IMPROVEMENT OF DUPIC PELLET FABRICATION PROCESSES BY USING SIMULATED FUEL

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ABSTRACT

A study to improve the DUPIC pellet fabrication process was carried out using simulated spent fuel. At present, 3 cycles of the OREOX treatment are conducted to convert a spent PWR fuel pellet into sinterable powder. But it takes a long time to treat spent PWR fuel material for 3 cycles of the OREOX treatment. Thus, 1 cycle of OREOX treatment was introduced for improving the powder process. The sinterability of 1 cycle-OREOX treated powder prepared by a simulated spent fuel pellet was investigated in terms of sintering temperature and compacting pressure. And, the effect of TiO_2 addition on the densification and grain growth was investigated. Good pellets with a sintered density of higher than 95% T.D. and average grain size of 8 . were obtained by using 1 cycle-OREOX treated powder. The density and grain size of the sintered pellet increased significantly with the addition of TiO_2.

1. INTRODUCTION

DUPIC (Direct use of spent PWR fuel in CANDU reactor) is a fuel recycling technology to fabricate CANDU fuel directly from spent PWR fuel material using a dry process. The heart of the DUPIC fuel fabrication is to produce sinterable powder from a spent PWR fuel pellet as a starting material [1,2].

The OREOX (Oxidation and REduction of OXide fuel) process was chosen to convert a spent fuel pellet into sinterable powder. DUPIC fuel pellet made from the powder treated by 3 cycles of the OREOX process satisfied successfully the requirements of a CANDU sintered pellet [3]. But it takes a long time to treat spent PWR fuel material for 3 cycles of OREOX treatment. Thus, 1 cycle of OREOX treatment and the addition of sintering aids like TiO_2 were introduced for improving the powder process.

Various methods to achieve a high sintered density of UO_2 have been considered; higher sintering temperature, longer sintering time, addition of sintering aids, control of the sintering atmosphere. The simple way to obtain a high sintered density without more powdering process is to raise the sintering temperature and to add sintering aids. Among the sintering aids, TiO_2 is known to greatly increase the rate of densification and sintered density of UO_2 [4-6].

A study on the preparation and characterization of sinterable powder was carried out using SIMFUEL (SIMulated high burnup FUEL) to avoid the high radioactivity of spent fuel. In this

study, the sinterability of a 1 cycle-OREOX treated powder was investigated in terms of sintering temperature and compacting pressure. And, the effect of the addition of TiO_2 on the densification and grain growth of a 1 cycle-OREOX treated powder was investigated.

2. EXPERIMENTAL PROCEDURES

2.1 SIMFUEL pellet fabrication

The fission product composition of irradiated UO_2 is determined by its starting enrichment and irradiation history. The ORIGEN (Oak Ridge Isotope Generation and Depletion) Code was used to calculate the fission product inventories to be added into the UO_2 powder for preparing SIMFUEL pellets. The fifteen elements listed in Table 1 represent the major fission products except for the volatile elements. The additives milled by a mortar were mixed with the UO_2 powder in a Turbula mixer. The wet attrition milling was used to obtain the homogeneous powder mixture. The powder mixture was pressed into green pellets at 300 MPa and sintered at 1700°C for 6 hours in an atmosphere of Ar-4%H_2. The SIMFUEL pellets having a sintered density of higher than 10.45 g/cm^3 and average grain size of 9 μm were used in this study.

2.2 Powder preparation

For the preparation of the powder from the pellet, the repetition of oxidation and reduction step, called the OREOX process, was carried out. The oxidation was performed at 500°C in air and the reduction at 700°C in Ar-4%H_2. Passivation was conducted at 70°C in Ar-2%O_2. Two kinds of powders, 1 cycle-OREOX powder and 3 cycles-OREOX powder, were prepared for the experiments. The 1 cycle-OREOX powder was produced by only one cycle of oxidation and reduction, whereas the 3 cycles-OREOX powder was made by 3 cycles of oxidation and reduction.

An attrition mill with a jar volume of 1.5 L was used to break the OREOX powder into a finer powder. The milling medium was zirconia balls with a 5 mm diameter. The OREOX powder was poured into the milling jar at a constant ball-to-powder weight ratio (40:1) and milled at 150 revolutions/minute. The milling of 1 cycle-OREOX powder and 3 cycles-OREOX powder were performed for 120 minutes and 15 minutes, respectively.

