintering, the oxygen is removed and carbides result but the compacts retain their form. The effect of temperature and time on this reaction is shown in Figures 10 and 11. X-ray diffraction studies, while not being capable of clearly detecting small amounts of uranium compounds in the presence of large amounts of thorium compounds, indicated that the thorium oxide to thorium dicarbide reaction was virtually complete after 15 minutes at 2400° C. At 1800°C the reaction is very slow and only traces of ThC_2 and ThC could be discovered after 40 minutes.

The unsintered compacts are quite stable thermally and show no change on cycling in nitrogen for 146 cycles. The sintered compacts compare with those prepared with metals and show only slight signs of breaking up after 68 cycles. The cycle times used were the same as described in Section 3.1.

3.5 Carbide Formation

Because of the interest in fissile material particle size, attempts have been made to discover the effect of sintering and carbide formation on the resulting fissile particle size. In the first instance this work was carried out using compacts containing only graphite and uranium. This avoided the marked handling difficulties associated with thorium carbides. Unsintered samples were very difficult to polish for microscopic examination due to inadequate cohesion in the compact. There was a marked tendency to tear the uranium metal particles out. In one of the samples, containing 65 to 75μ uranium, it was possible to observe some uranium particles and these were spheroidal in shape.

After heating the sample for half an hour at 2500°C, its appearance had changed considerably and the cohesion improved greatly, making the material easier to polish. The appearance of this sample is seen in Figure 12, which shows cavities ringed with a shell of finely dispersed carbide. It is difficult to say whether the large cavities are a real part of the structure or represent the area from which UC_2 was removed on polishing.

However, the structure is not suitable for use as a fuel because the very fine distribution of fissile material would retain few fission fragments, resulting in great damage to the matrix. Therefore attempts were made to modify the structure. On the assumption that the diffuse structure of the carbide indicated flow of molten carbide because of the high temperature of sintering, new samples were prepared, one heated to 2000° C and the other to 2600°C. The sample heated to 2000°C, though not so strong, showed discrete carbide particles. The one heated to 2600°C once again showed a diffuse structure. Photographs of these specimens are shown in Figures 13 and 14.

4. DISCUSSION

4.1 Compaction of Graphite

Provided the graphite was freshly ground and of a suitably fine size, it could be compacted without trouble to form strong, non-friable cylinders of high theoretical density. Bodies 1 cm diameter by 1.5 cm long made in this way were sufficiently strong for an $^1/_8$ inch diameter hole to be drilled. If the length to diameter ratio was raised to more than about 2 to 1, the compacts showed a marked tendency to cap. Train (1956) showed that this capping effect is due to both the force distribution in the compact when under load, and the relative movement of the powder. The compacts expanded after removal from the die and also on thermal cycling, indicating relief of some of the stresses remaining in the compact after pressing.

The verb "to compress" is used in this report when describing the densification process. Thus if a powder compresses and coheres, it is considered to compact. The fact that ground graphite compacts to bodies of such high theoretical density (85 to 86%) under a load of 60 t.s.i. is remarkable. Much higher pressures are needed to achieve similar theoretical densities with metal powders. It is understandable that graphite compresses well because it has good lubricating properties which help in interparticle slippage and hence closer packing. However, as it does not undergo local welding in the same way as metal powders do, it is not clear why graphite coheres and hence makes sound compacts.

It has been shown that the final density of the compacts is lower if other than freshly ground graphite is used. For instance, powder stored in air, nitrogen or over water, or heated in an air oven at 120° C prior to compaction has a lower BET nitrogen adsorption surface area and produces compacts of lower density and lower strength than freshly ground graphite. Leached graphite powder also has a lower BET nitrogen adsorption surface area and gives lower density compacts, but this is probably closely associated with the drying of the graphite in the air oven at 120° C after leaching. As the grinding time of the graphite is increased, the particle size decreases and the BET nitrogen adsorption surface area increases, and it would appear that the BET nitrogen adsorption surface area and the compacting properties of the graphite are related. This is further shown by the fact that the as-ground graphite, having a Micromerograph size 50% passing 9.5 microns, has a surface area of 13.2 m^2/g and compacts very readily. After heating it to 2500°C in argon, the surface area reduces to 6.9 m^2/g which is very close to the surface area of a graphite powder having a Micromerograph size of 50% passing 18 microns. Neither of these latter powders compact.

However, it is a well known disadvantage of the BET nitrogen adsorption method of surface area measurement that the results are markedly affected by the pretreatment of the powder. In an effort to standardise the results, all samples have been outgassed at 200°C. However, this does not allow for differences in treatment of the powder prior to outgassing. Therefore, it is not surprising that graphite as ground would give a result different to the same powder after heating to 2500°C in argon, even though both powders have a very similar geometrical surface area.

The loss of compacting properties by heating the powder prior to compaction was also observed by Livey (1958). He found that vacuum annealing at 1000°C removed the compacting properties and these were not restored by exposure of the graphite to air, argon, hydrogen or water vapour, but were partially restored by regrinding in argon. The powders still compressed but would not cohere. Savage (1948) also found that vacuum annealing removed the lubricating properties of the graphite. He showed that the lubricating properties were due to adsorbed vapour films and, although they were removed by vacuum annealing they could be restored by exposure to the required vapours. Thus the lubricating properties of the graphite are not the most important factors in the achievement of high density on compaction.

Measurements of the compressed heights of the powders show that the coarser powder does not compress to the same extent as the finer powder. This is understandable since the coarser powder cannot be packed to the same density as the finer powder. Allowing for the slightly smaller weight of powder taken, the graphite powders 50% minus 10μ, both as-ground and after heating, compress to the same extent. However, expansion measurements on releasing the load show that the heated powder expands nearly twice as much. Thus, even though the heated powder compresses satisfactorily, there is no cohesion to bond the particles together and hence the powder simply expands on releasing the load. This work shows the importance of both the compression and the cohesion steps in the compaction process. It also shows that breakage of the powder under load is not sufficient to give bonding.

A possible explanation for the achievement of high densities is the production of "active sites" on grinding. In the compacting process these serve to bond graphite to graphite and hence the greater the number of "active sites" available for bonding, the higher the compact strength and density. Some of these sites can be occupied by adsorbed gases and are hence lost for bonding. They are also destroyed on heating. Once destroyed the production of new "active sites", and hence restoration of compacting properties, requires regrinding.

The above hypothesis that "active sites", produced on grinding and on breakage of particles in the compression of the powder, bond the graphite together to give the very high density product achieved in this work has yet to be proved conclusively. This would require a detailed investigation of the "active sites", something which is out of the scope of our present work. However, the work of Mrozowski (1952, 1959 and private communication) on the paramagnetic resonance properties of graphite shows that on grinding graphite in vacuum or in helium, "active sites" which bond oxygen are formed. It also has been shown that these "active sites" are associated with unpaired electron centres and are destroyed on heating above 700°C. The results of this work are certainly not in conflict with the present hypothesis and further investigation in this field may well bring to light the information needed to fully understand the mechanism of graphite compaction.

4.2 Thermal Cycling

The instability of the unsintered metal–containing compacts on thermal cycling in nitrogen and argon to 800°C is apparently due to chemical reaction of the highly reactive metal powders with impurities in the furnace atmosphere. X–ray diffraction studies have shown that large quantities of oxides are present after cycling. Smaller quantities of thorium nitride have also been noted. Once these chemical reactions have been avoided, by sealing under pure helium in stainless steel, the compacts are quite stable to rapid thermal cycles up to 800°C.

4.3 Sintering

The higher the temperature of sintering and the longer the time at temperature, the greater is the strength improvement in the compacts containing metals. This strength improvement seems to be associated with the diffusion of the carbide material through the graphite matrix, since there is a very marked increase in strength near the melting points of the carbides. Microscopic examination of sintered compacts supports this claim but the work is incomplete. The strength improvement with compacts containing 60% w/w uranium is not as great as with those containing 60% w/w uranium and thorium, since the volume percentage carbide produced on sintering in the former case is lower.

The range of fission fragments in graphite has been estimated to be between 10 and 20μ depending on the mass of the fragments (Durand, Klein, Nykiel, 1954) and somewhat less in uranium oxide and uranium metal. Preliminary experimental and theoretical work (Durand, Klein, Nykiel, 1954; Lock, Slyh, Duckworth, 1954; Kernohan, 1954; Hunter, 1959) shows that fissile particles greater than 50μ would be needed to limit the damage by fission fragment release to a small fraction of that suffered in the homogeneous case. Thus it is desirable to finish fabrication with the fissile material, uranium dicarbide, as discrete particles greater than 50μ in the graphite matrix. Some work has been commenced to produce this type of structure. It would seem that if the sintering temperature is kept below the melting points of the carbides, such a structure can result. Certainly this is so for compacts containing only graphite and uranium as starting materials. However, due to difficulties in handling compacts containing thorium carbides, the microscopic examination of compacts containing both uranium and thorium is incomplete.

5. CONCLUSIONS

5.1 Artificial graphite, if ground to 50% minus 10μ, can readily be cold compacted without the use of binders to give strong, non–friable cylinders of high density.

5.2 Uranium and thorium metal powders can be incorporated into the graphite and cylinders made from the mixtures. These cylinders can then be heated, with only small dimensional changes, to give uranium and thorium dicarbides in a graphite matrix. Such cylinders could be used for an H.T.G.C. fuel provided their stability on irradiation was satisfactory.

5.3 Handling of cylinders containing ThC_2 is very difficult due to very rapid hydrolysis in moist air at room temperature. Hydrolysis of compacts containing UC_2 at room temperature is very slow.

5.4 Thermal cycling studies of sintered and unsintered compacts in inert atmospheres have shown that they are stable to rapid temperature cycles up to 800°C. Thus the carbide forming reactions could be allowed to proceed after loading the fuel into the reactor. This procedure would obviate handling difficulties due to hydrolysis.

5.5 Cold compaction of uranium and thorium oxides with graphite is not considered a satisfactory route for the manufacture of carbide fuels due to the reduction in density and somewhat friable nature of the cylinders on removing the oxygen.

5.6 Strength and density measurements and thermal cycling studies have shown that compacts containing UO_2 and ThO_2 would be satisfactory for low temperature fuel applications provided the results of irradiation studies were promising.

6. RECOMMENDATIONS

It is recommended that further work be carried out in the following spheres.

6.1 A series of irradiations to test the effect of burn–up on the fuel compacts.

6.2 Studies of the amount of solid solution of UC_2 in ThC_2 and of the control of size and shape of the UC_2 and ThC_2 particles in the graphite matrix.

6.3 Thermal cycling tests to show the effect these have on the mechanical properties of the compacts.

6.4 Hydrolysis studies of the sintered fuel compacts to give a better understanding of the handling precautions needed.

6.5 Determination of the temperature at which rates of the UO_2–graphite and ThO_2–graphite reactions become appreciable.

