

UO₂–Gd₂O₃ solid solution formation from wet and dry processes

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Gadolinium oxide homogeneously mixed with uranium oxide nuclear fuel is used as burnable poison in modern LWR.

Solid solutions of UO₂ with Gd₂O₃ additions of between 5 and 10 wt% have been prepared according to the following routes: (a) mechanical mixing of both ceramic powders; (b) AUC and ADU coprecipitation. Microstructural analyses have been carried out by optical ceramography and electron microprobe for observation of heterogeneities. Sintered densities as well as O/U ratios of the ceramic pellets have also been measured.

1. Introduction

Brazilian involvement in nuclear fuel research can now be considered to be in a development phase. The Nuclear and Energy Research Institute – IPEN – has been largely interested in acquiring knowledge in various areas related to the fuel cycle. Efforts have always been directed towards keeping pace with new developments and therefore with carrying out research in the fabrication process of burnable poison fuels. This approach involves also adapting known procedures to suit the conditions prevailing in the country in order to build up a domestic capability in this field.

A burnable poison is a material used in reactors to provide a negative moderator coefficient at the beginning of reactor life and help shape core power distributions [1]. It is added to a reactor core in order to burn out during mainly the first operating cycle; consequently the poison is consumed during operation and at the end of life, the burnable poison rod assembly is discharged [2].

The poison material should have a high macroscopic neutron absorption cross section and form daughter products with low absorption cross sections. Then, as the fluence increases, the material burns up and the macroscopic cross sections decrease. From a long list of elements for reactor control (Gd, Sm, Eu, Cd, Dy, B, Ir, Hg, In, Er, Rh, Im, Lu, Hf, Au, Re, Ag, in decreasing order of mean microscopic thermal neutron cross-section), an important number could be eliminated for different rea-

sons, such as very high cost, very high or very low absorption cross-sections for the LWR.

From a nuclear viewpoint, gadolinia is an excellent burnable poison, having a high neutron absorption cross-section coupled to a burn up rate that, if properly designed, can match approximately the ²³⁵U depletion. This poison is universally used in BWRs, but its use in pressurized water reactors is more recent and in general requires higher levels of Gd₂O₃.

Table 1
Impurity analysis of UO₂ and Gd₂O₃ powders

UO ₂		Gd ₂ O ₃	
Element	Concentration (ppm)	Element	Concentration (ppm)
Al	< 14	Sm	< 60
Fe	< 40	Eu	< 30
Cr	< 5	Tb	< 30
Ni	< 6	Yb	< 20
Si	< 30	Cd	< 10
Zn	< 10	B	< 0.1
F	< 10		
Mo	< 2		
Ca	< 2		
B	< 0.1		
BET (m ² /g)	5.5 ± 0.2	BET (m ² /g)	7 ± 3
O/H	2.15 ± 0.02		

Several researchers report on the sintering of UO_2 - Gd_2O_3 mixed oxides, a number of them pointing to difficulties in sintering good fuel pellets with high levels of Gd_2O_3 . Consequently, the purpose of this investigation is to begin a study on this mixed oxide solid solution formation, starting from wet and dry processes.

2. Experimental procedure

The metallurgical development of UO_2 - Gd_2O_3 pellets has taken place following different routes: (a) sol-gel [5], (b) coprecipitation [6-8], (c) dry mixing powder [9-11]. In this paper, $U_{1-x}Gd_xO_2$ solid solutions samples have been prepared following three routes, e.g., coprecipitation from ADU and AUC, and the mechanically dry mixing UO_2 and Gd_2O_3 powders. Therefore, the UO_2 - Gd_2O_3 pellets with Gd_2O_3 content in the 0 to 10 wt% range were fabricated according to the flow diagram shown in fig. 1.

The gadolinium oxide, purity 99.9%, was supplied from

Ventron Alfa Produkte, FRG. The UO_2 powder used in the dry blended powders process was obtained from uranium hexafluoride via the AUC (ammonium uranyl carbonate) conversion [12]. The main impurities of the two powders are listed in table 1.