2.3 Stimulated DUPIC pellet fabrication

Zinc stearate powder was added as a lubricant and mixed with the milled powder in a Turbula mixer for 25 minutes at 25 rpm. Then the mixed powder was pressed into green pellets at a pressure range of 100 to 400 MPa using a single acting hydraulic press. Green pellets were sintered at 1700 to 1800°C for 6 hours in an atmosphere of Ar-4%H_2 with a flow rate of 3 L/min. The heating and cooling rate was controlled at 4°C/min.

The milled 1 cycle-OREOX powder and TiO_2 powder were mixed in a Turbula mixer to make a homogeneous mixture for 1 hr. After mixing with a lubricant, zinc stearate, and compacting at 300 MPa, the green pellets were sintered at 1750°C for 6 hours.

2.4 Characterization of the powder and the pellet

The mean particle size was measured using a laser particle size analyzer (Malvern, UK). The specific surface area of the powder was determined by the BET method. The powder morphology was observed by a scanning electron microscope (SEM). The densities of the green pellets and sintered pellets were determined by the geometric dimension and water immersion method (Archimedes' principle), respectively. The grain size of the sintered pellet was determined by a linear intercept method. The microscopic distribution of Ti was analyzed by an electron probe microanalyzer (EPMA).

3. RESULTS AND DISCUSSIONS

3.1 Powder characteristics

The physical properties of the 1 cycle-OREOX powder in comparison with the 3 cycles-OREOX powder are shown in Table 2. The 1 cycle-OREOX powder produced by only one step oxidation and reduction treatment has a lager mean particle size and a lower specific surface area than those of the 3 cycles-OREOX powder. The specific surface area of the 1 cycle-OREOX powder was increased significantly by attrition milling due to the reduction of the particle size into the submicron range, thus resulting in the improvement of powder sinterability.

Figure 1 shows SEM micrographs of the cyclic OREOX treated and milled powders. The 1 cycle-OREOX powder (Figure 1. (a)) shows generally coarse and angular shape with large cracks, less breakable than the 3 cycles-OREOX powder (Figure 1. (b)) showing the shape of sponge-like particles with internal cracks. But, the 1 cycle-OREOX particles were easily broken into submicron particles by a attrition mill for 120 minutes milling. The 1 cycle-OREOX powder was easily agglomerated after milling, due to increasing of the specific surface area and reducing of the particle size. The 1 cycle-OREOX powder milled for 120 minutes was densely agglomerated comparing with the 3 cycles-OREOX powder milled for 15 minutes.

The bulk and tap densities of the cyclic OREOX powders are greatly increased after milling. Therefore, a higher packing density of the cyclic OREOX powder during compaction would be obtained. Figure 2 shows the variations of green density as a function of compacting pressure. The 1 cycle-OREOX powder shows higher densities than the 3 cycles-OREOX powder.

3.2 Sinterability of 1 cycle-OREOX powder

The densification of the green pellet is the process of decreasing the free energy by means of a decrease in the surface area. Therefore, The sinterability of the 1 cycle-OREOX powder at the same sintering temperature will be worse than that of the 3 cycles-OREOX powder due to a lower specific surface area of the 1 cycle-OREOX powder. Thus, the sinterability of the 1 cycle-OREOX powder was investigated with a sintering temperature of 1700 to 1800 °C. Figure 3 shows the variation of the sintered density with sintering temperature. The sintered densities of the 1-cycle OREOX powder were increased from 10.25 (95.08% TD) to 10.35 g/cm^3 (96.01% TD) with increasing the sintering temperature.

Figure 4 shows the effect of the compaction pressure on the sintered density of the 1 cycle-OREOX powder in comparison with the 3 cycles-OREOX powder. The sintered densities of the 1 cycle-OREOX powder sintered at 1800°C were increased from 10.29 to 10.37 g/cm^3 with a compaction pressure of 150 to 400 MPa. Sound pellets without any defects were obtained in this pressure range [7]. Pellet densities of the 1 cycle-OREOX powder sintered at 1800°C were

higher than those of the 3 cycles-OREOX powder sintered at 1700°C. The average grain size of a sintered pellet for the 1 cycle-OREOX powder ranged from 7 to 9 μm.