7. ACKNOWLEDGMENTS

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APPENDIX 1 – FURNACE DETAILS

1. Graphite Resistance Furnace

The furnace used for the high temperature sintering studies was a horizontal graphite resistance furnace. The layout of this furnace is shown in Figure 15. The heating element is 16 in. long, 1½ in. internal diameter with ¼ in. thick walls, threaded at both ends to screw into the water–cooled brass terminal blocks. The element is made from reactor grade A graphite. Cylinder argon is purged through the heating tube and also into the pelletized lamp–black insulation at about 8 ft^3/hr. One terminal block is free to slide on a brass support thereby allowing for the expansion of the heating element. The ends and base of the furnace are Sindanyo which gives the necessary electrical insulation. A brass water jacket, split longitudinally to avoid inductive heating, makes up the outer casing. Water flow rate to the terminal blocks is about 2½ gal/min.

The heating current used is from a 25.6 kVA single phase B.G.E. furnace transformer with off–load tap changing. The power required depends on the age of the tube but, for a new tube, about 1800 amps at 9 volts enables 2800° C to be reached and held. A temperature of 3200°C has been reached without much trouble. However, the life of the resistance tube is considerably shorter with such high temperature operation. The temperature is measured by a disappearing filament optical pyrometer sighting horizontally through a quartz glass window at the gas inlet end of the furnace.

Operation of the furnace has been satisfactory, although tube life has been short at temperatures above 2500° C. Ten hours running is all that can be expected at this temperature. Figure 16 shows the type of failure of the heating element; most of the damage occurs on the outside of the tube. It is thought that this is associated with adsorbed oxygen on the lamp–black insulation. The packing is not sealed from the atmosphere at the end where expansion of the heater tube occurs and hence there is fairly ready access of oxygen to the packing and the outside of the tube. It is proposed in a new design to seal this end with a bellows; it is hoped that damage to the tube will then be limited to sublimation of the graphite.

Temperature control and reproducibility is difficult with the present control system. Temperature control of better than ± 50° C is hard to maintain through a half–hour run. This is due to the nature of the transformer and it is hoped to adapt a form of automatic control to the new design, whereby reproducibility and control of ± 20° C or better can be achieved. The temperature profile of the furnace is almost symmetrical and Table 6 gives some typical figures of the longitudinal temperature gradient at a centre temperature of 2600° C.

The sample holders for the small 1 cm diam. x 1.5 cm long samples are made of graphite and have been designed to allow the maximum number of samples to be enclosed in the shortest longitudinal distance in the furnace. Thus ten samples can be heated in a 2 in. length of the furnace tube, thereby reducing the effect of temperature gradients.

2. Thermal Cycling Furnace

This furnace consists of two parts, a cold zone and a hot zone mounted vertically above it. The hot zone consists of a 1½ in. internal diameter x 12 in. long grooved silica tube wound with Nichrome resistance wire and packed in powdered vermiculite insulation. The sample is made to cycle between the two zones on a prearranged time cycle by a reciprocating mechanism driven by a small electric motor and controlled by two timers. The layout of the furnace is shown in Figure 17.

A thermocouple passed into the furnace through the hollow stainless steel sample holder, is used to measure the temperature of the sample. The furnace control has been found to be very flexible. Temperature control is by a Sunvic controller and has been very satisfactory. The actuating mechanism has been reliable and readily changeable to give the desired temperature cycles. A typical temperature cycle used in the work is shown in Figure 18.

Purging gas, either cylinder nitrogen or cylinder argon, is fed into the bottom of the furnace. In order to cut down the back diffusion of oxygen into the system, the top of the furnace has been modified and another gas inlet included as shown in Figure 17. Unfortunately, this has not succeeded in stopping the ingress of oxygen into the furnace.

APPENDIX 2 – PROPERTIES OF MATERIALS

1. Particle Size

All particle sizes have been measured using a Sharples Micromerograph. Figure 19 shows sizes of the materials used. The plus 300 mesh B.S. material has been screened out of the uranium powder prior to size analyses. The size of each batch of ground graphite varied slightly but the distribution shown is typical. These slight variations in size almost certainly account for some of the variations in compressive strengths of compacts made from different batches of graphite.

2. Chemical Composition

2.1 Graphite

The graphite used in this work had an ash content generally less than 0.1% and an iron content of about 0.05% but these figures depend on the particular batch. A more detailed study of the graphite used has been reported earlier (May and Warner, 1959).

2.2 Uranium

This was calcium reduced natural uranium from the U.K. Table 7 shows the uranium content of the various size fractions of the powder used. The minus 300 mesh fraction had an iron content of 200 p.p.m.

2.3 Thorium

The thorium used in the work was calcium reduced U.K. material and had an iron content of 180 p.p.m.

2.4 Uranium Oxide

This was unstabilized non stoichiometric UO_2 of U.K. origin. It had a total uranium content of 85.3% and an iron content of 40 p.p.m.

2.5 Thorium Oxide

Two batches of thorium oxide have been used, one calcined at 300°C and the other at 1100°C. The percentage ThO_2 in the first batch was 92.5% and iron content 80 p.p.m. The loss on ignition at 1100°C was 7.1% indicating incomplete calcination. The second batch contained 99.4% ThO_2 and 80 p.p.m. iron.

TABLE 1

Compacting Properties as Function of Compacting Pressure for Graphite Compacts

Compacting Pressure	Density		Compressive Strength	
	Average g/cc	Standard Deviation	Average p.s.i.	Standard Deviation
20 t.s.i.	1.76	1.1%	910	7.4%
40 t.s.i.	1.91	0.2%	2150	6.9%
60 t.s.i.	1.93	0.3%	2700	2.8%
80 t.s.i.	1.95	0.2%	2930	3.8%

TABLE 2

Compacting of Graphite in Various Diameter Dies

Die Size Diameter cm	Density	
	Average g/cc	Standard Deviation
1	1.95	0.3%
1.5	1.95	0.6%
2.0	1.96	0.5%

TABLE 3

Effect of Powder Conditioning on Graphite Compaction

Type of Powder Treatment	Density		Compressive Strength	
	Average g/cc	Standard Deviation	Average p.s.i.	Standard Deviation
Original powder	1.94	1.6%	4080	4.9%
Air Oven 120°C 1 week	1.90	1.7%	3150	4.2%
Nitrogen 2 weeks	1.89	0.1%	3180	2.4%
Air 2 weeks	1.90	0.7%	3550	6.9%
Over Water 2 weeks	1.89	0.6%	3700	2.7%
Over Water 10 weeks	1.89	0.8%	2400	9.1%

TABLE 4

Expansion of Graphite Powders on Removing Load

Powder	Weight of Powder		Compressed Height		Expansion	
	Average g.	Stand. Dev.	Average mm.	Stand. Dev.	Average %	Stand. Dev.
50%–10μ as ground	2.403	0.13%	13.45	0.18%	8.7	1.0%
50%–10μ heated 2400°C	2.378	0.17%	13.13	0.92%	21.1	5.0%
50%–12.6μ	2.400	0.08%	13.61	0.02%	10.3	0.6%

TABLE 5

Compaction and Sintering of Graphite Containing Uranium and Thorium

Metal Content 30:1, Th:U Atoms		Before Sintering				
		Density			Compressive Strength	
% Wt.	% Vol.	Theoret. g/cc	Exp. g/cc	Stand. Dev.	Average p.s.i.	Stand. Dev.
0	0	2.26	1.92	0	2550	2.0%
20	4.7	2.69	2.30	0.4%	2870	6.5%
40	11.7	3.32	2.83	0.4%	2900	4.4%
60	23.0	4.35	3.74	0.3%	3040	5.1%
Metal Content 30:1, Th:U Atoms		After Sintering				
		Density			Compressive Strength	
% Wt.	% Vol.	Theoret. g/cc	Exp. g/cc	Stand. Dev.	Average p.s.i.	Stand. Dev.
0	0	2.26	1.80	0	2460	5.1%
20	4.7	2.72	2.18	0.5%	6130	9.9%
40	11.7	3.41	2.71	0.5%	9140	1.9%
60	23.0	4.59	3.66	0.3%	13190	4.6%

TABLE 6

Longitudinal Temperature Gradient of Graphite Resistance Furnace

Distance from Centre of Furnace	4 in.	3 in.	2 in.	1 in.	Centre
Temperature	1820°C	2160°C	2350°C	2510° C	2600°C

TABLE 7

Uranium Content of Size Fractions of Calcium Reduced Natural Uranium

Size (B.S. Sieves)		Uranium Content
Mesh	Aperture (Microns)	
+200	+76 μ	98.0%
− 200+240	65μ	98.3%
−240+300	53 μ	98.1%
−300	−53μ	97.3%

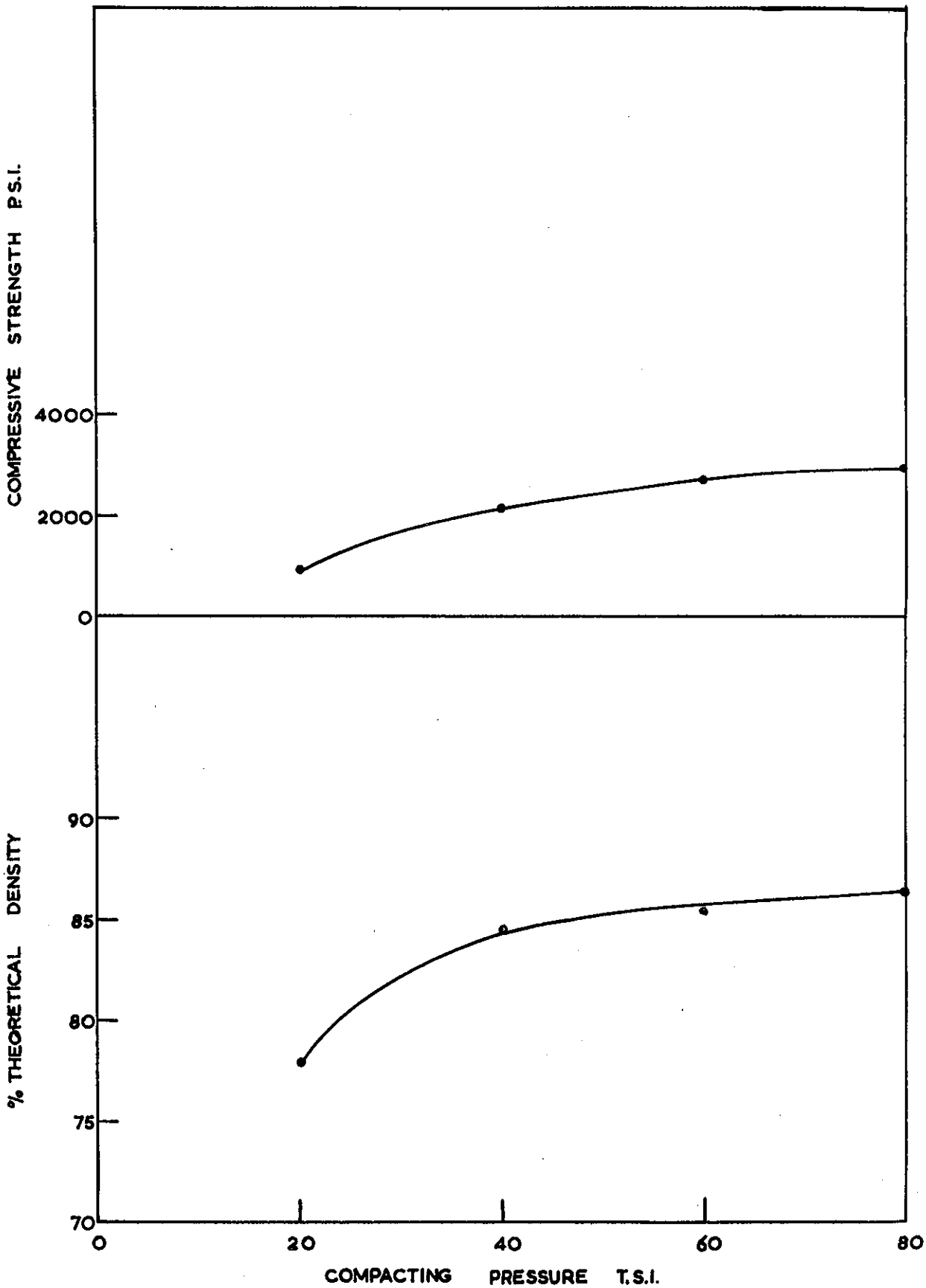


FIG. 1 COMPACT PROPERTIES AS A FUNCTION OF COMPACTING PRESSURE
(GRAPHITE ONLY)

