DEVELOPMENT OF INERT-MATRIX MATERIALS FOR PLUTONIUM BURNING OR ACTINIDE-WASTE ANNIHILATION

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ABSTRACT

Significant effort is underway internationally to develop a non-UO_2-based inert-matrix fuel capable of hosting fissile isotopes without generating new plutonium or high-mass carcinogenic actinides. The intention is to be able to dispose of military or reactor-grade plutonium, or eliminate carcinogenic actinides. AECL has a program that focuses on the development of SiC as the candidate material for this new form of fuel; the program includes accelerator-simulation studies of in-reactor behaviour of SiC, fabrication of SiC, compatibility of SiC with water and Zircaloy, waste disposal of SiC, as well as examining reactor physics issues related to SiC. CANDU reactors have been shown to be uniquely suited for this purpose. Results of this AECL program are described.

1. INTRODUCTION

A worldwide effort is underway to find the best ways to dispose of the military plutonium that is being freed by dismantling of nuclear weapons from the United States and Russia. The United States Department of Energy (USDOE) has set this as one of its primary goals for the near and intermediate future. Towards this end, Canada is investigating the potential of burning mixed-oxide (MOX) fuel in one or two of its CANDU reactors [1]. In the United States, underground disposal of the military plutonium as a waste-glass is also under serious consideration. And, a number of institutions, including AECL, are investigating a new form of fuel, termed *inert-matrix* fuel, as a way of burning the plutonium without generating new plutonium at the same

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time as MOX or any uranium-based fuel does. This paper addresses this last topic—inert-matrix fuel.

In Europe, a significant program is underway, not on the disposition of military plutonium, but on the annihilation of certain long-lived, carcinogenic actinides produced during normal reactor operation, and concentrated by reprocessing of the fuel*. Here, the intent is to make an inert-matrix fuel incorporating these actinides (^{237}Np, ^{241}Am, ^{244}Cm) together with plutonium that is usually separated with these actinides. The plutonium provides sufficient fissile material and the neptunium, americium and curium are transmuted or fissioned to shorter-lived, less carcinogenic nuclides. Without ^{238}U in the fuel matrix, further production of these actinides does not occur. The challenge to develop an inert-matrix material is the same as for plutonium annihilation, above. Thus there are two separate possible applications for a proven inert-matrix fuel material—plutonium annihilation and actinide-waste destruction.

There is also a third potential application—burning reactor-grade plutonium. The US efforts on developing an inert matrix is for this application. The amount of plutonium produced in the next 10 to 20 years, intended for use in MOX fuel or fast-reactor fuel, may necessitate the use of inert-matrix fuel to help dispose of the plutonium.

CANDU reactors are particularly suited for all three of these applications [3] because no major modifications to reactor design are required and because the neutron economy of CANDU reactors means the annihilation of plutonium/actinide waste is more complete.

This paper surveys briefly programs that are underway worldwide and then describes AECL's program and progress. It is an update of material given at the last CANDU conference [4].

2. PROGRAMS AND CANDIDATE MATERIALS

The major European effort is a multi-national program called EFTTRA *(Experimental Feasibility of Targets for Transmutation),* which is directed towards actinide-waste annihilation. The program includes fast-reactor irradiations of candidate materials. At the last EFTTRA meeting, the participants issued an invitation to Russia and Canada to take part in a 2-d workshop in Paris in mid-1998 to "compare the different approaches on the topics of *matrices* and *actinides without uranium*". Although main results and approaches will be shared, detailed results from the EFFTRA irradiations are proprietary, shared only by the countries participating.

Japan has a program directed towards annihilation of military plutonium (particularly Russian military plutonium), which they call PROFIT (Plutonium Rock-like Fuel In-Reactor Technology). Their idea is to use a combination of materials to produce a multi-phase inert-matrix material that will resemble ordinary rock, even after irradiation, and thus facilitate underground burial as a waste.

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* For deep geological disposal of spent fuel in an underground repository, Canadian assessments have shown that the radiological risk from the actinides is negligible [2]

The US program on inert-matrix material development, smaller than EFTTRA and PROFIT, focuses on zirconia (ZrO_2). Zirconia is one of the few materials that has already been shown to behave acceptably as a fuel material (with the addition of ^{235}U). Its major disadvantage is its poor thermal conductivity (slightly lower than UO_2), which means that fuel temperatures will be as high as, or higher than, those in today's fuels. Most researchers are searching for an inert-matrix material that, besides its ability to function acceptably as fuel host in-reactor, has a higher thermal conductivity than UO_2 does so that fuel temperatures will be lower, fission-gas release from the fuel will be lower, and safety margins will be increased.

A listing of candidate materials and the properties that make them suitable as inert-matrix candidates can be found in Ref. 2. Those that we have worked with include $ZrSiO_4$ (zircon), $MgAl_2O_4$ (spinel), CeO_2, $CePO_4$, ZrO_2-doped with Ca, Ce, Er or Y, and SiC. Cerium oxide (CeO_2) has the same crystal structure as UO_2, and was thought therefore that it would behave well in-reactor. Zircon is a stable mineral found in the earth's crust, and therefore at least should be a stable waste form. It is being evaluated as a candidate for hosting military plutonium for direct burial in the ground. Cerium phosphate is a candidate supplied to us from the Netherlands (via the Transuranium Institute in Germany).