Good pellets with sintered density of higher than 95% T.D. and an average grain size of 8 μm could be obtained from the milled powder after a 1 cycle of OREOX treatment. Thus, the fabrication of a good quality DUPIC pellet would be possible by using the powder produced by 1 cycle of OREOX treatment.

3.3 Effect of TiO_2 addition on the density and grain size

Figure 5 shows the sintered density of the 1 cycle-OREOX powder with a concentration of TiO_2. Sintered density increased significantly from 10.30 to 10.69 g/cm^3 with increasing the TiO_2 concentration. The sintered density is slightly increased in the concentration range of 0.15 wt.% TiO_2, but greatly increased to the extent of 0.24 g/cm^3 at 0.2 wt.% TiO_2. More than 0.2 wt.% TiO_2 is needed to promote the higher densification of the simulated DUPIC pellet. It is supposed that the addition of TiO_2 enhanced the densification of the green pellet fabricated from 1 cycle-OREOX powder because TiO_2 (as Ti_3O_5) is interstitially dissolved in the dissolved surrogate oxides-UO_2 to accelerate the densification rate similar to a pure UO_2 pellet [6].

Figure 6 shows the pore distributions of the sintered pellets with a concentration of TiO_2. The number of fine pores decreased and the pore shape became round as the TiO_2 concentration increased.

Figure 7 shows the effect of TiO_2 addition on the grain size of sintered pellet. The grain size of a sintered pellet increased slightly from 8 to 15 μm by the addition of 0.15 wt.% of TiO_2, but is greatly increased to 19 μm by the addition of 0.2 wt.% of TiO_2. Figure 8 shows the secondary phase in a sintered pellet with 0.2 wt.% of TiO_2. A secondary phase is precipitated on the grain boundary in the sintered pellet. The profile of Ti concentration across the secondary phase shows that the secondary phase has higher Ti concentration than the matrix. It is known that UO_2 and TiO_2 form a new eutectic phase with a melting point of 1600 to 1620°C [4]. Thus it can be deduced that TiO_2 and the dissolved surrogate oxides-UO_2 may form a eutectic phase. The liquid phase is formed on the grain boundary at the sintering temperature, and the material transport could be significantly enhanced through the liquid phase. The increase in grain growth by TiO_2 addition is assumed to be the presence of a liquid phase during sintering [6].

4. CONCLUSIONS

The sinterability of the 1 cycle-OREOX powder was investigated in terms of sintering temperature and compacting pressure. And, the effect of TiO_2 addition on the densification and grain growth was investigated. From the results discussed above, the following conclusions can be drawn:

- Good pellets with a sintered density of higher than 95%T.D. and an average grain size of 8 μm were obtained using the 1 cycle-OREOX powder prepared by 120minutes milling.
- Sintered density of the 1 cycle-OREOX powder could be the same as that of the 3 cycles-OREOX powder by increasing sintering temperature.
- TiO_2 addition enhanced the densification of the pellet and increased the grain growth of the pellet.

ACKNOWLEDGEMENTS

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TABLE 1. CONTENTS OF SURROGATES OF THE FISSION PRODUCTS ADDED TO UO_2 (SIMULATED BURNUP: 35 MWD/Kg U, COOLING TIME: 15 YEARS)

Fission products	Surrogates	Added quantity (g/1000g UO2)
Nd(Pr, Sm)*	Nd_2O_3	6.6945
Zr	ZrO_2	4.7803
Ce(Pu, Np)*	CeO_2	9.1126
Mo	MoO_3	4.7826
Ru(Tc)*	RuO_2	3.8053
Ba	$BaCO_3$	2.5228
Pd	PdO	1.5200
La	La_2O_3	1.8405
Sr	SrO	0.8414
Te	TeO_2	0.5628
Y	Y_2O_3	0.5597
Rh	Rh_2O_3	0.5255

*Elements in parenthesis were replaced by the element in front of parenthesis

TABLE 2. CHARACTERISTICS OF POWDER

Properties	1 cycle-OREOX		3 cycles-OREOX	
	As produced	After milling	As produced	After milling
Mean particle size (μm)	7.8	0.4	4.2	0.6
Specific surface area (m^2/g)	1.88	3.75	4.55	4.79
Bulk density (g/cm^3)	1.76	2.09	0.71	1.63
Tap density (g/cm^3)	2.86	3.41	1.87	3.05