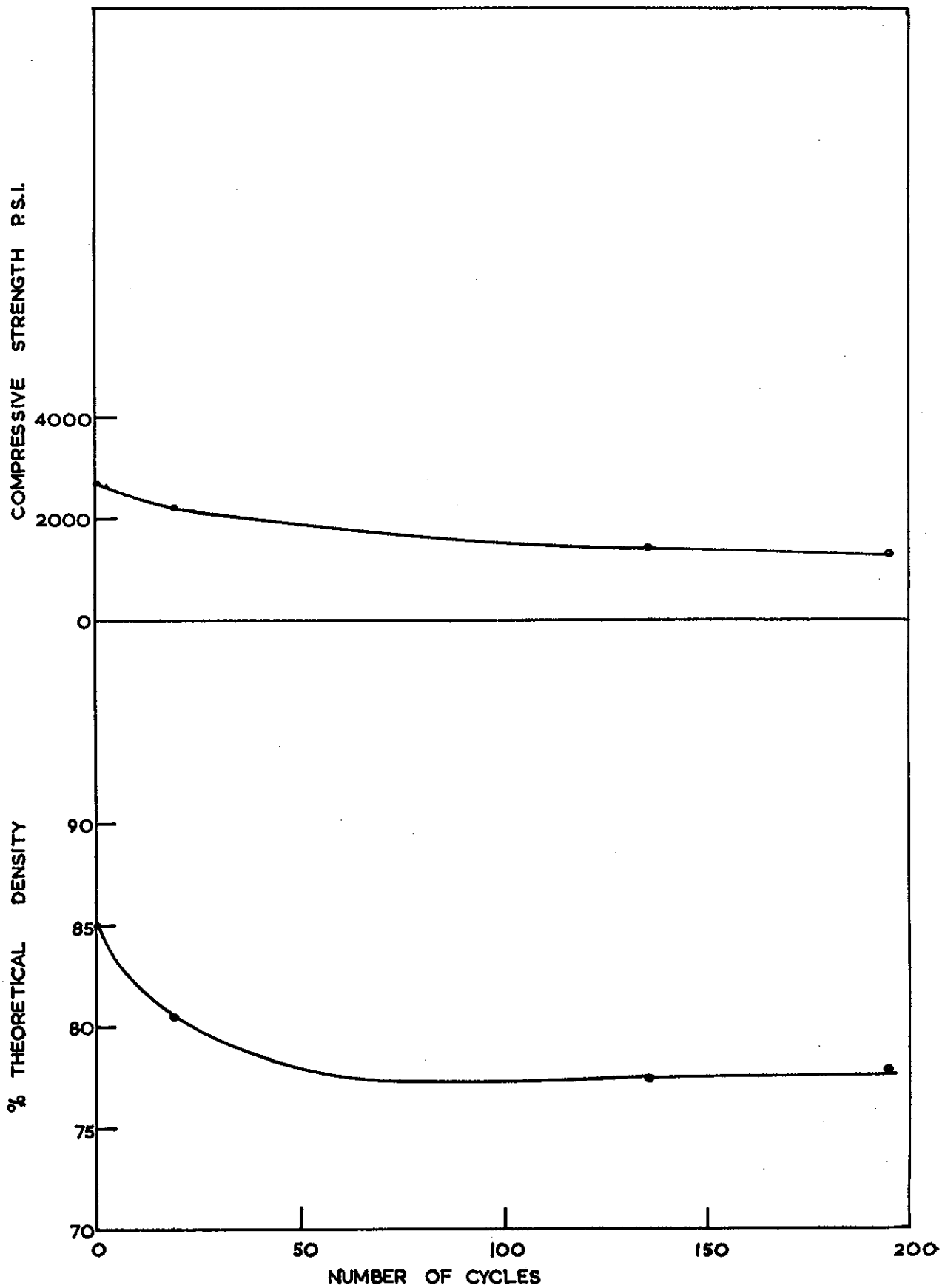


FIG. 2 THE EFFECT OF THERMAL CYCLING ON COMPACT PROPERTIES

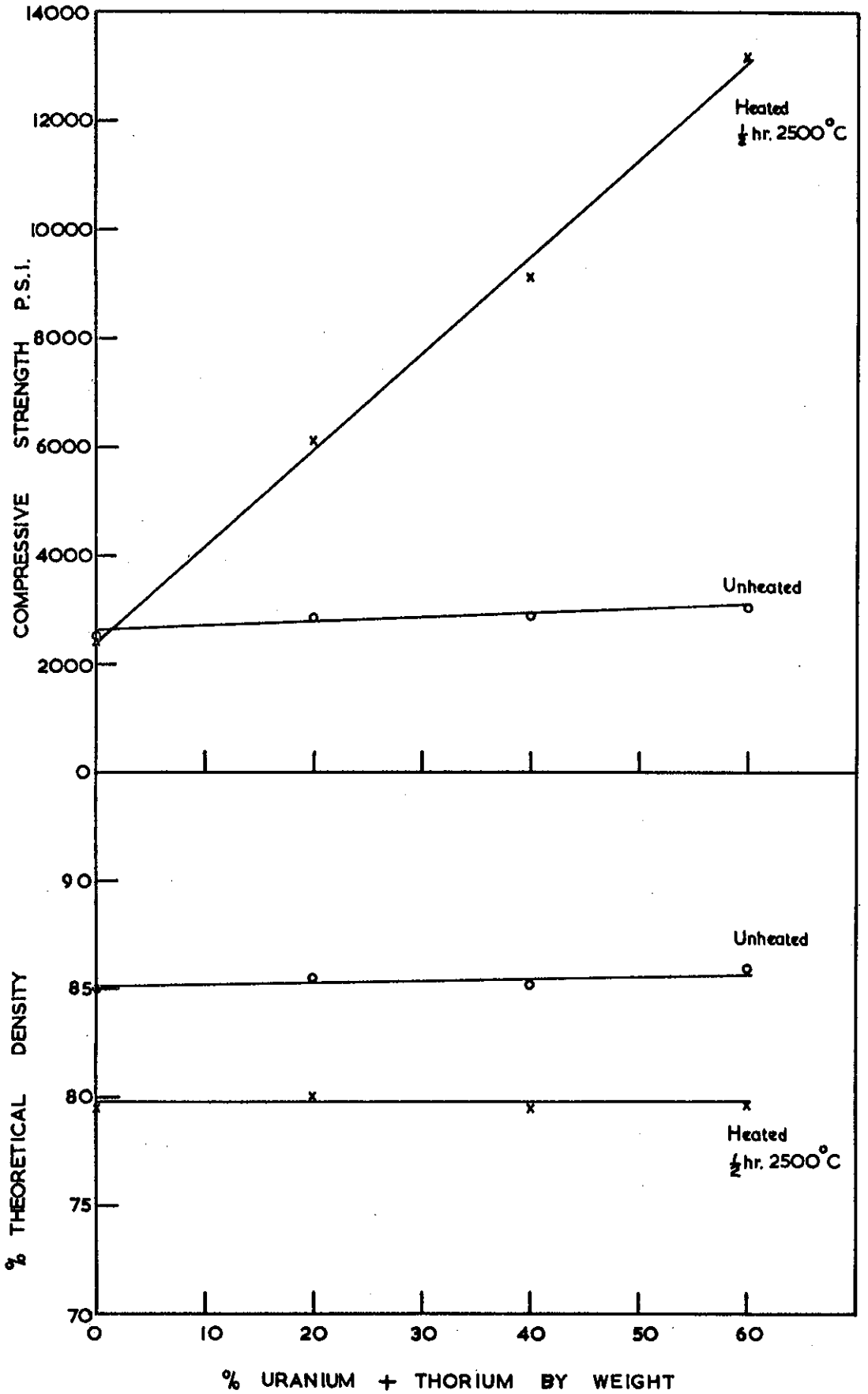


FIG. 3 COMPACT PROPERTIES AS A FUNCTION OF METAL CONTENT
(GRAPHITE PLUS URANIUM AND THORIUM)