3. AECL'S PROGRAM

Silicon carbide stood out early as a promising candidate material because of its high melting temperature, very high thermal conductivity and known resistance to attack by many corrosive agents, including oxygen, even at high temperatures. Because no other laboratory in the world was examining SiC for this purpose, AECL focused its efforts on SiC, although the Tandem Accelerator studies described in the next paragraph were used for many candidate materials. The overall program was aimed at examining all issues that would be important in the selection of SiC as an inert-matrix fuel candidate.

Because of the large number of candidate materials, we utilized the Tandem Accelerator to simulate in-reactor conditions to help sort out those candidate materials that would behave well as a fuel. The critical unknown issue for candidate materials is how they will behave in-reactor under the severe damage inflicted by fission fragments blasting through the matrix at energies greater than 70 MeV. Especially, will the candidate materials become amorphous or undergo an unacceptable volume-change? Producing fuel from each candidate material for in-reactor tests is expensive, particularly with plutonium, so the Tandem Accelerator at AECL was used to bombard the candidate materials with a beam of 72 MeV iodine ions. This beam substitutes for fission fragments, and the bombarded areas were examined for damage, especially swelling. To increase the number of candidate materials available for testing, and to foster international collaboration, AECL tested candidate materials from the countries of the European Union and the United States, as well as its own.

Besides these accelerator-simulation tests, the program on SiC consisted of assessing:

- reactor-physics aspects of SiC fuels in CANDU reactors

- fabrication issues associated with SiC —high sintering temperatures, handling plutonium, and characterization of microstructures that form with the addition of plutonium and several sintering aids
- compatibility of SiC with water at reactor coolant conditions and with groundwater for eventual storage
- compatibility of SiC with Zr-based sheath materials under accident temperatures
- waste-disposal aspects.

4. REACTOR PHYSICS

Detailed fuel-management simulations demonstrate that an existing CANDU reactor can burn inert-matrix fuel containing plutonium or actinides without major modification. Fuelling rate, channel power, bundle power and element power ratings are all within current limits. The reference fuel, described in the next paragraph, would destroy 94% of the fissile plutonium.

The reference Pu-SiC fuel for Pu-annihilation contains 250 g of weapons-derived plutonium mixed uniformly with SiC in the outer 30 elements of a standard 37-element bundle. The central element contains 20 g of gadolinium. Another 40 g of gadolinium are distributed uniformly over the 6 elements in the next ring. The distribution of the gadolinium, which has a very high depletion rate, was optimized to suppress the excess reactivity of the fresh fuel and to minimize the power ripple that is due to refuelling.

Detailed fuel-management simulations using a uniform 2-bundle-shift refuelling scheme in a Bruce A reactor indicated that the maximum instantaneous channel power is below 7.1 MW and the maximum instantaneous bundle power is below 970 kW. Both are within the current licensing limits. The fuelling rate is about 15 bundles per full-power day of operation, which is within the current fuelling machine capability.

For this Pu-SiC fuel, as well as for all the conventional MOX options, void reactivity is negative. Hence there would be no power pulse in a postulated LOCA, and the safety and licensing analyses would be greatly simplified.

The fuel temperature coefficient is very slightly positive, about 12 μk/°C; however, this is irrelevant in the safety analysis since any increase in heat in the fuel would immediately be transferred to the coolant because of the high thermal conductivity of the SiC, thus reducing the coolant density and producing a negative reactivity feedback because of the negative void-reactivity coefficient.

For the actinide-waste-burning option, results are similar for reactor-physics assessments of SiC. The actinide additive to the SiC consists of plutonium and minor actinides recovered from spent LWR fuel. As in the Pu-burning option, gadolinium is also added. Several combinations of actinide inventory and gadolinium loading were considered. The best result in a CANDU 6 type reactor would be achieved using a full-core loading of actinide-SiC fuel containing 400 g of actinides in the outer 30 elements of the standard 37-element bundle and 60 g of gadolinium in the inner 7 elements. The actinide mix consists of the minor actinides and plutonium from spent PWR fuel; specifically, 356 g of plutonium and 44 g of neptunium, americium, and curium. About 60% of the initial actinide inventory is destroyed (as is 90% of the initial fissile plutonium inventory). The fuelling rate is 9.2 bundles per full-power day, resulting in the destruction of 0.68 Mg of actinides in a CANDU 6 reactor per year (assuming an 80% capacity factor). Maximum instantaneous channel power was less than 7.0 MW, and maximum instantaneous bundle power was less than 1000 kW. Fuel element power is expected to be below the current safety limit because of the high thermal conductivity of the SiC matrix. Fuel temperature coefficient is slightly positive, 12.2 μk/°C, and the coolant-void reactivity is -4.2 mk. The power coefficient is expected to be significantly negative because of the negative coolant-void reactivity and the high heat conductivity of the SiC matrix.

5. TANDEM ACCELERATOR TESTS

Since preliminary results were reported in 1995 [4], we have exhaustively tested many candidate materials, $ZrSiO_4$ (zircon), $MgAl_2O_4$ (spinel), CeO_2 (ceria), $CePO_4$, ZrO_2-doped with Ca, Ce, Er or Y, as well as SiC, from ambient temperature to 1200°C, and over a wide range of doses (10^{14}-10^{17} ions/cm^2)*. After accelerator bombardment of each sample, the surface relief of the 3-mm-diameter beam spot was measured. Significant height of the spot above the original surface was taken as an indication that in-reactor swelling would occur. In general, results were not strongly dependent on dose—if a candidate material showed swelling at high dose, it also showed swelling at low dose. The results were also reasonably independent of temperature. The materials that showed the best results (least swelling) were SiC and ZrO_2 with any of its dopants. These candidate materials did not show *any* swelling; i.e., laser profilometry could not detect any surface relief at the implantation spots. Ceria turned out to be one of the poorest candidate materials on the basis of these tests. All other candidate materials showed some surface relief, implying that swelling could be expected when used in-reactor as a fuel.