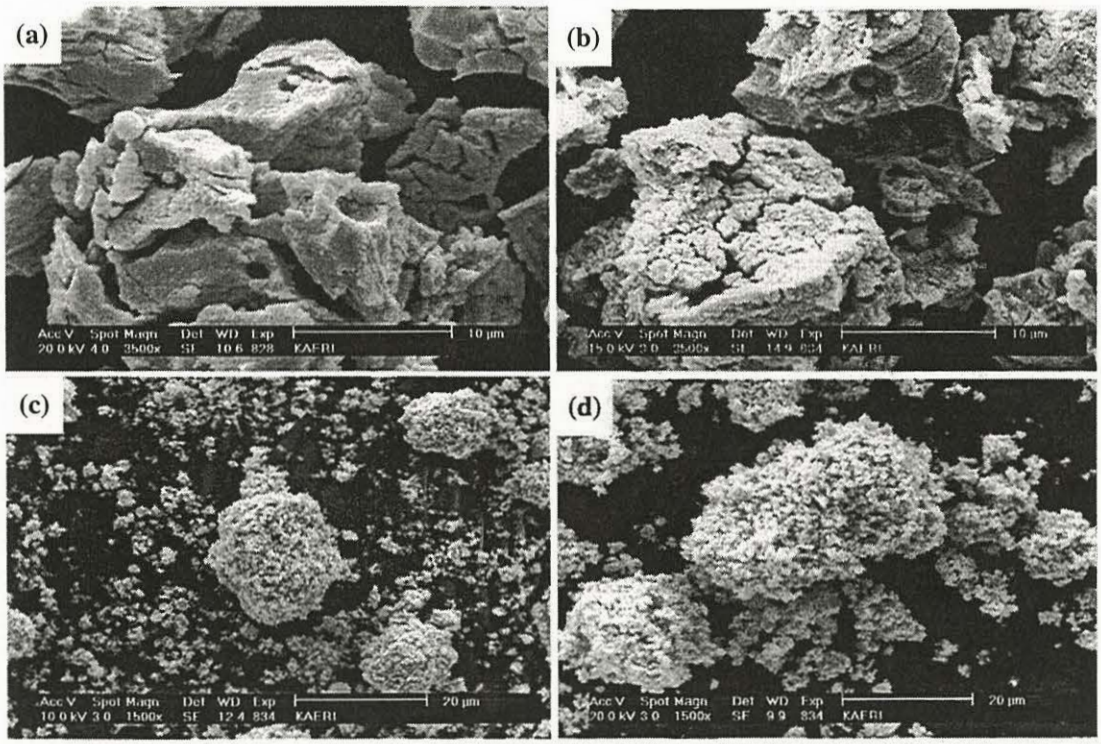

FIGURE 1. MORPHOLOGIES OF POWDERS; (a) 1 CYCLE-OREOX POWDER, (b) 3 CYCLES- OREOX POWDER, (c) 120 MINUTES MILLING, 1 CYCLE-OREOX POWDER, (d) 15 MINUTES MILLING, 3 CYCLES-OREOX POWDER