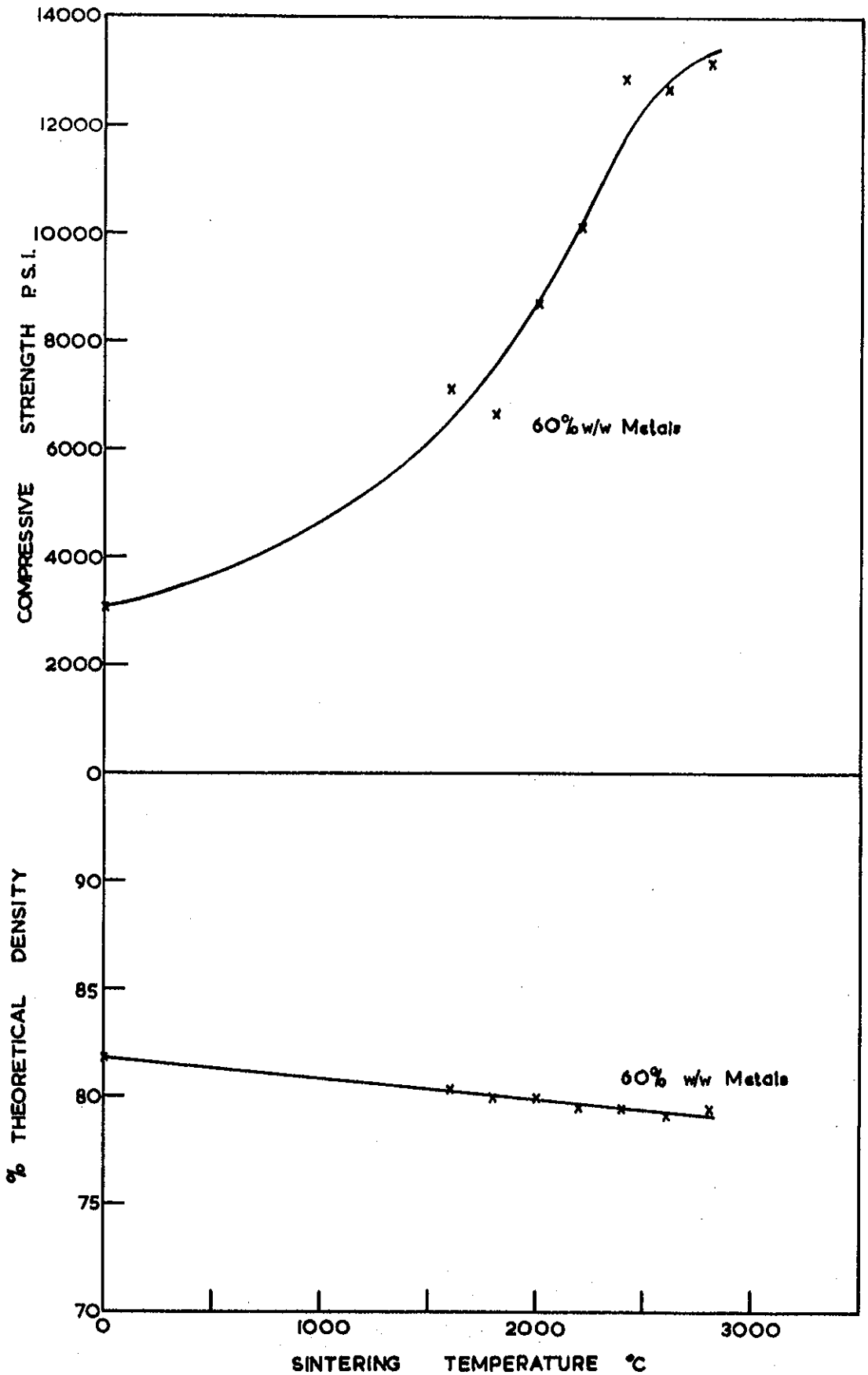


FIG. 4 COMPACT PROPERTIES AS A FUNCTION OF SINTERING TEMPERATURE
(GRAPHITE PLUS URANIUM AND THORIUM)

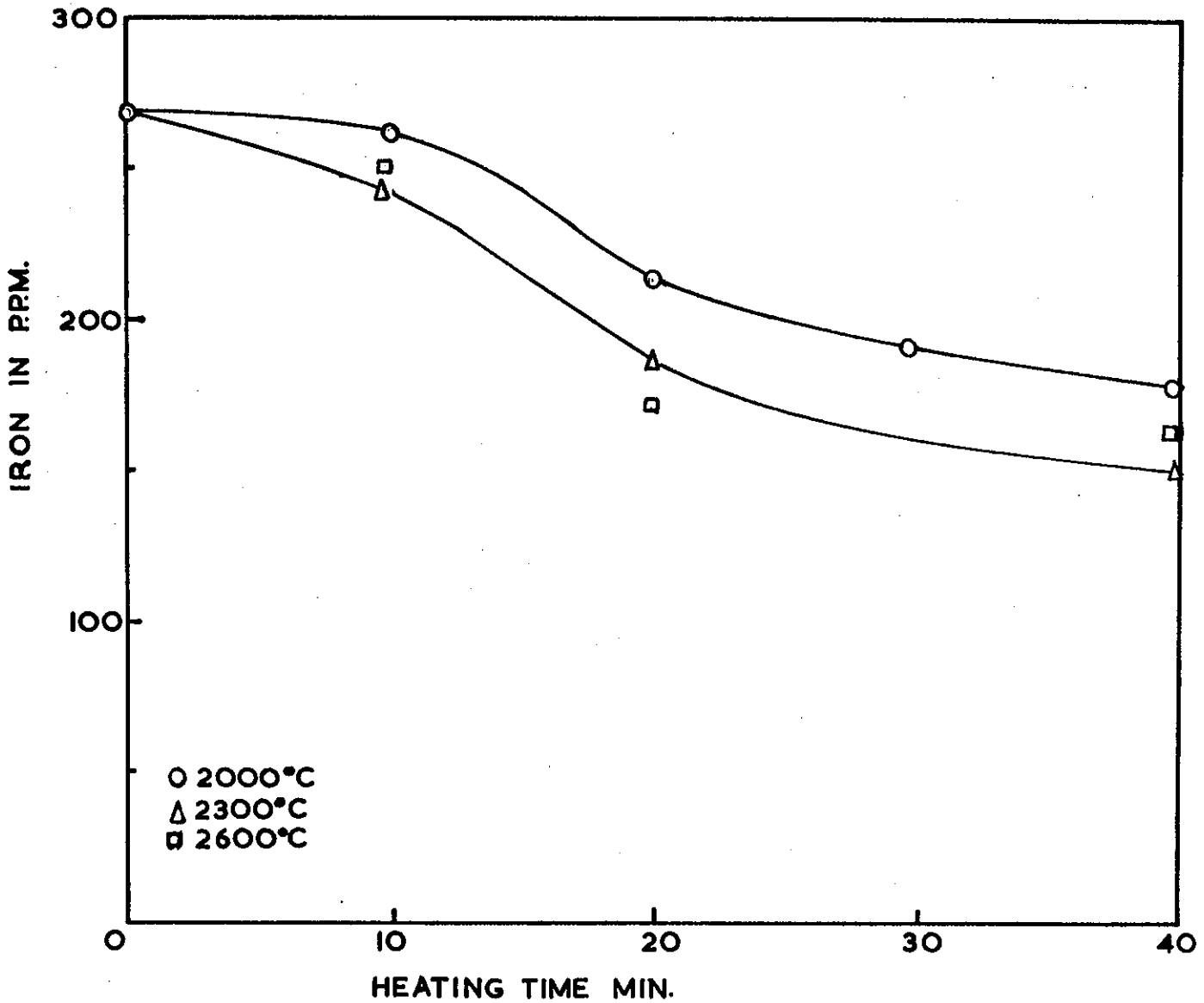


FIG. 5 EFFECT OF TIME AND TEMPERATURE ON IRON REMOVAL FROM COMPACTS CONTAINING GRAPHITE PLUS URANIUM AND THORIUM

Fig. 6 Photograph showing the effect of hydrolysis on sintered compacts.
(Approximately 2 hrs. under laboratory conditions)

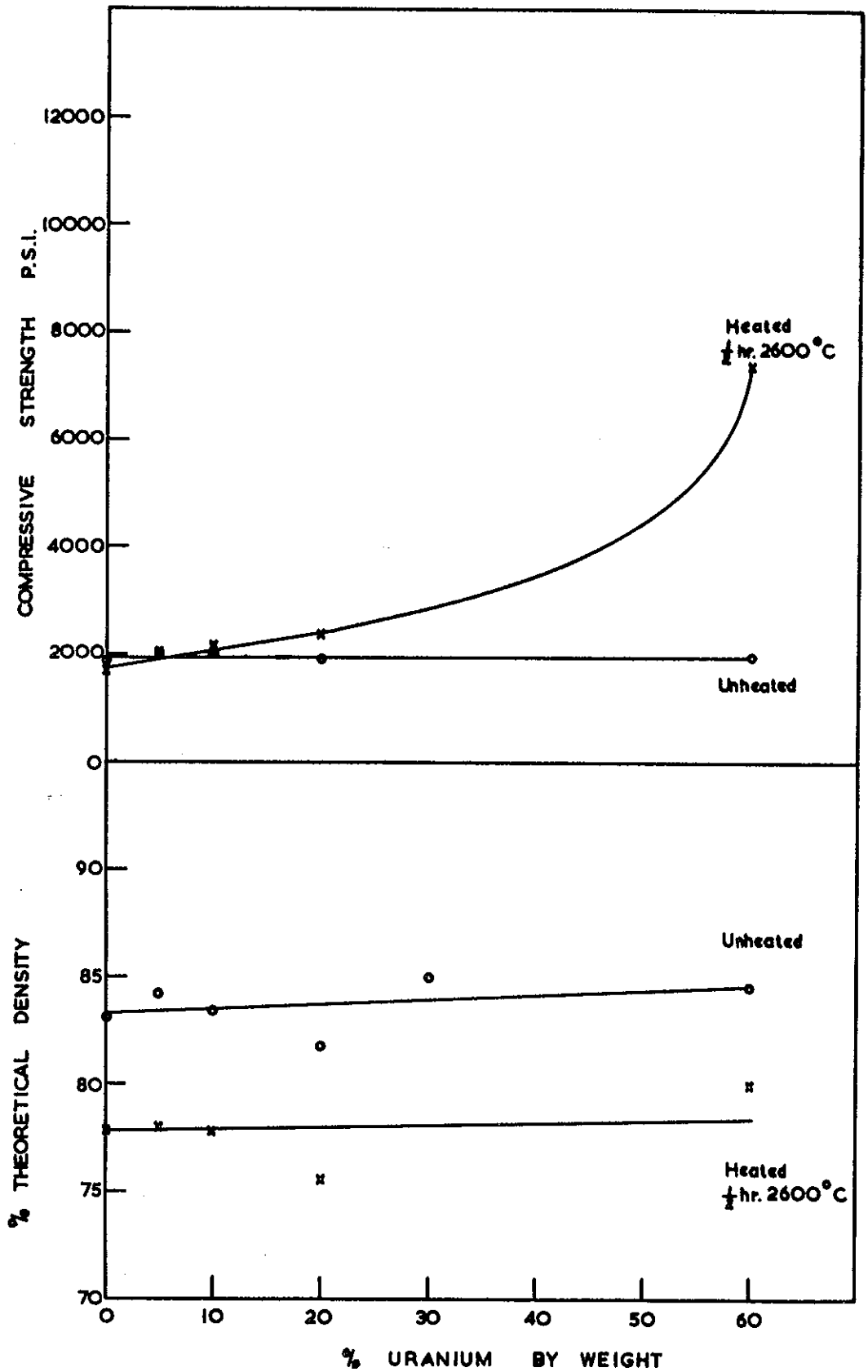


FIG. 7 COMPACT PROPERTIES AS A FUNCTION OF METAL CONTENT
(GRAPHITE PLUS URANIUM)