Figs. 1-8 show typical results. Figs. 1 and 2 are for $MgAl_2O_4$ (spinel) at 100°C and 900°C, respectively, each showing the results for three doses (5×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2). Only the lowest dose spot (5×10^{14}) at 100°C shows little relief; the same dose at 900°C is clearly visible. Relief is about 1 to 2 μm. However, recent measurements with a new and recently calibrated stylus profilometer indicates that the calibration for the laser profilometer is about a factor of 5 too high. Thus relief for spinel is actually only 0.2 to 0.4 μm. Figure 3 shows a $ZrSiO_4$ (zircon) run at 1200°C to a dose of 1×10^{15} ions/cm^2; relief of a few micrometres is again clearly visible. Figure 4 shows a SiC single-crystal sample with 3 beam spots, 1×10^{15} at 1200°C, and 1.3×10^{14} and 1×10^{15} at ambient temperature. There is no sign of any of the spots even though mild discolouration at the spot sites can be seen on the sample surface by eye†. Figures 5 to 7 show sintered SiC, prepared at Queen's University, at 200°C, 900°C, and 1150°C, all taken to a relatively high dose of 1×10^{16} ions/cm^2. Again, there is no sign of the beam spots.

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[*] 10^{17}ions/cm^2 is approximately equivalent to a CANDU fuel burnup of 20 MW•h/kg U.

[†] indicating that nothing had accidentally prevented the beam from bombarding the sample.

6. MANUFACTURING

Pressureless sintering of SiC normally requires temperatures of 1900°C and higher; we have been working with Queen's University to develop methods of fabrication at lower temperatures, more representative of UO_2 sintering. In addition, fabrication tests were performed with Ce as an additive, Ce being generally considered, worldwide, as a reasonable chemical substitute for plutonium. No SiO_2 was used in these tests; the objective was only to determine what microstructures would develop.

Because of the largely covalent nature of the bonding in SiC, diffusion and, therefore, sintering do not occur easily. Usually, up to 5 wt % Al_2O_3 and 8 wt % Y_2O_3 is added to SiC powder to aid in sintering and reduce the temperatures required to achieve densities <90% TD to about 1900°C. Because this is still high, additional additives were examined in an attempt to reduce sintering temperatures even further. In particular, SiO_2 was examined since it was thought that this would melt and assist by *liquid-phase sintering.*

Reasonably good results were achieved with SiO_2 additive; densities of >95% were achieved at a sintering temperature of 1770°C (and 87% at 1730°C).

Unexpectedly, when fabrication tests with CeO_2 were done, not with the intent of lowering sintering temperatures, but rather to produce samples and observe microstructures, the CeO_2 proved a better sintering aid than SiO_2. At 1670°C, with the lowest amount of CeO_2 tested, 5 wt.%, a density of 96.5% was achieved; at 1700°C, 97%.

In the samples with 5 to 10% CeO_2, a garnet phase ($3Y_2O_3{\cdot}5Al_2O_3$) and an oxide phase ($CeAlO_3$) formed. At sintering temperatures $\leq$1700°C, these were very finely distributed among the 2 to 3-μm-sized SiC grains.

7. COMPATIBILITY WITH WATER

Previous results [4] showed that SiC had negligible interaction with water at typical CANDU coolant conditions, 300°C and a pH of 10.3. To determine the robustness of SiC, tests were performed under stagnant acidic conditions, pH of 3 and 300°C, for 32 d, even though it is not expected that CANDU coolant would ever exist under such conditions. Eleven samples, weighing 75 to 400 mg were tested. Some interaction with the water occurred; visibly, a gray oxide layer formed and some samples broke into two or more pieces. Weight changes were small, however; samples decreased in weight by 1 to 1.5 mg.

Additional tests were performed to examine the stability of SiC as a waste under attack by groundwater. The SiC samples used were ceria-doped, also with alumina sintering aid, prepared at Queen's University. The 20 mL water sample was at 2.9 pH at 96°C, and test duration was 119 h. (Groundwater in a fuel disposal vault is not expected to have such low pH, but is a check under "extreme" conditions.) Because attack at these low temperatures was so small, weight measurements were not used; rather, the chemistry of the water was examined for dissolved components, and the surface of the sample was examined by X-ray photoelectron spectroscopy (XPS).

After the test, the water analysis indicated 0.53 mg/L Al, 11.8 mg/L Ce, and 11.3 mg/L Si. Since the water volume was 20 mL, total dissolved amounts were 0.011 mg Al, 0.24 mg Ce, and 0.23 mg Si. A similar test with UO_2 has not been performed under these conditions, so direct comparison is not possible, at present. However, these amounts are very low, especially considering the high acidity level of the water, and indicate that dissolution rates are not likely to be a problem for SiC waste. The XPS analysis of the surface (2-3 monolayers) showed a change—the concentration of cerium was lower than the concentration of cerium in an unused sample.