In the coprecipitation method, the aqueous solutions of uranyl nitrate, $UO_2(NO_3)_2$, and gadolinium nitrate, $Gd(NO_3)_3$, were prepared by dissolving U_3O_8 and Gd_2O_3 powders with 7N nitric acid. The precipitation of AUC and ADU was carried out in a batchmanner.

The uranyl and gadolinium nitrate solutions were thoroughly blended together in varying proportions up to 10 wt% Gd_2O_3 . An uranyl nitrate solution containing 400 g U/l mixed with Gd-nitrate solution was slowly added to freshly prepared 10% ammonium carbonate solutions to produce AUGdC precipitates. Stirring was applied with a glass rod during the addition of the solution. The precipitation temperature was 60°C and the final pH value close to 8.3. The AUGdC slurry was filtered in vacuum and washed with ethanol to improve the drying rate.

A variety of ADU precipitates with different Gd_2O_3 quantities was prepared by adding NH_4OH to

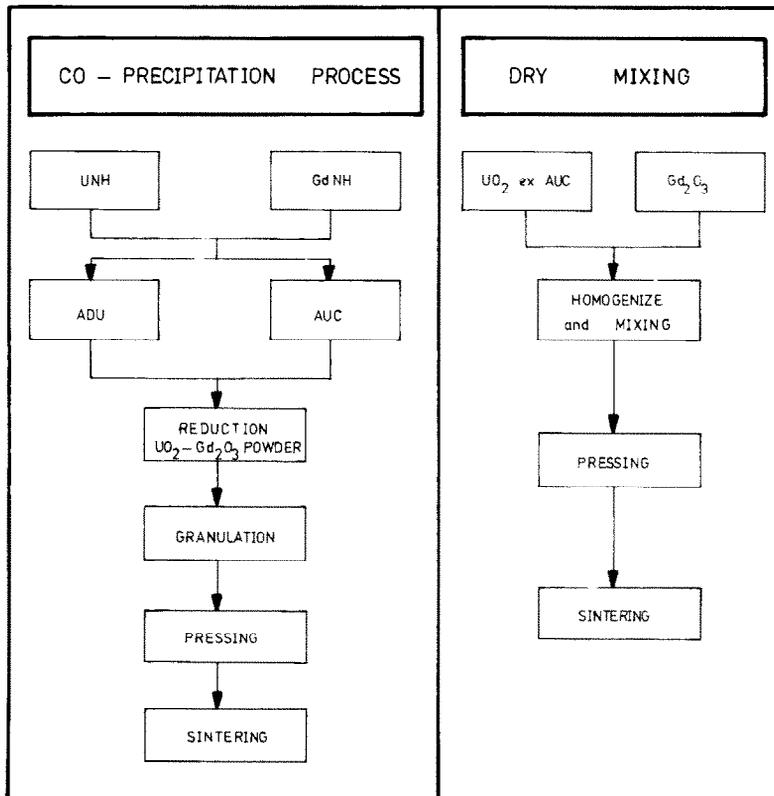


Fig. 1. Flow diagram of wet and dry process (UNH and GdNH: Uranyl and gadolinium nitrate).