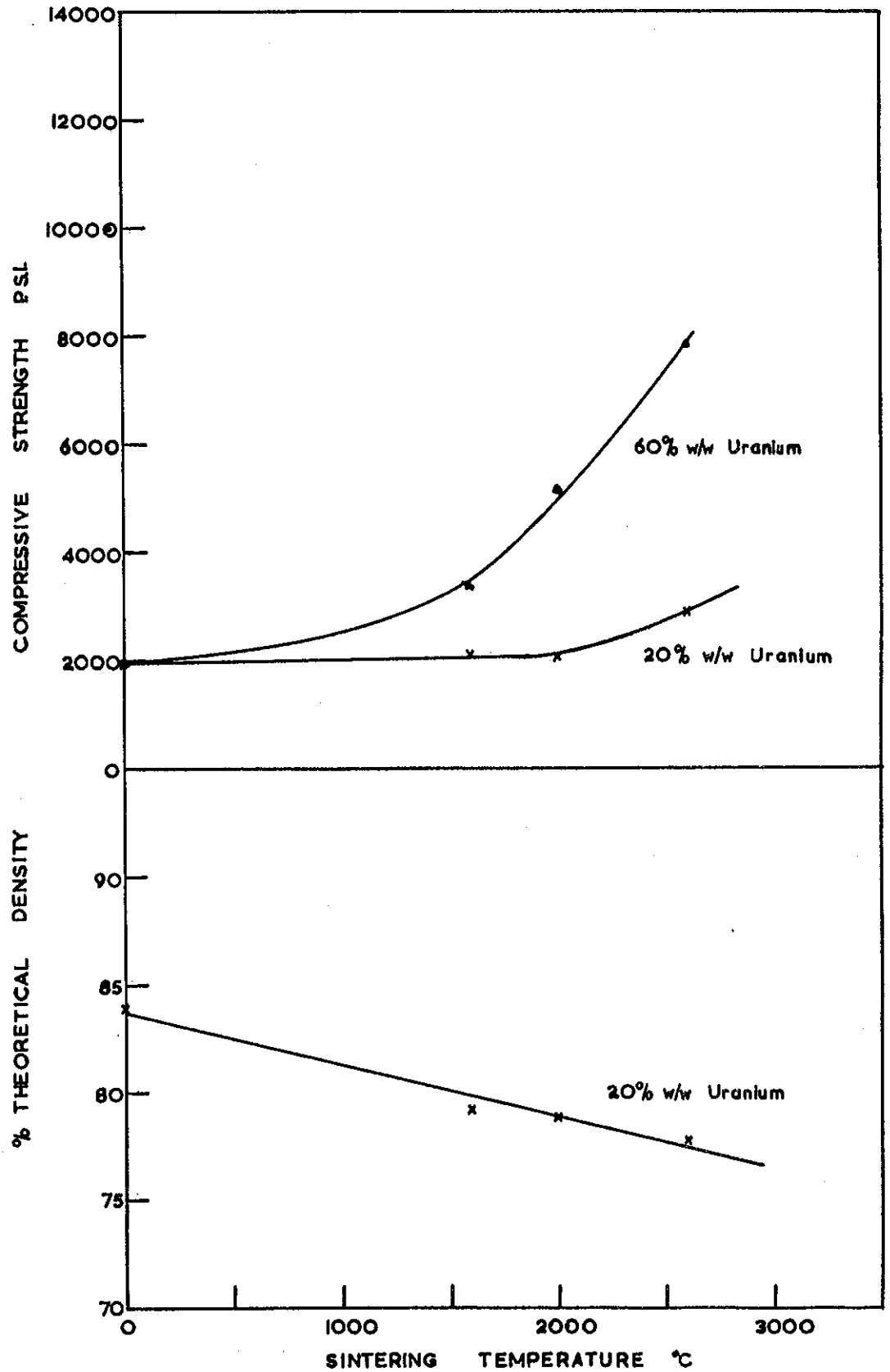


FIG. 8 COMPACT PROPERTIES AS A FUNCTION OF SINTERING TEMPERATURE
(GRAPHITE PLUS URANIUM)

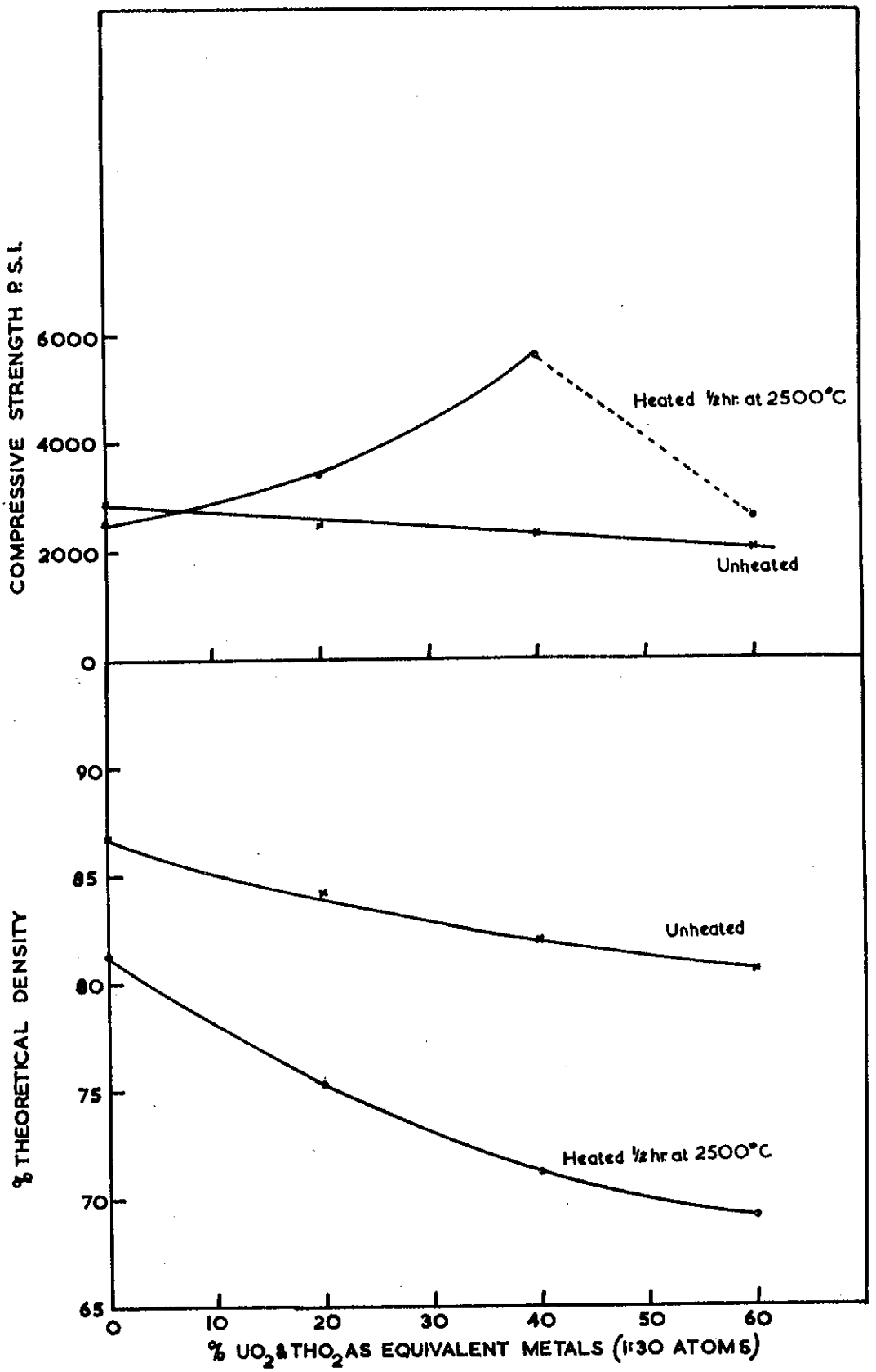


FIG. 9 COMPACT PROPERTIES AS A FUNCTION OF OXIDE CONTENT (GRAPHITE PLUS UO_2 AND ThO_2)

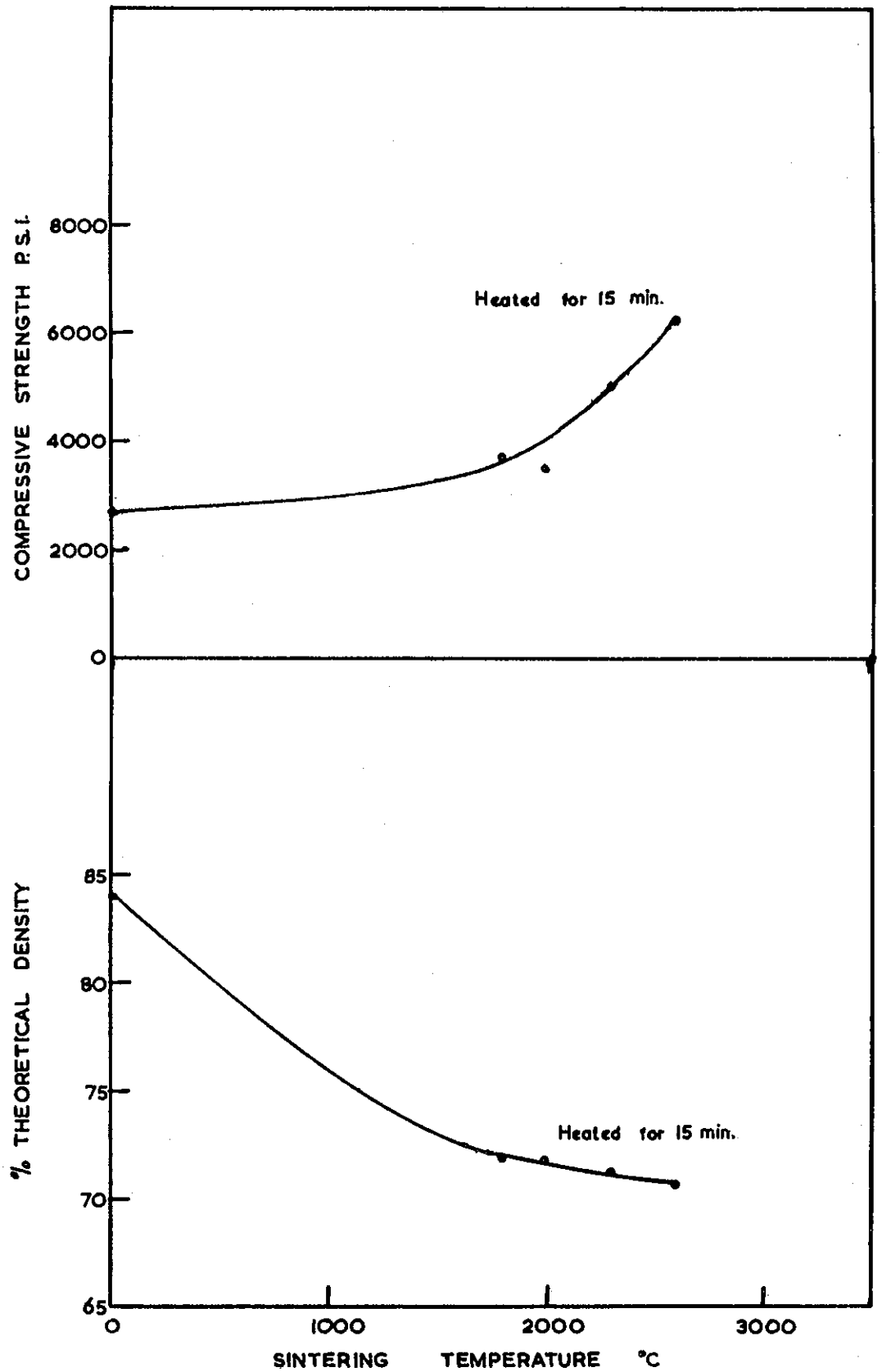


FIG. 10 COMPACT PROPERTIES AS A FUNCTION OF SINTERING TEMPERATURE (GRAPHITE PLUS UO_2 AND ThO_2)