8. HIGH-TEMPERATURE CHEMICAL REACTIVITY BETWEEN SIC AND ZIRCALOY-4

Tests were performed by holding polished disc specimens of SiC and Zircaloy-4 under a light pressure and an argon atmosphere in a molybdenum cell at 1000°C, 1500°C and 1700°C. Temperatures were maintained for 1 h at 1000°C and 1500°C and for 15 min at 1700°C. Two types of SiC specimens, fabricated at Queen's University, were used; both contained alumina as a sintering aid, and one contained titania, the other ceria. Extra carbon had been added to all specimens during sintering to ensure that no free Si was present in the final products. After cooling and sectioning, the specimens were examined by optical and scanning electron microscopy to study the extent of interaction.

Although no significant interaction occurred at 1000°C, at 1500°C there was clear evidence of a diffusion-based reaction to form ZrC and free Si. Diffusion of free Si into the Zircaloy disc led to the formation of a molten Zr-Si-rich eutectic phase. This reaction was more pronounced in the 1700°C test specimens, where the amount of molten eutectic phase was sufficient to cause partial dissolution of the Mo-cell sidewalls.

The test results indicate that formation of a molten Zr-rich phase could conceivably occur during a hypothetical reactor accident at temperatures significantly lower than the melting point of unoxidized Zircaloy cladding (1760°C). This possibility is of concern because it would allow further accelerated attack on the SiC carrier material, thereby allowing any fission products that had exsolved from the plutonium phase to be released. However, UO_2 interaction with Zircaloy begins at about 1200°C [5], and it dissolves into molten Zircaloy at 1760°C. The rate and extent of UO_2–Zircaloy interaction depends on the amount of oxygen present; however, it seems that the SiC interaction with sheath is, at least, no worse than the UO_2 interaction. Tests using SiC pellets clad with Zircaloy-4 sheathing, for more direct comparison are being evaluated.

9. WASTE-DISPOSAL

Considerations of SiC-based fuel as a waste form can be summarized:

- The SiC matrix itself, with sintering aids used to date will not generate long-lived activation products in-reactor. Care needs to be taken to minimize the impurity levels of N and Cl to eliminate concerns about their activation products ^{14}C and ^{36}Cl.

- Silicon carbide itself is extremely stable and resistant to corrosion. Its performance as a waste form will depend on its ability to encapsulate and retain high-burnup plutonium-containing particles. It is likely that the plutonium-rich phase will remain encapsulated, and hence be protected from leaching. This needs to be verified by post-irradiation examination and leach-testing of irradiated inert-matrix fuel materials.

10. CONCLUSION

Practical realization of an inert-matrix fuel for burning plutonium or actinide waste is 10 to 20 years off, at least partly because the incentive, while real, is not urgent. Silicon carbide and doped ZrO_2 are the 2 candidate materials that most clearly pass the accelerator-simulation test, but tests in-reactor are the final arbitrator. Compatibility of SiC with water does not seem to be an issue, either as a fuel for compatibility with coolant or as a waste form for compatibility with groundwater. Compatibility of SiC with Zircaloy does not seem to be worse than compatibility of SiC with UO_2-Zircaloy interactions. A small amount of melt phase above 1700°C may be acceptable in safety evaluations. A concern for the actinide burning application may be that SiC is a carbide rather than an oxide, and americium carbide, which could form when the actinide waste is incorporated in the SiC, is unstudied, and mounting a program to investigate it will be expensive because americium is highly alpha-active (MATZKE Hj., private communication, 1996). Americium oxide, on the contrary, has already been studied. For plutonium burning, and for actinide burning if the americium carbide issue can be resolved, SiC appears to be an excellent candidate material.

11. REFERENCES

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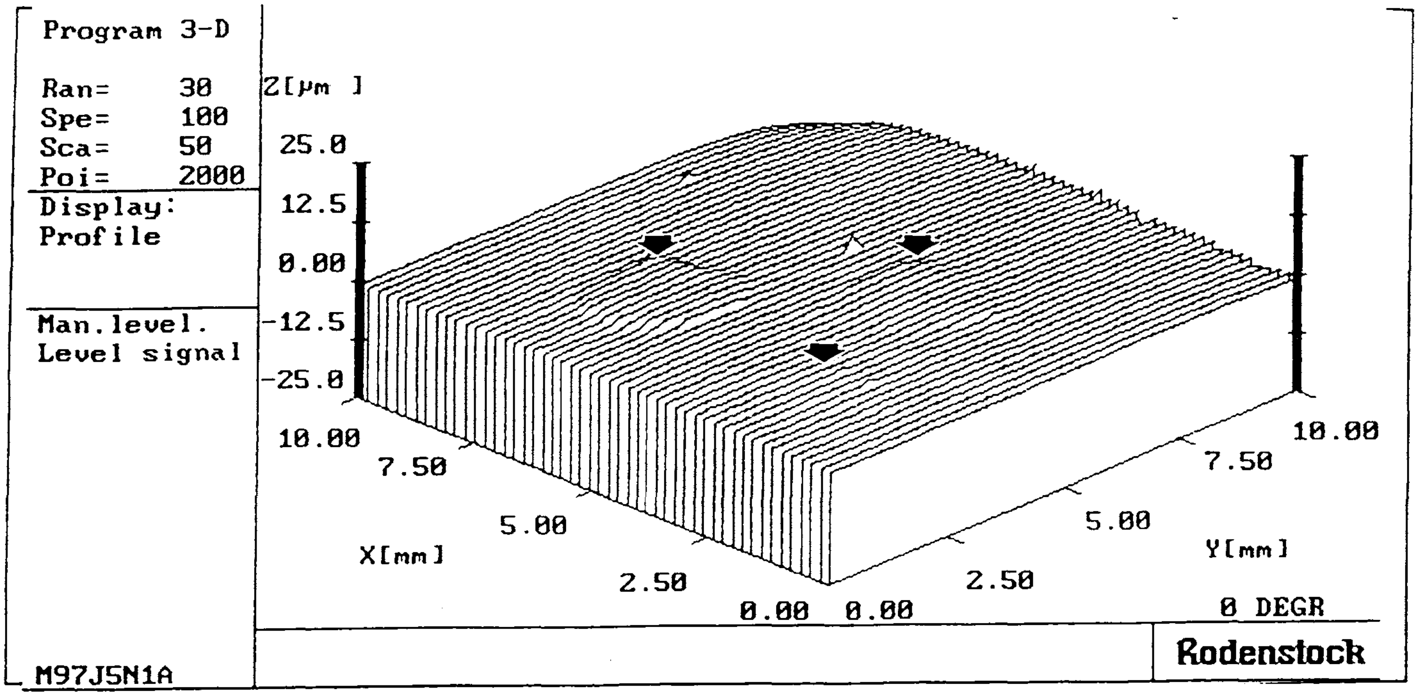