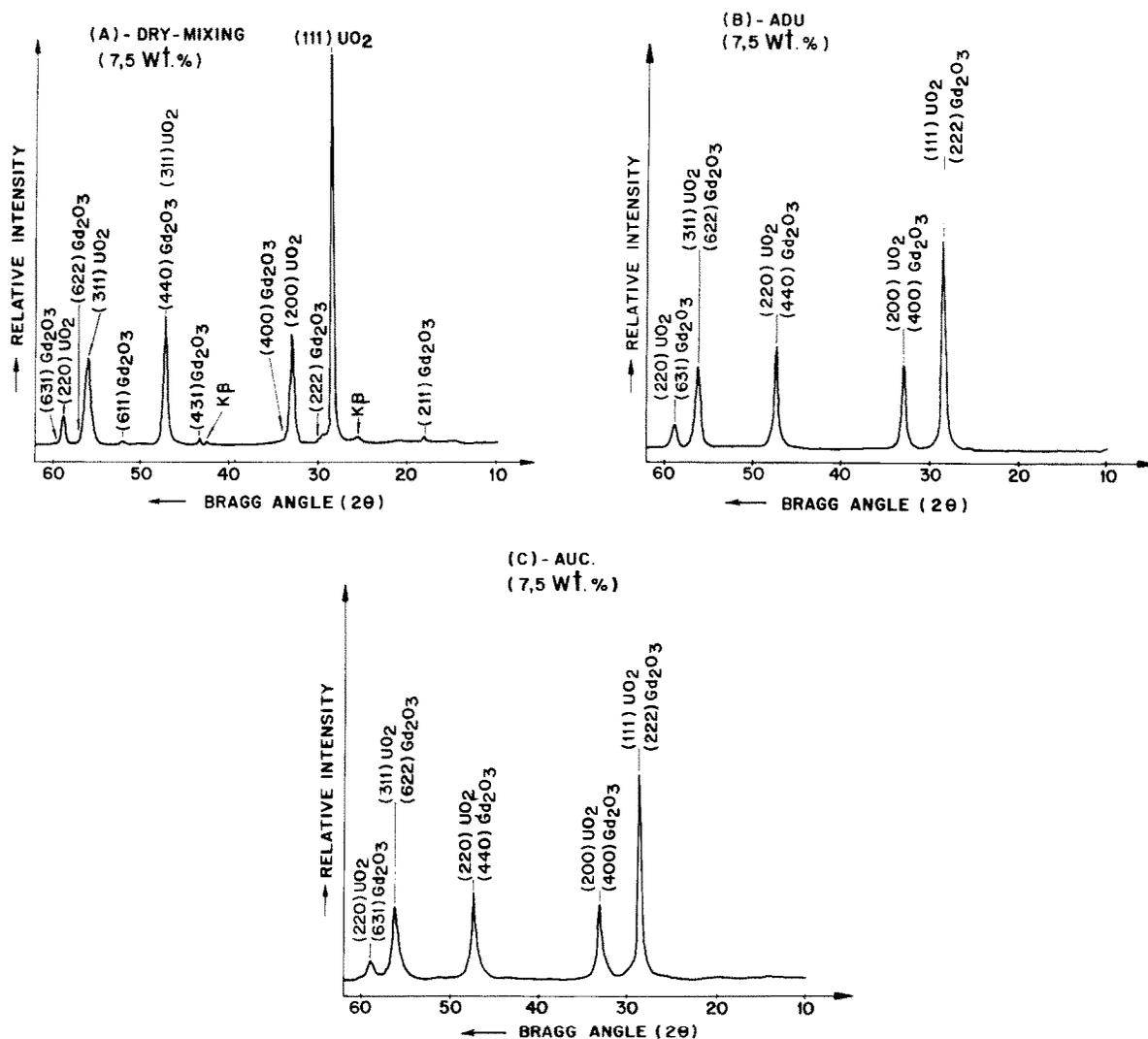


Fig. 2. X-ray diffractograms of UO_2 powder containing 7.5 wt% Gd_2O_3 ; (A) dry mixing method, (B) ADU method, (C) AUC method.

$UO_2(NO_3)_2-Gd(NO_3)_3$ solution at $60^\circ C$ and pH 9. Vacuum filtration was performed by using a funnel with perforated plate. After filtration, the wet precipitates were dried in an oven at $80^\circ C$ during 24 h.

The dried precipitates contained in a stainless steel tray were reduced to uranium-gadolinium oxide in a tubular furnace at $650^\circ C$ in hydrogen atmosphere. The AUC powder from UF_6 was also reduced to UO_2 in the tubular furnace at $650^\circ C$ and water vapor/hydrogen atmosphere [13]. This UO_2 powder was used in the mechanical mixing method. Gd_2O_3 and UO_2 powders were dry blended in a Turbula T2C shaker mixer.

Fig. 2 shows the X-ray diffractograms of UO_2 powders containing 7.5 wt% Gd_2O_3 , obtained by the different

methods. In the X-ray diffraction pattern (A) of the sample prepared by the dry blended method, the Gd_2O_3 bcc phase is detected. In addition, it can be shown that the (B) and (C) X-ray diffraction peaks are broader than the (A) lines. A considerable fraction of solid solution phase with fluorite structure exist in the powder samples prepared by co-precipitation methods.