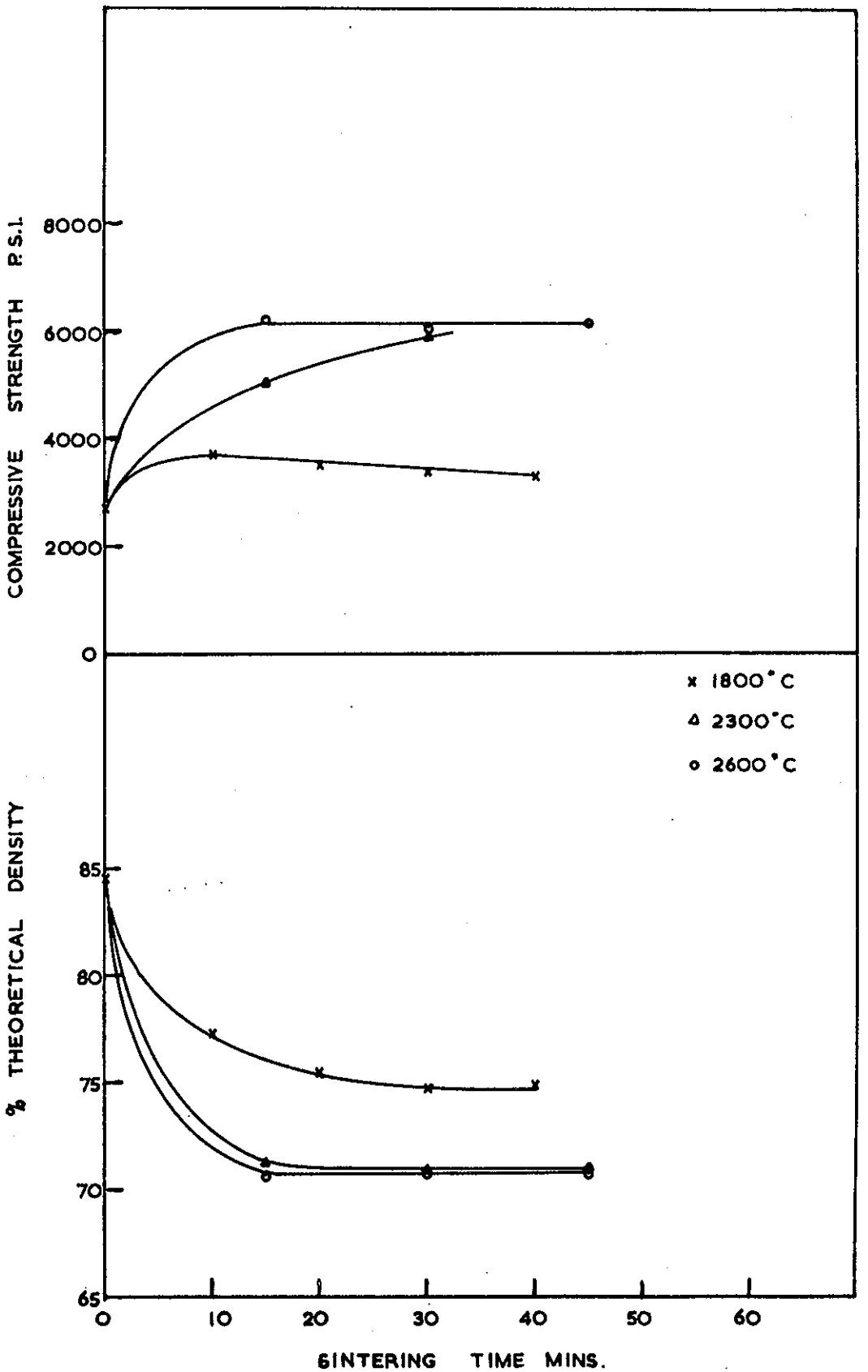


FIG. 11 COMPACT PROPERTIES AS A FUNCTION OF TIME AT TEMPERATURE (GRAPHITE PLUS UO_2 AND ThO_2)

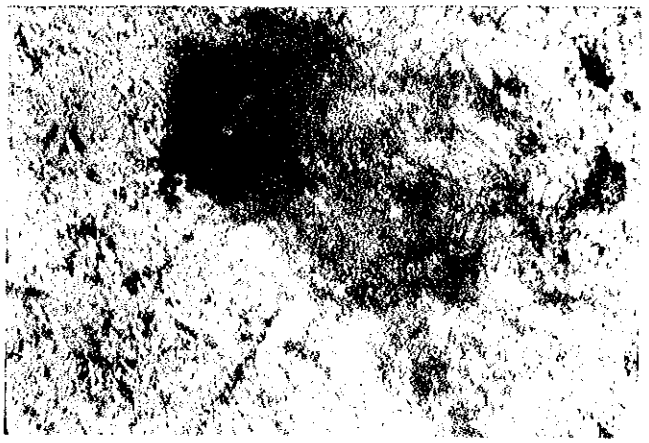


Fig. 12 Photomicrograph of compact containing graphite and uranium (30% w/w) after sintering for ½ hr. at 2500°C (X 500)

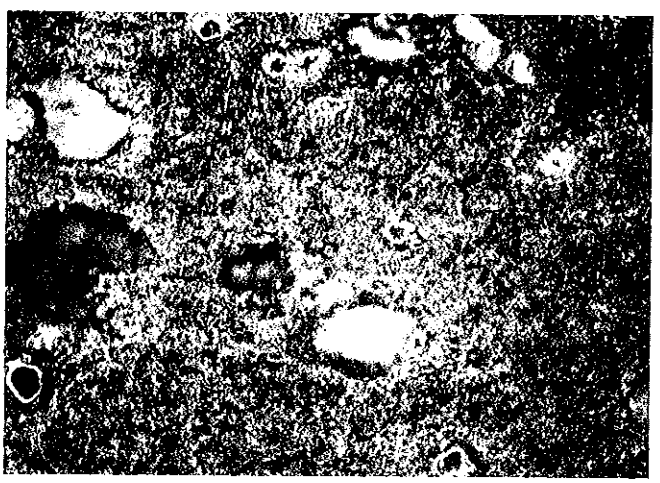


Fig. 13 Photomicrograph of compact containing graphite and uranium (30% w/w) after heating for ½ hr. at 2000°C (X100)

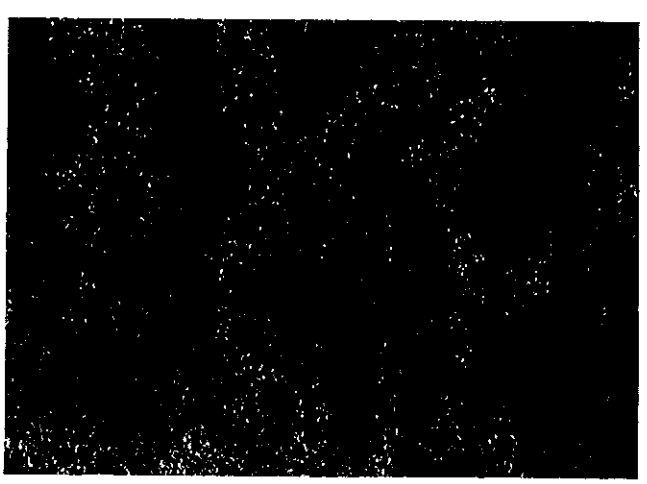


Fig. 14 Photomicrograph of compact containing graphite and uranium (30% w/w) after heating for ½ hr. at 2600°C (X50)

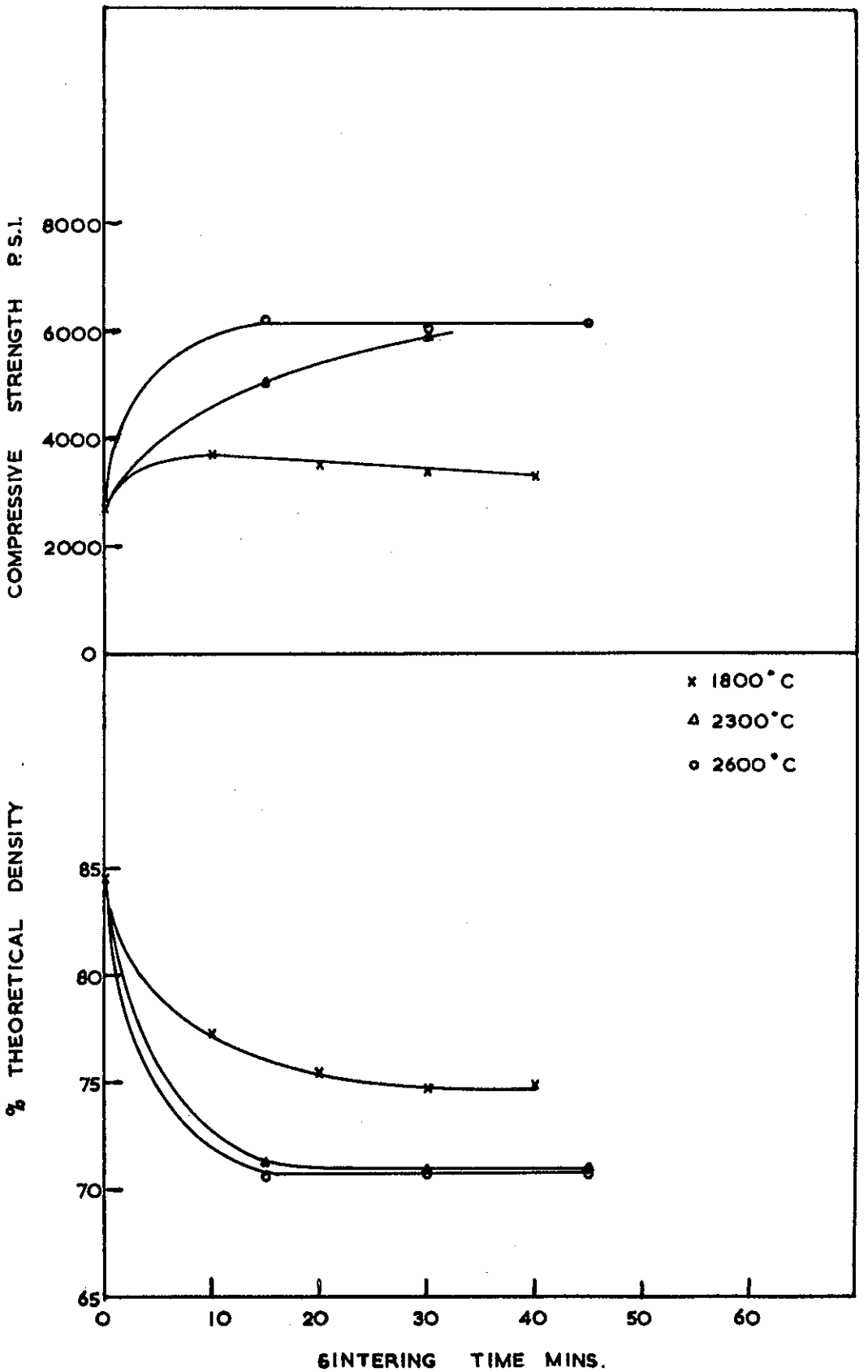


FIG. 11 COMPACT PROPERTIES AS A FUNCTION OF TIME AT TEMPERATURE (GRAPHITE PLUS UO_2 AND ThO_2)