FIGURE 1. SINGLE-CRYSTAL SPINEL (100) WITH THREE IMPLANTATION DOSES AT 100°C OF IODINE AT 72 MeV (5×10^{14}, 1×10^{15}, 5×10^{15} IONS/CM^2).

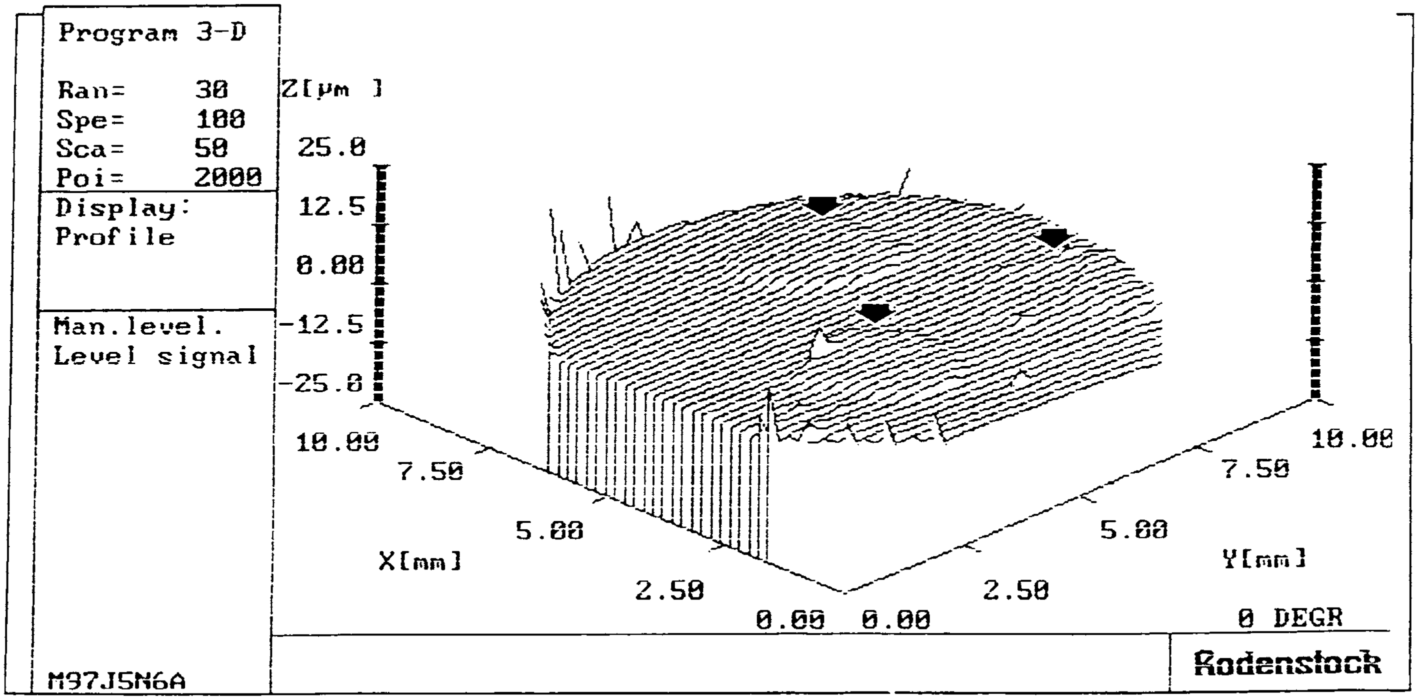

FIGURE 2. SPINEL AT 900°C, IMPLANTED WITH IODINE TO 5 x 10^{14}, 1 x 10^{15}, AND 5 x 10^{15} IONS/CM^{2}.