The particle size distributions for UO_2 , Gd_2O_3 and $UO_2-7.5$ wt% Gd_2O_3 are shown in fig. 3. The UO_2 powder containing 7.5 wt% Gd_2O_3 prepared by ADU process consists of very fine particles with an average size of about $2.5 \mu m$.

The different mixed oxide powders were pressed into pellets in the $2.5-4.0$ tf/cm^2 range and sintered in a hy-

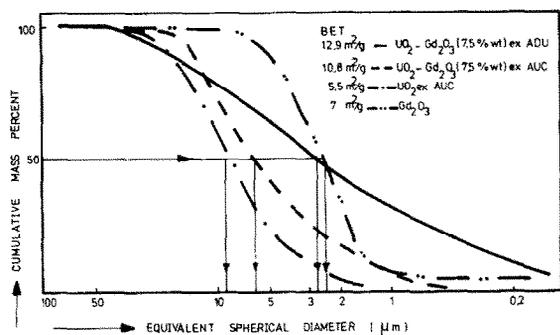


Fig. 3. The particle size distributions of UO_2 , Gd_2O_3 and UO_2 -7.5 wt% Gd_2O_3 powders.

drogen atmosphere at $1650^\circ C \pm 20^\circ C$ for 3 and 6 h.

The pressing of green pellets was carried out in a hydraulic press without any additive, but the walls of the die were lubricated with a thin oil film. Fig. 4A shows the influence of increasing percentages of Gd_2O_3 on the sintered density of pellets obtained by mechanically dry-mixing powders. In this route, the presence of gadolinium strongly inhibits the sinterability of the UO_2 , as already reported by Assmann [9], Manzel [10], Une [14] and Dörr [15]. Dörr [15] mentioned the existence of a diffusion barrier around the Gd_2O_3 particles, and consequently the interdiffusion process decreases the sintering rate and shifts the densification to higher temperatures. For the ADU route (fig. 4B), the sintered density of the pellets was reduced after low Gd_2O_3 additions, although, irrespective of the addition content, higher sintered densities have been achieved. A maximum value between 6 and 8 wt% Gd_2O_3 has been observed. A possible explanation for this densification behaviour is that a low Gd_2O_3 content produces lattice defects widely separated with no significant impact of the additions. At a certain concentration level, about 3 wt% Gd_2O_3 , oxygen vacancies and U^{+5} ions are both formed, resulting in enhanced sinterability. Consequently, in the process of formation, a solid solution may be produced according to the reaction:

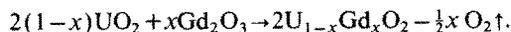


Fig. 4C gives the sintered density of the $(U,Gd)O_2$ pellets prepared by AUC coprecipitation. These data indicate that the densification mechanism resembles that of ADU coprecipitation (fig. 4B). These results are in good agreement with those reported by Ho [16] and Littlechild [17].

The coprecipitation method is largely used to provide a $(U,Gd)O_2$ homogeneity better than the one obtained by mechanical blending. This trend has also been observed in our specimens. Fig. 5 shows a stain-etched ceramograph of the UO_2 -7.5 wt% Gd_2O_3 pellets prepared by coprecipitation and by mechanical blending. While the samples by the latter method had small amounts of is-

lands with high UO_2 or Gd_2O_3 concentrations, they are not observed in pellets obtained by the former method.

The X-ray diffractograms show that all samples are single-phased with fluorite structure, with no visible indication of free gadolinia. On the other hand, electron probe microanalyses indicate some inhomogeneity in pellets obtained by dry blending, with some up to 20 diameter low gadolinia content areas. In fig. 6 diagrams taken with an electron microprobe in $(U,Gd)O_2$ pellets sintered at