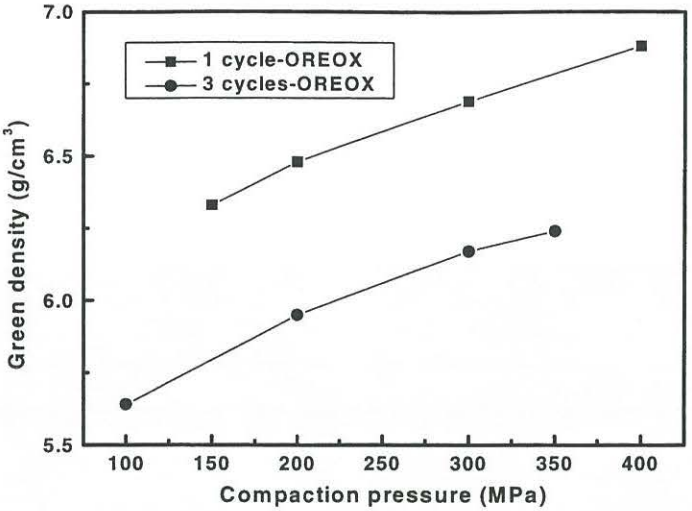

FIGURE 2. THE VARIATION OF GREEN DENSITIES WITH COMPACTING PRESSURE

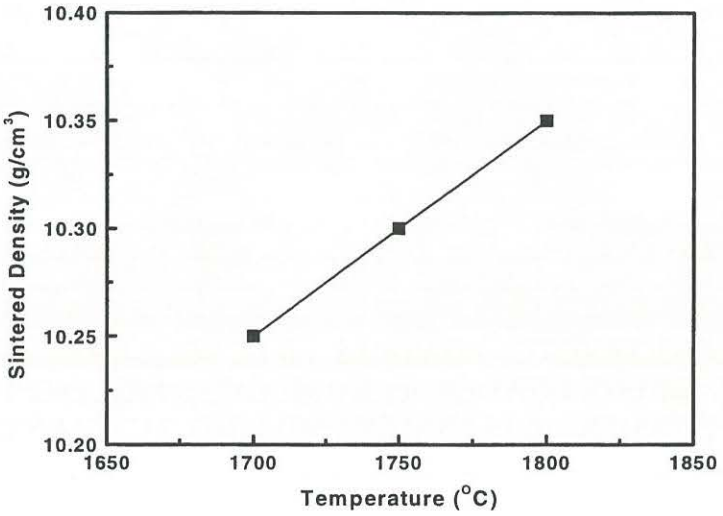

FIGURE 3. THE VARIATION OF SINTERED DENSITY OF THE 1 CYCLE-OREOX POWDER WITH SINTERING TEMPERATURE (COMPACTING PRESSURE: 300 MPa)