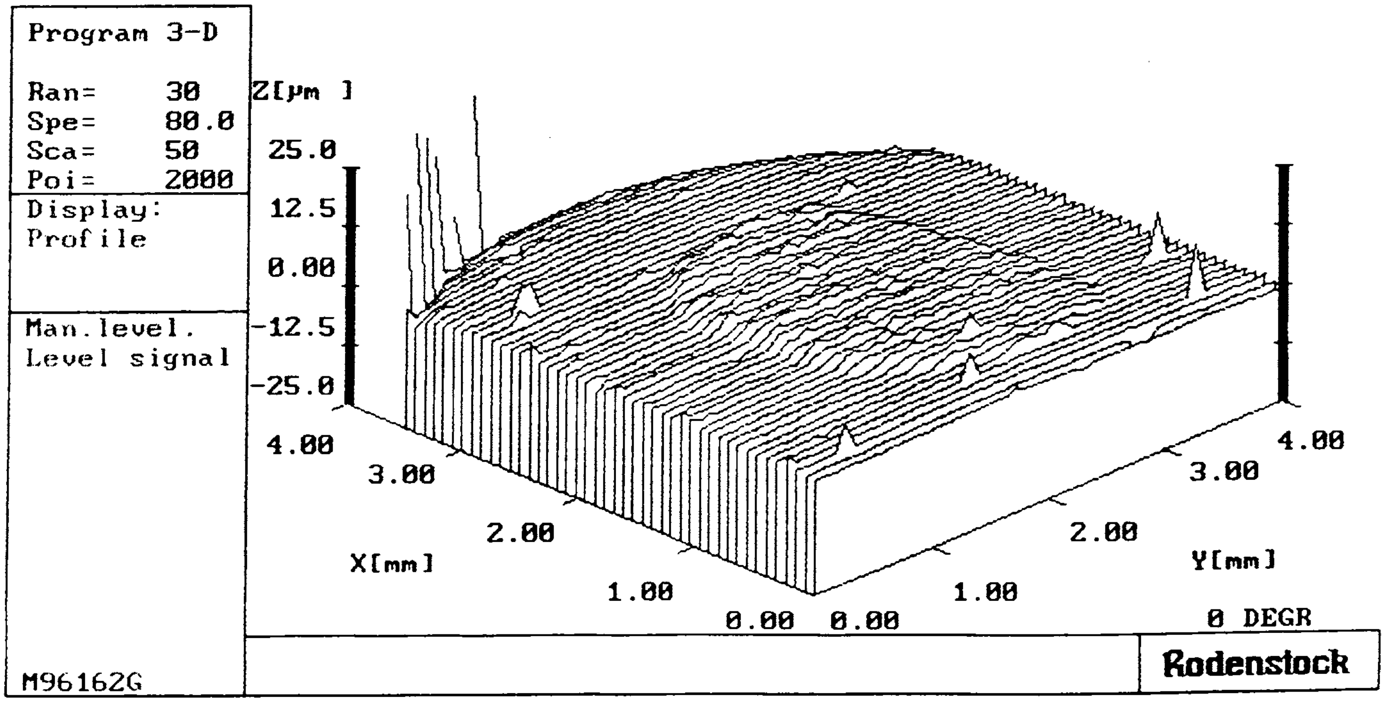

FIGURE 3. ZIRCON AT 1200°C, IMPLANTED WITH IODINE TO 1 x 10^{15} IONS/CM^{2}.