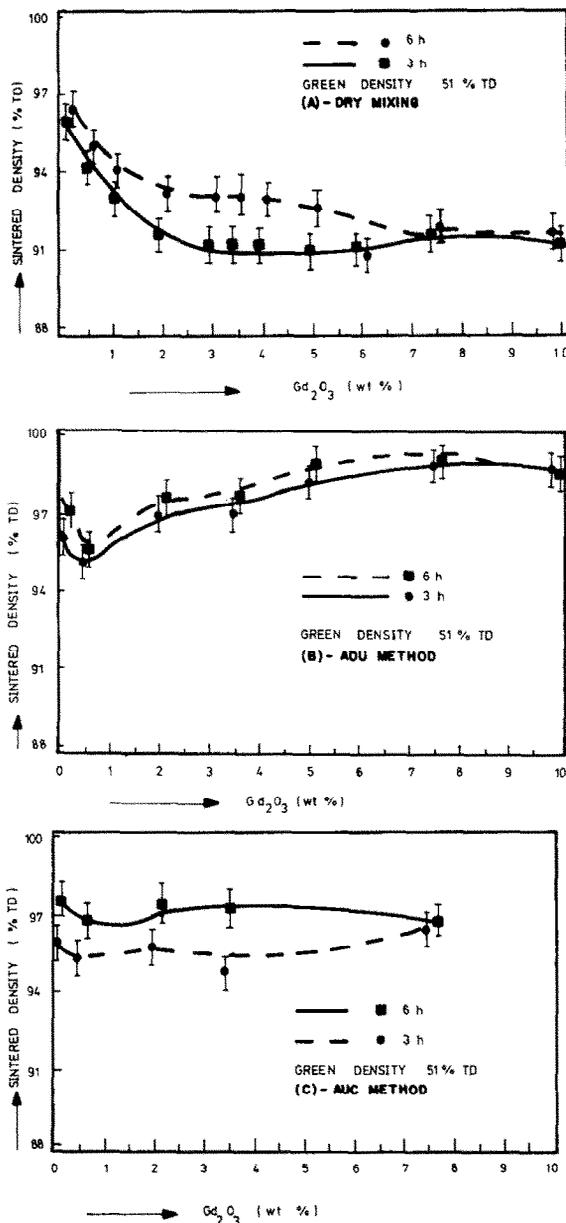


Fig. 4. Effect of gadolinium content on sintered density of fuel pellets prepared by (A) dry mixing, (B) ADU method, (C) AUC method.