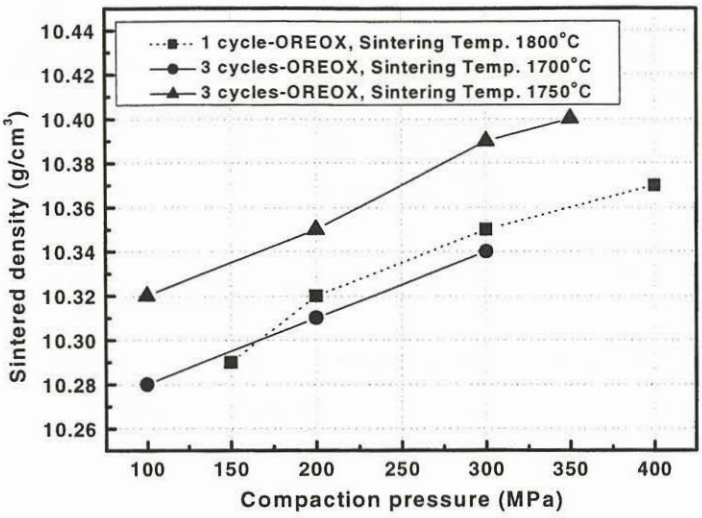

FIGURE 4. EFFECTS OF THE COMPACTING PRESSURE ON SINTERED DENSITIES

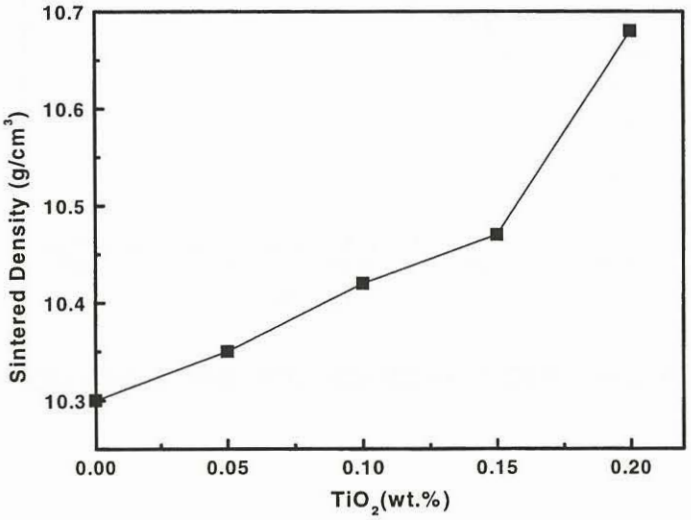

FIGURE 5. THE VARIATION OF SINTERED DENSITY WITH TiO_2 CONCENTRATION

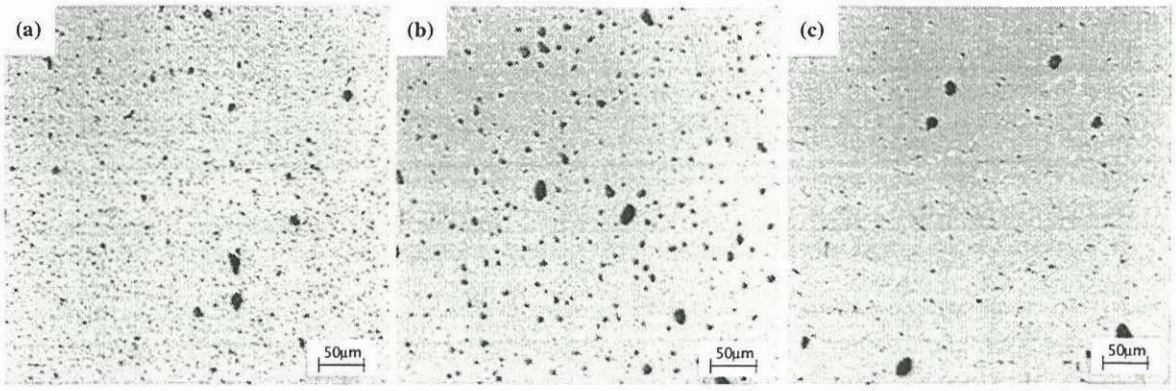

FIGURE 6. MICROSTRUCTURES OF SINTERED PELLETS WITH TiO_2 ADDITIONS; (a) 0 wt.%, (b) 0.15 wt.%, (c) 0.2 wt.%

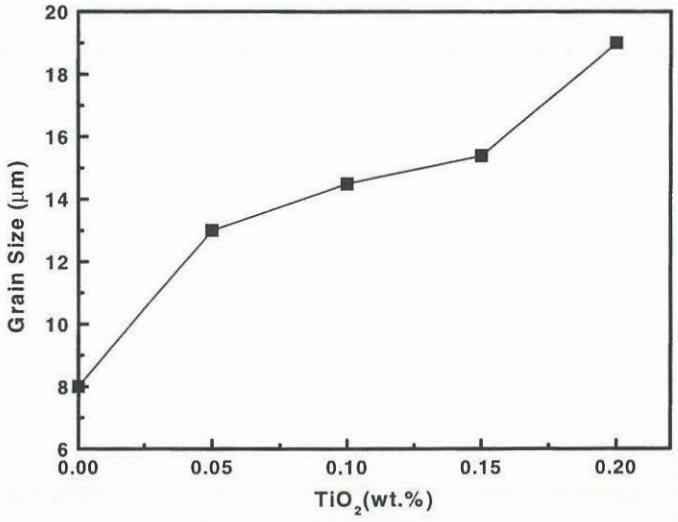

FIGURE 7. THE VARIATION OF GRAIN SIZE WITH TiO_2 CONCENTRATION

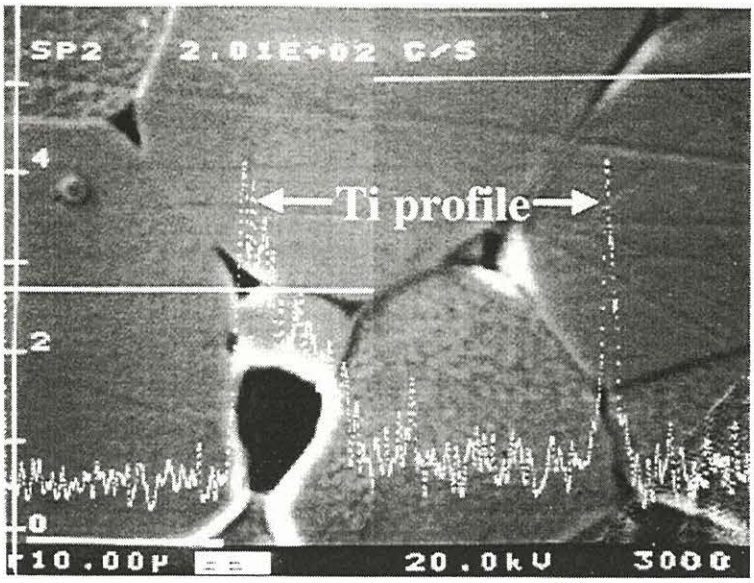

FIGURE 8. SEM MICROGRAPH SHOWING THE SECONDARY PHASE FORMED ON THE GRAIN BOURNADRY