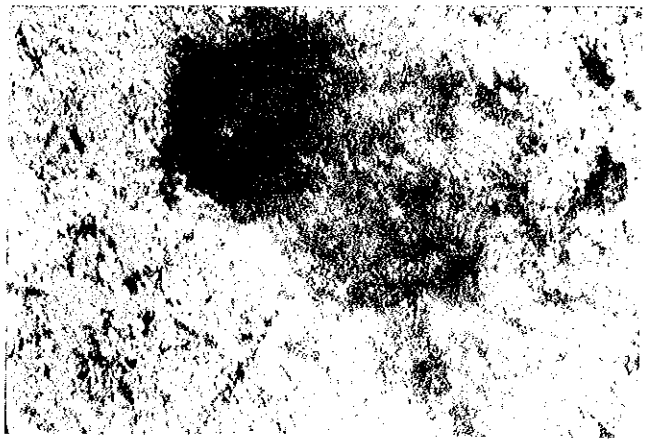


Fig. 12 Photomicrograph of compact containing graphite and uranium (30% w/w) after sintering for ½ hr. at 2500° C (X 500)

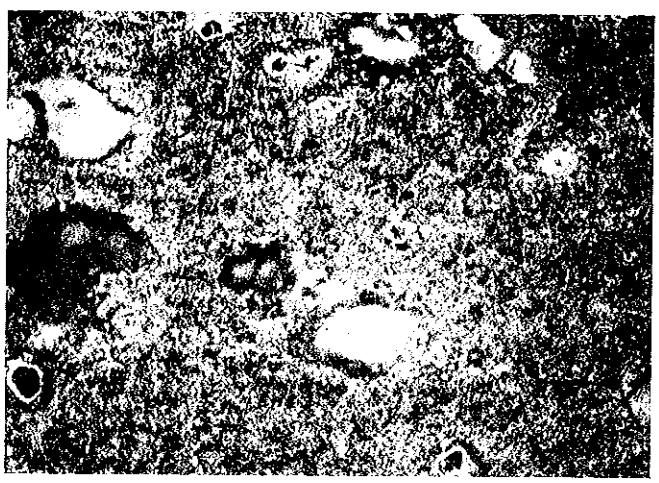


Fig. 13 Photomicrograph of compact containing graphite and uranium (30% w/w) after heating for ½ hr. at 2000° C (X100)

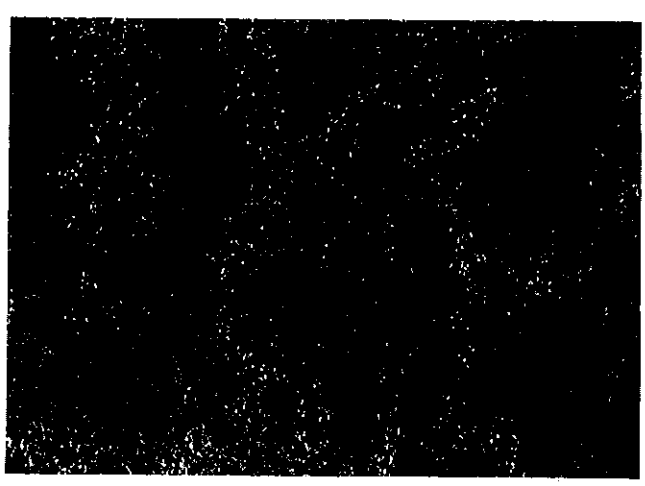
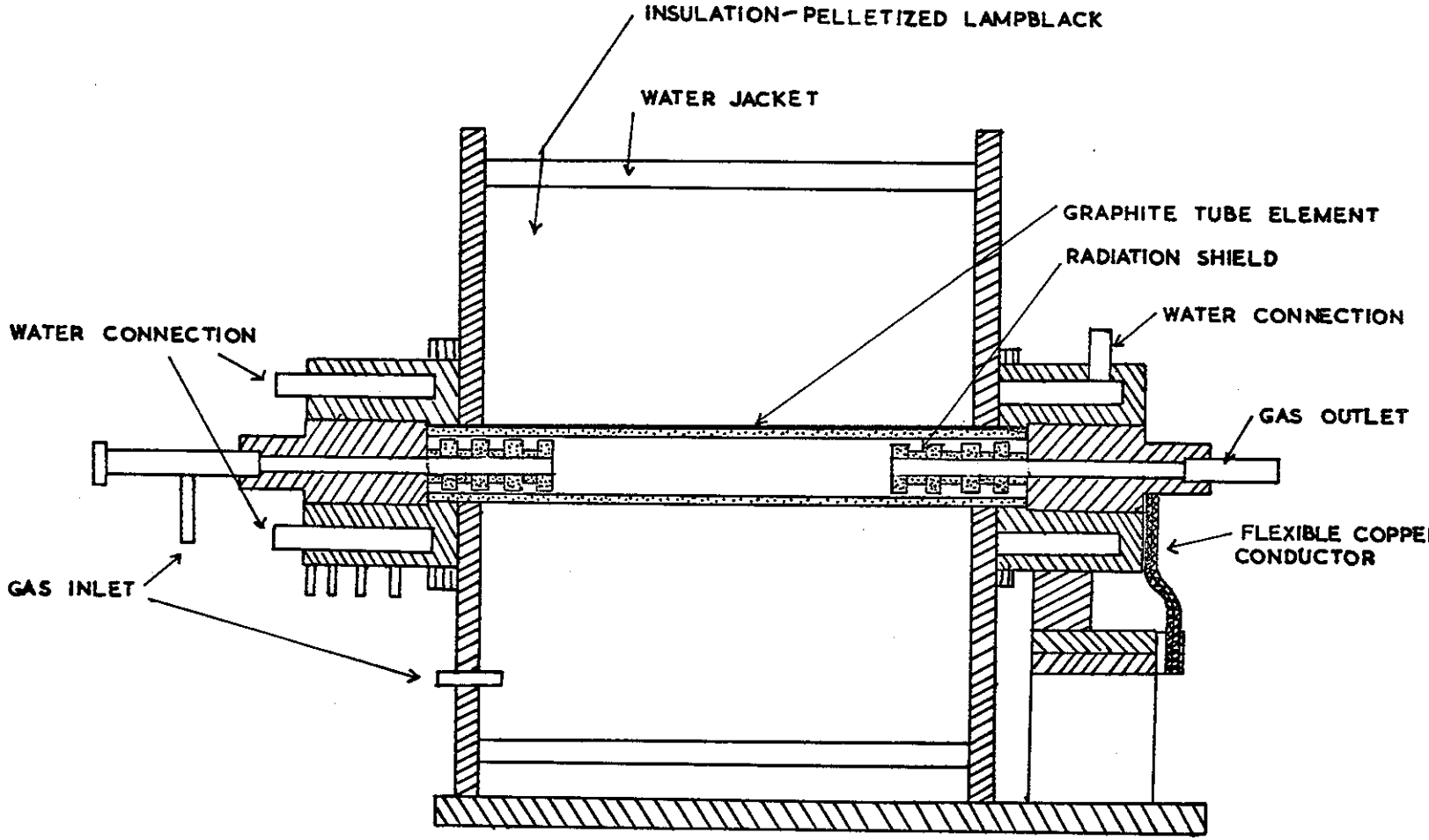


Fig. 14 Photomicrograph of compact containing graphite and uranium (30% w/w) after heating for ½ hr. at 2600°C (X50)



GRAPHITE RESISTANCE FURNACE.

FIG. 15 GRAPHITE RESISTANCE FURNACE

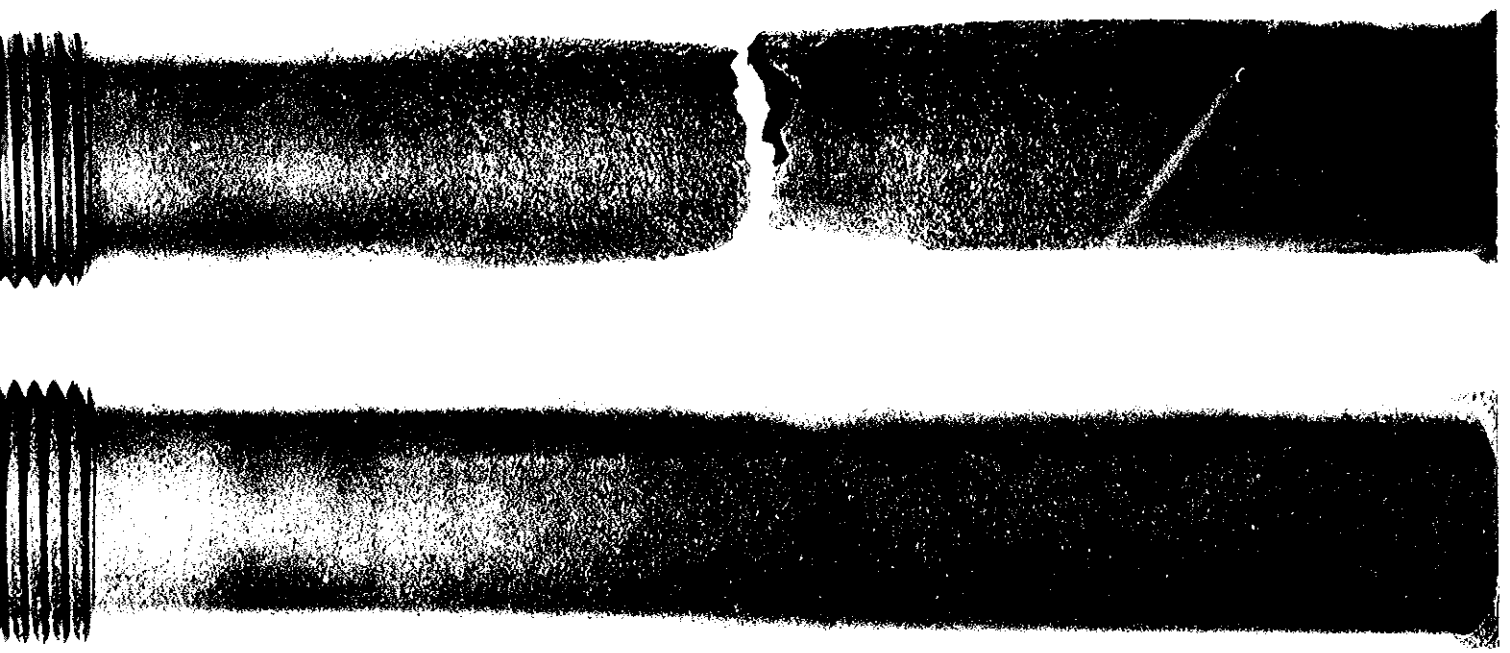


Fig. 16 Photograph showing a new and a fractured heating element for the resistance furnace