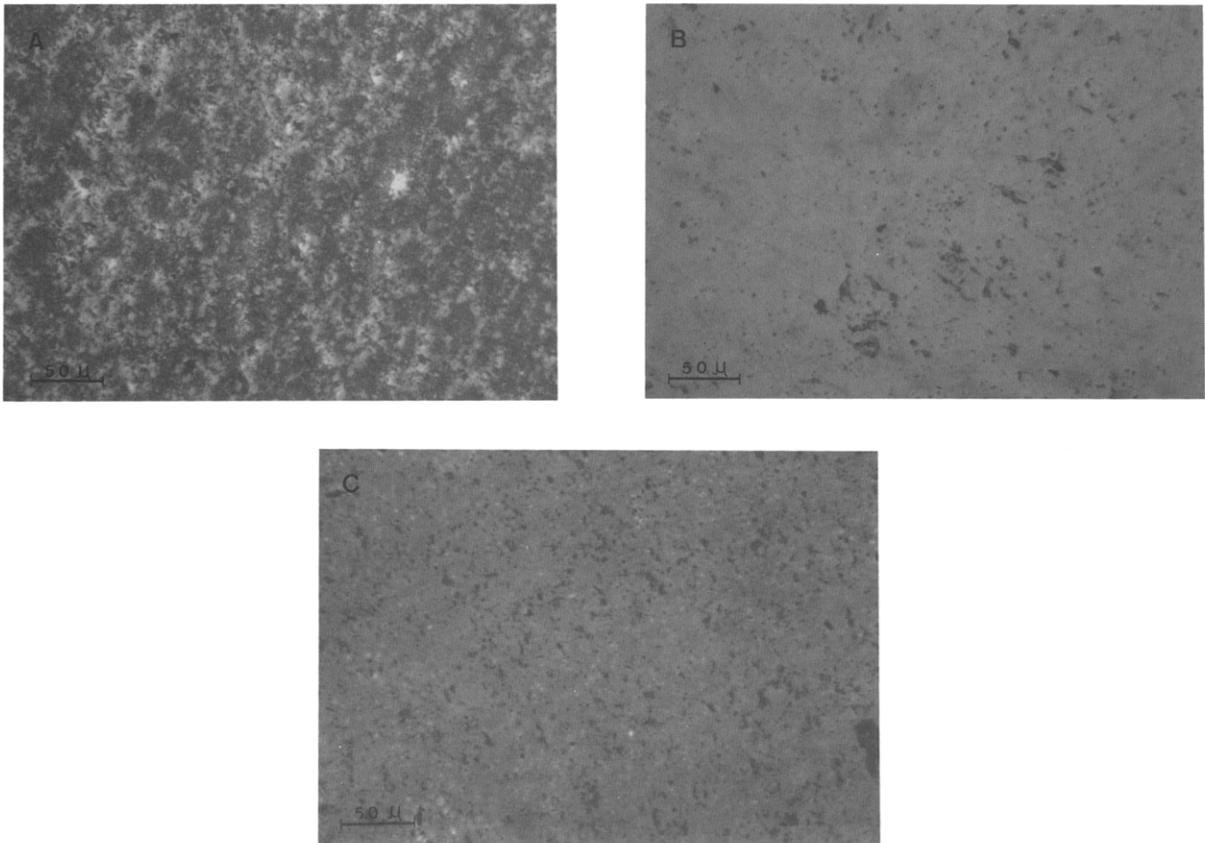


Fig. 5. Stain-etched ceramograph of the UO_2 -7.5 wt% Gd_2O_3 ; (A) dry mixing, (B) ADU process, (C) AUC process.

$1650^\circ C \pm 20^\circ C$ for 3 h in dry hydrogen atmosphere are shown. The samples prepared by ADU-AUC coprecipitation (figs. 6B and 6C, respectively) show continuous solid solutions with an average concentration slightly less than the nominal compositions, e.g. 7.5 wt% Gd_2O_3 . On the contrary, the sample obtained by mechanical mixture still contains particles with high Gd_2O_3 concentration up to 25 wt%. As seen from fig. 6A, mainly two mixed oxide phases with about 15% and 7% of mass fraction Gd_2O_3 seem to be detected.

Microprobe analyses in pellets prepared from mechanical blended uranium and gadolinium oxides show that the formation of the solid solution is not complete after sintering for 3 h at $1650^\circ C$. Pellets sintered for 6 h show an homogeneous distribution of Gd in the fuel, as observed in fig. 7.

The oxygen/metal ratio of $(U,Gd)O_2$ pellets has been

determined by the gravimetric method [18]. As has also been observed [16,17], the addition of oxygen deficient Gd_2O_3 causes a reduction in the O/M ratio.

As shown on the micrograph (fig. 8), a slightly homogeneous pore structure (fig. 8A) of a pellet obtained by mechanical mixture can be compared with a typical granule structure (figs. 8B and 8C) of pellets obtained by ADU-AUC coprecipitation, respectively. Due to the gadolinium effect, the fuel grain size cannot be interpreted only as a function of sintering time and temperature. It has been observed that the grain size is largely reduced by even small Gd_2O_3 additions [17]. This effect has also been noticed with other rare earth oxides such as Eu_2O_3 and Dy_2O_3 [20]. This trend is observed in our experiments. The phenomenon is probably due partly to the lower solid solution surface and grain boundary energies [17].