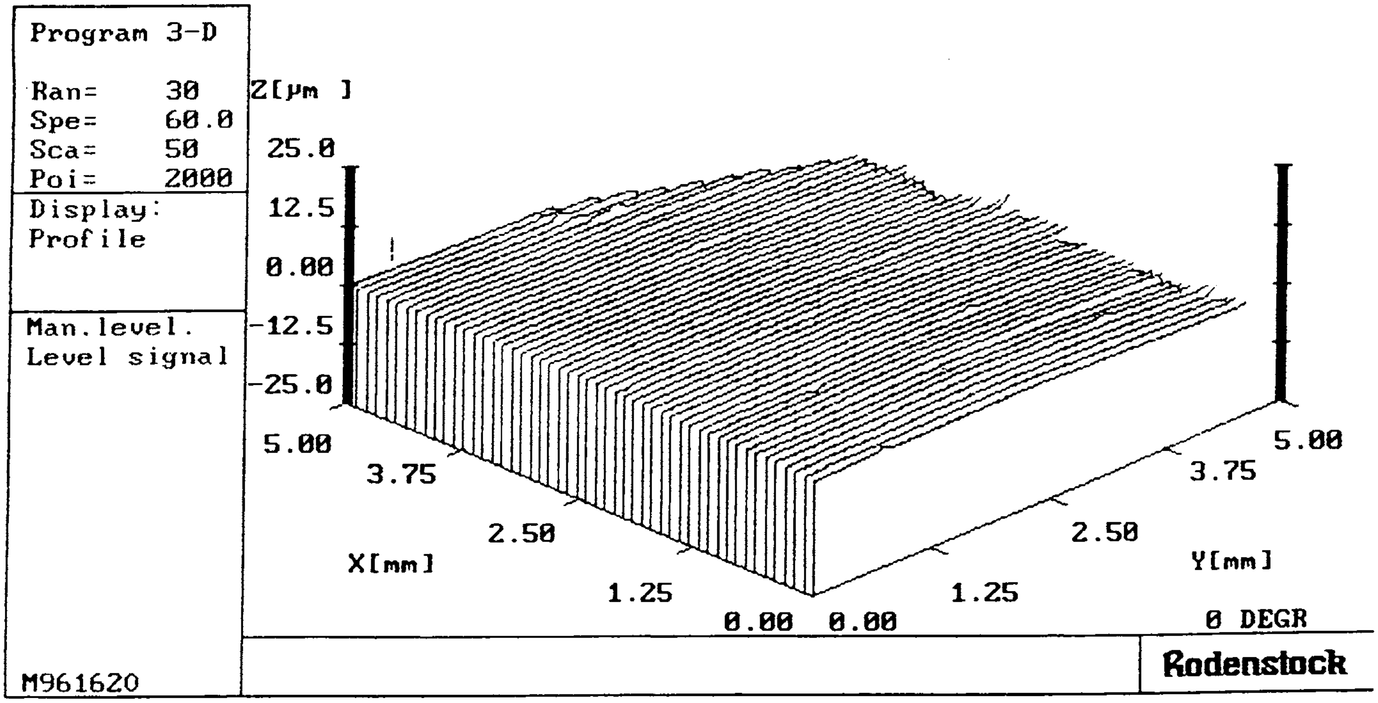

FIGURE 4. SINGLE-CRYSTAL SiC, WITH THREE DOSES OF IODINE: 1 x 10^{15} AT 1200°C; 1.3 x 10^{14} AND 1 x 10^{15} IONS/CM^2 AT AMBIENT TEMPERATURE.

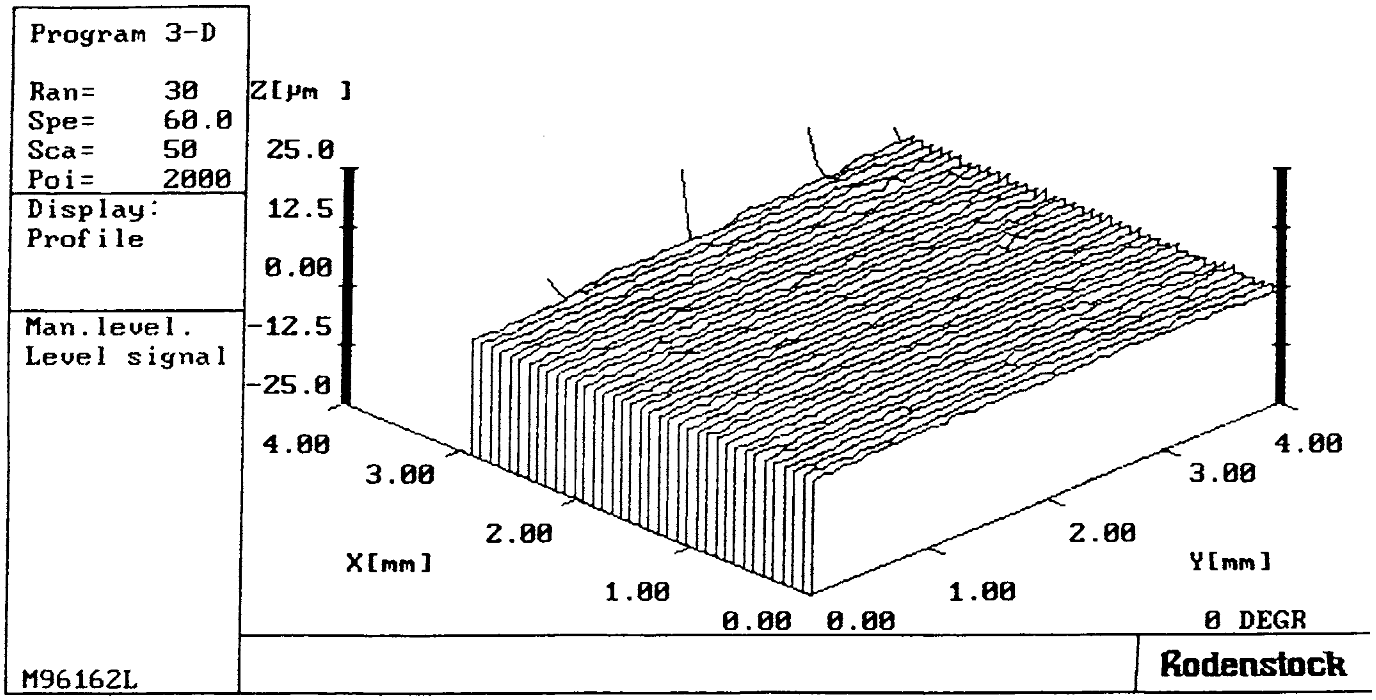

FIGURE 5. SiC AT 200°C WITH IODINE AT 72 MeV TO A DOSE OF 1 x 10^{16} IONS/CM^2.