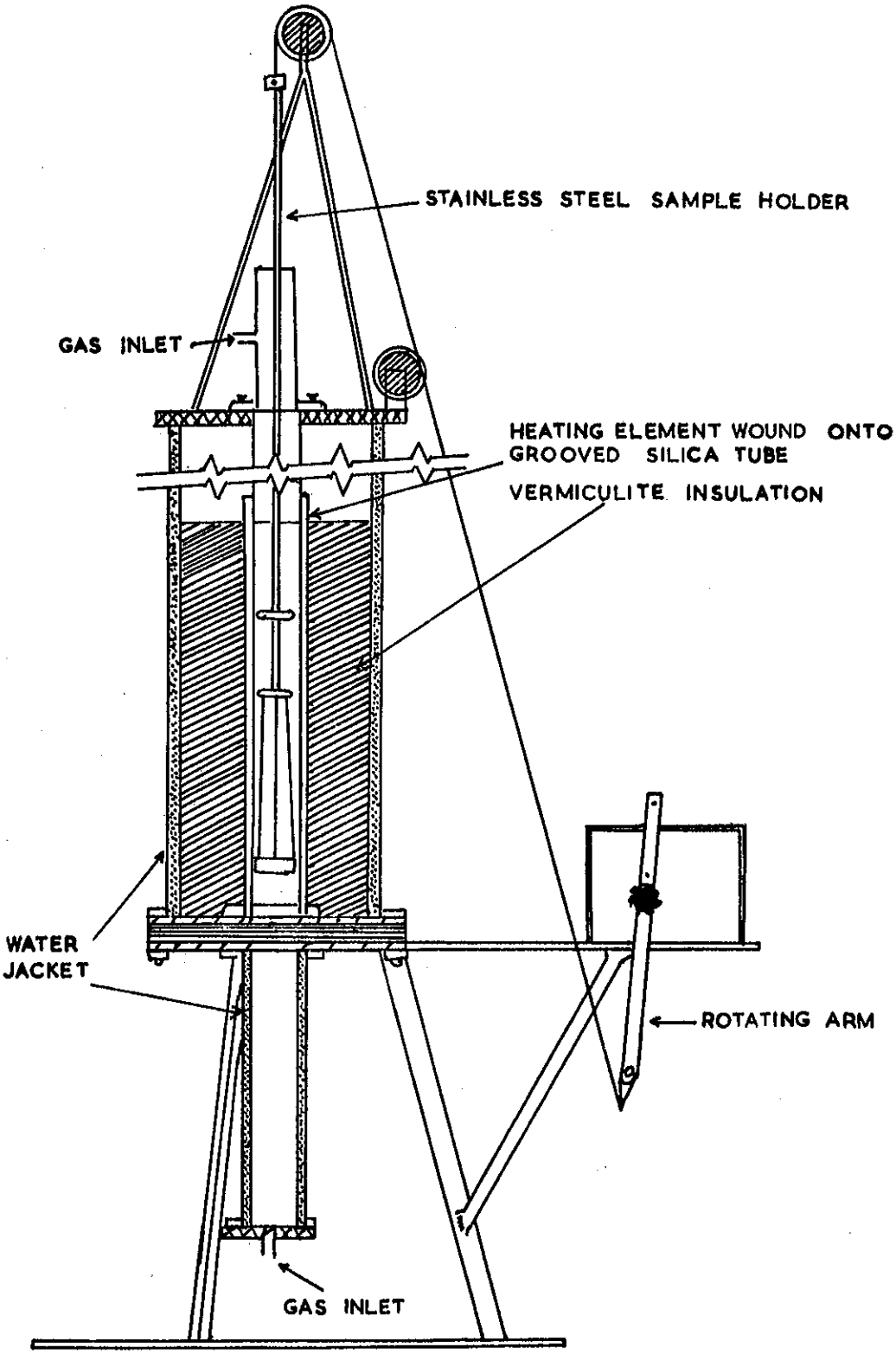


FIG. 17 THERMAL CYCLING FURNACE

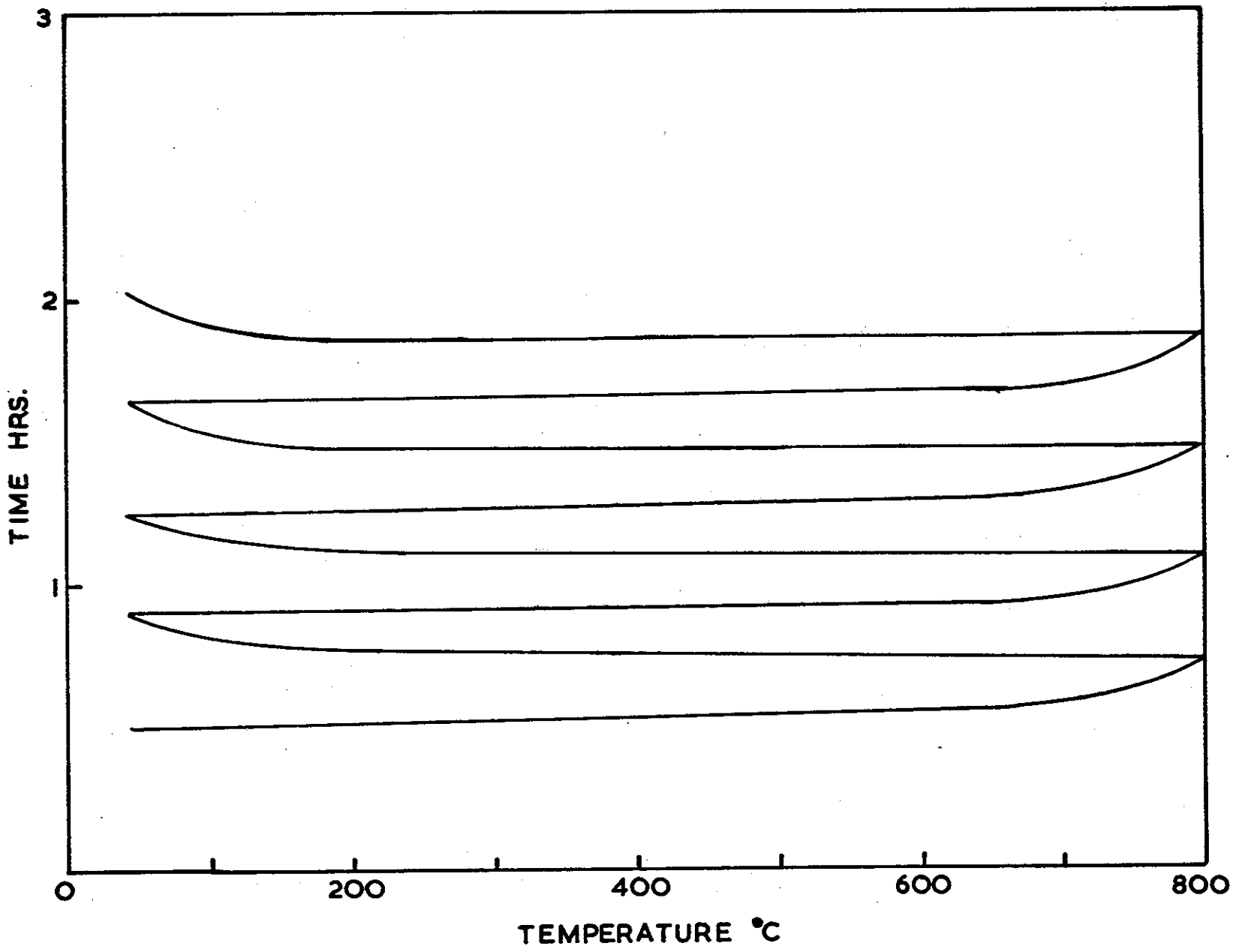


FIG. 18 TYPICAL SERIES OF HEATING AND COOLING CYCLES FOR THE THERMAL CYCLING FURNACE

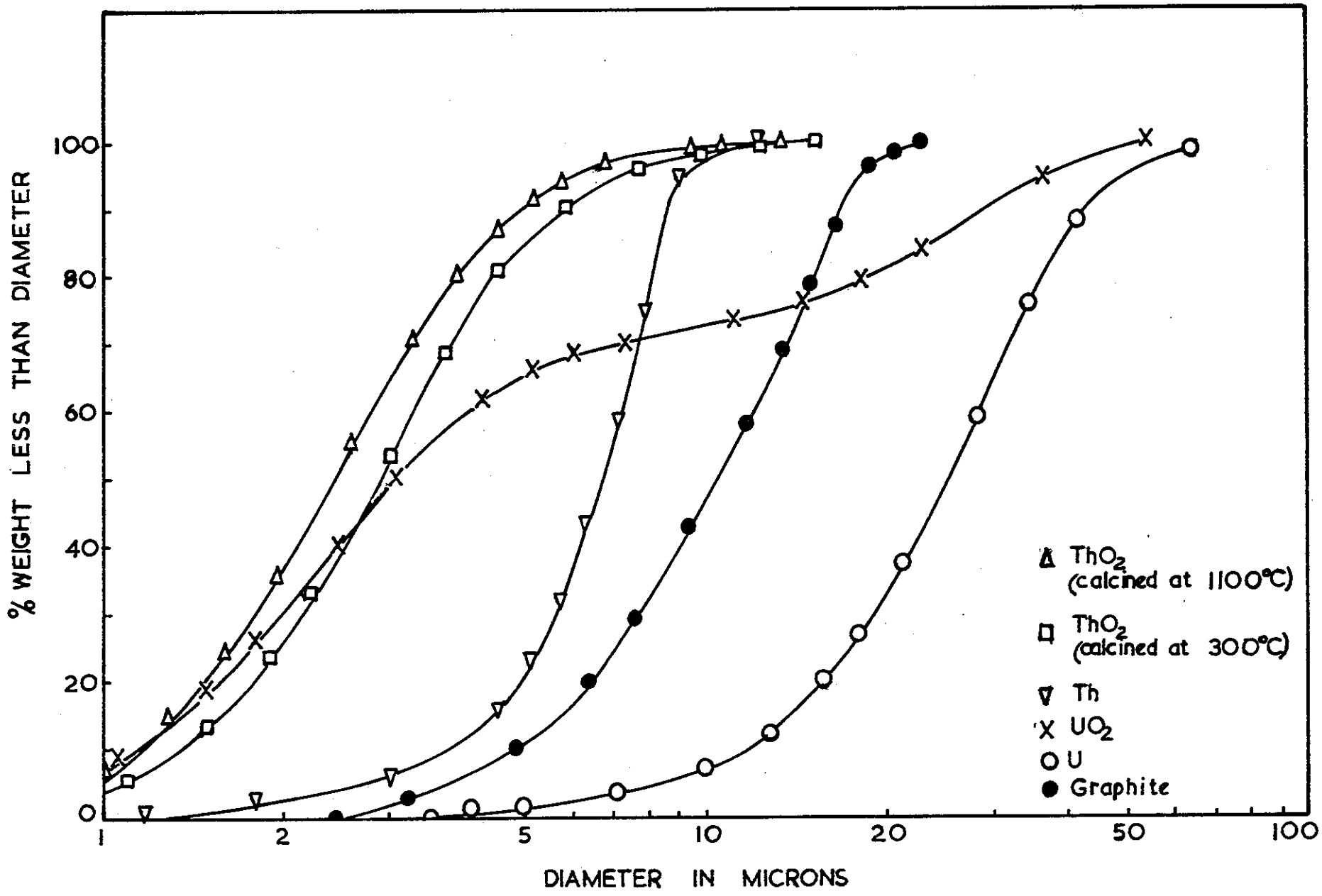


FIG. 19 PARTICLE SIZE DISTRIBUTIONS OF MATERIALS USED
(MEASURED WITH A SHARPLES MICROMEROGRAPH)