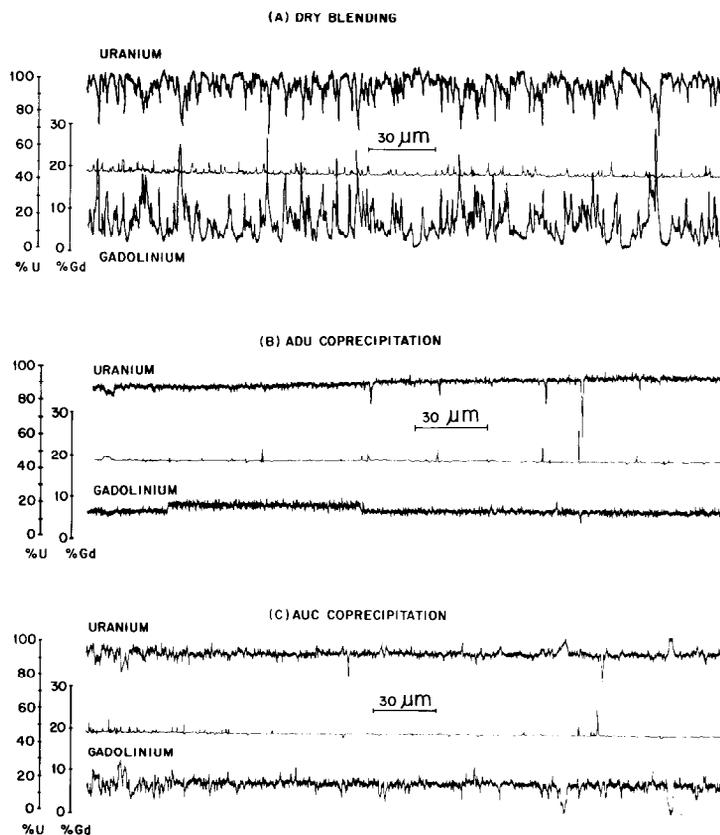


Fig. 6. Electron microprobe in UO_2 -7.5 wt% Gd_2O_3 pellets sintered at $1750^\circ C$ for 3 h; (A) mechanical dry blending, (B) ADU coprecipitation, (C) AUC coprecipitation.

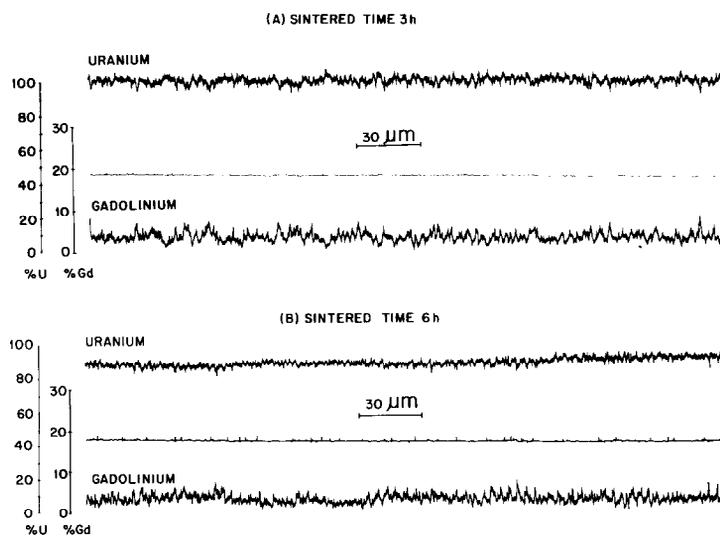


Fig. 7. Electron microprobe diagram of a UO_2 -3.5 wt% Gd_2O_3 pellet prepared by ADU coprecipitation and sintered at $1650^\circ C$ under H_2 ; (A) 3 h, (B) 6 h.