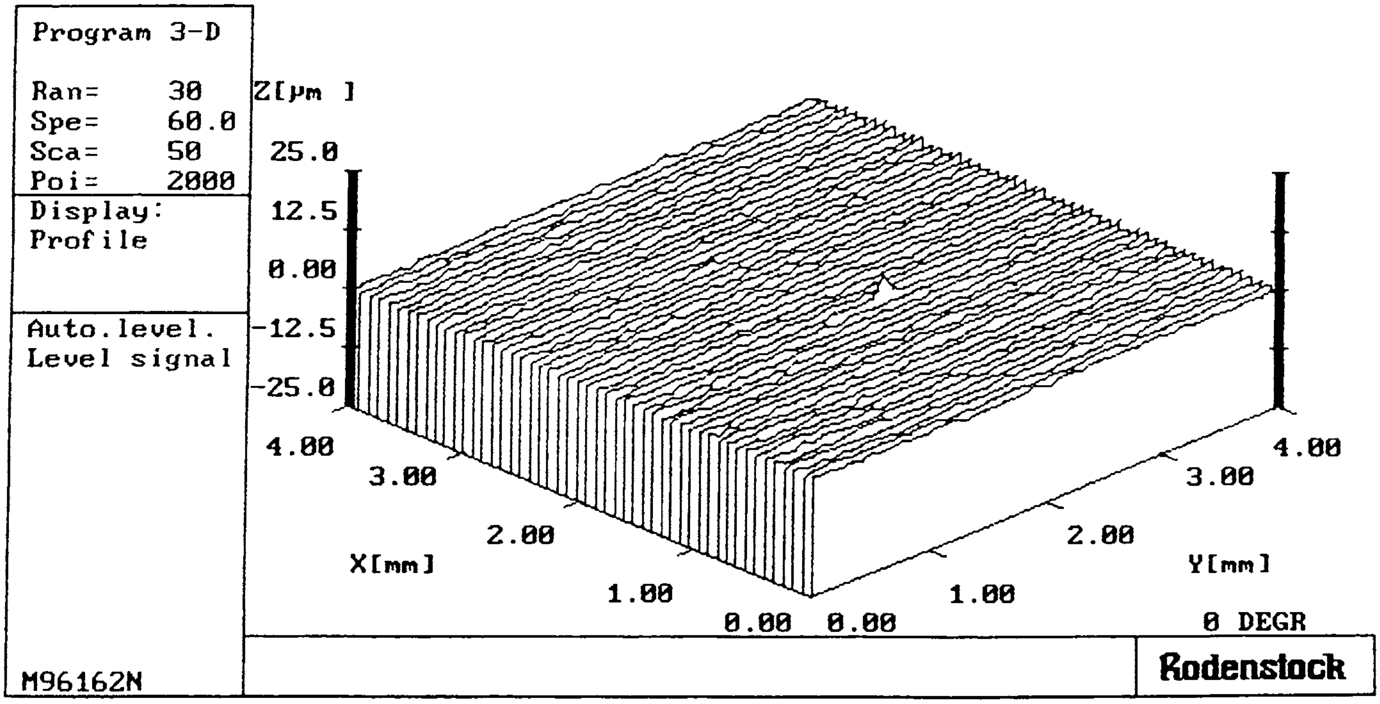

FIGURE 6. SiC AT 900°C WITH IODINE AT 72 MeV TO A DOSE OF 1x10^{16} IONS/CM^2.

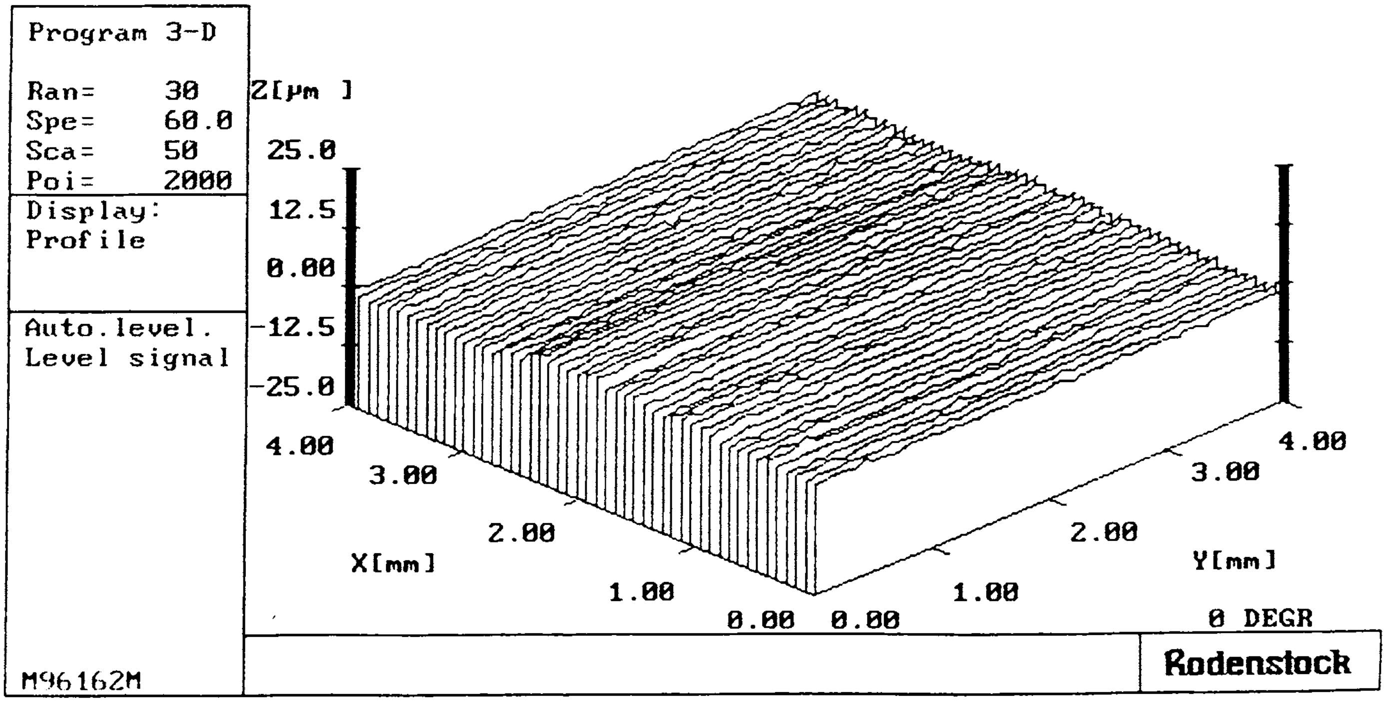

FIGURE 7. SiC AT 1150°C WITH IODINE AT 72 MeV TO A DOSE OF 1 x 10^{16} IONS/CM^2