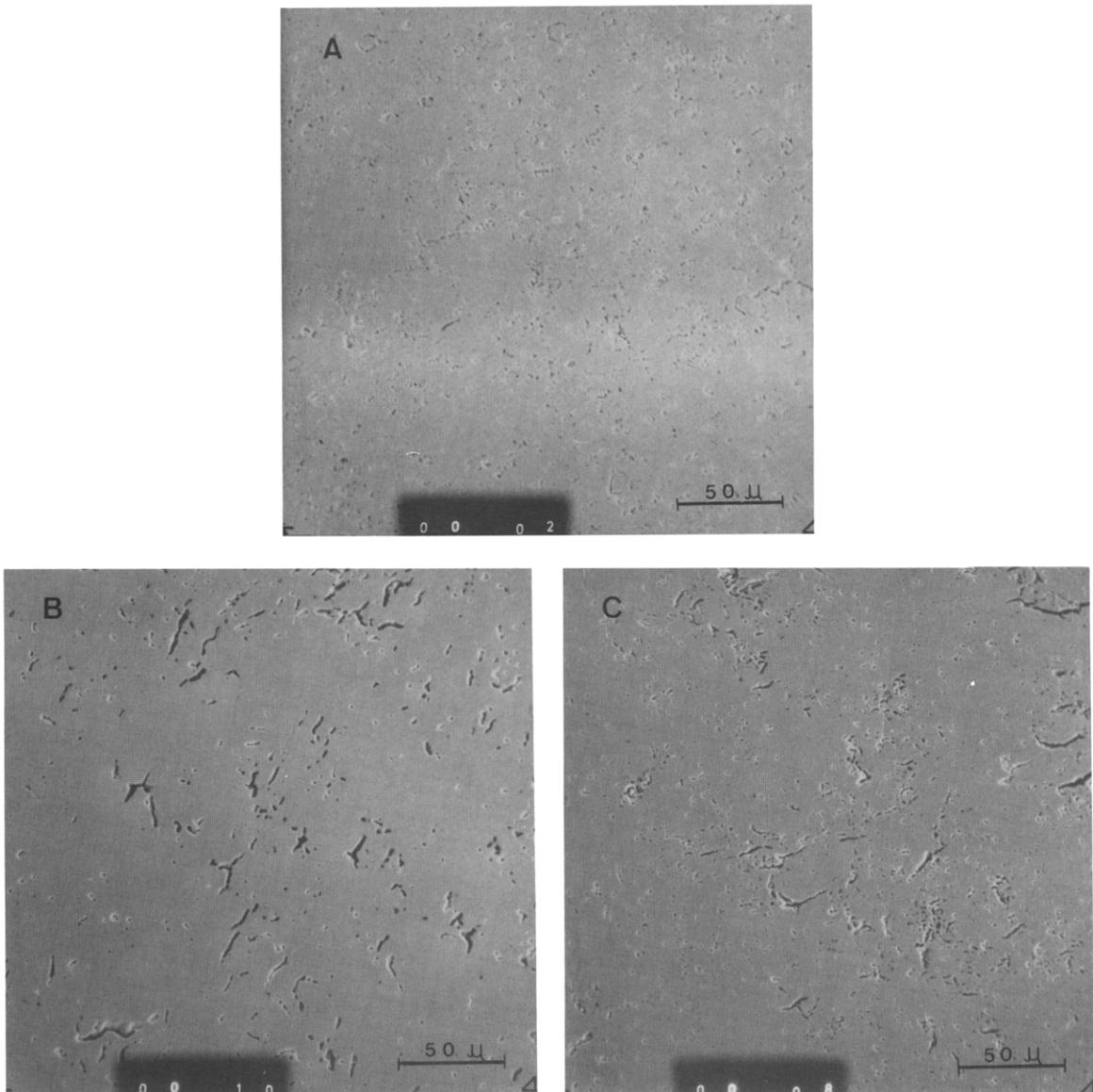


Fig. 8. The pore structure of UO_2 -3.5 wt% Gd_2O_3 pellets; (A) mechanical dry mixture, (B) ADU method, (C) AUC method.

3. Conclusions

Extensive studies were carried out to establish a flow sheet for production of UO_2 pellets containing up to 10 wt% Gd_2O_3 . The results indicate that the sinterability of the $(U,Gd)O_2$ pellets obtained from dry blended powders is markedly different from that of pellets prepared by AUC-ADU coprecipitation. Higher sintered densities

have been achieved in samples prepared following the coprecipitation route. The typical mechanical mixture of powders always yielded pellets with lower densities.

The X-ray diffraction patterns of the powder samples from coprecipitated UO_2 - Gd_2O_3 powders show no gadolinium oxide peaks, indicating that the gadolinium is incorporated into the UO_2 lattice in the early stages of processing. This is advantageous in sintering, since single

phase material behaviour always gives better results.

Moreover we observed that the fuel grain size is largely reduced by even small Gd₂O₃ additions.

Further experiments are still necessary to fully understand the sintering behaviour of UO₂-Gd₂O₃ pellets.

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