



Escola Politécnica
Universidade de São Paulo



PMT 3531 - PROCESSAMENTO DE COMBUSTÍVEIS NUCLEARES II

HUMBERTO GRACHER RIELLA

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- Estudo do Processamento do Combustível UO_2 -7% Gd_2O_3 Via Mistura Mecânica com Reutilização dos Rejeitos do Processo de Fabricação e Aditivos de Densificação

LITERATURA:

Sintering Behavior of the UO_2 - Gd_2O_3 Nuclear Fuel
Michelangelo Durazzo and Humberto Gracher Riella
Lambert Academic Publishing ISBN 978-3-8454-0784-5/2014 page 179

Otimização do Combustível

- aumento do tempo de queima -- aumento do intervalo de recarga
- precisa de um excesso de reatividade no início do ciclo de queima
precisa aumentar o enriquecimento
excesso de reatividade deve ser controlado

Controle da Reatividade nos Reatores nucleares

BARRA DE CONTROLE: é o sistema mais comum

- barras móveis contendo material absorvedor
- movimentação elétrica, pneumática ou hidráulica
- controle fino do reator
- controla a reatividade de curta duração

BARRA DE SEGURANÇA:

- reatividade negativa do reator
- desligamento em condições normais ou em caso de acidente
- paralelas ao eixo vertical do reator
- características iguais às da barras de controle

CONTROLE FIXO DE LONGO PRAZO:

- forma fixa no núcleo do reator
- ajustar as variações de reatividade causadas por processos com ciclo de tempo longo (consumo do combustível e o envenenamento pela formação de produtos de fissão com alta seção de choque e absorção de nêutrons). Providencia a compensação de variação de reatividade de longa duração, que ocorre ao longo de toda vida útil do núcleo do reator.

VENENO QUEIMÁVEL: absorver nêutrons gerando um isótopo de baixa seção de choque de absorção de nêutrons

tipos:- heterogêneo ou discreto-absorvedor e diluente (past. $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$)

- homogêneo ou integrado (past. $(\text{U-Gd})\text{O}_2$)

vantagens:- aumento da carga e do enriquecimento do combustível

- quantidade suficiente para obter reatividade inicial = reatividade final
- colocado em posições estratégicas diminui os fatores de pico

TIPOS VENENOS QUEIMÁVEIS INTEGRADOS DISPONÍVEIS

Tabela 1 – Comparação entre tipos de venenos queimáveis integrados disponíveis (laea-Teodoc-844, 1995)

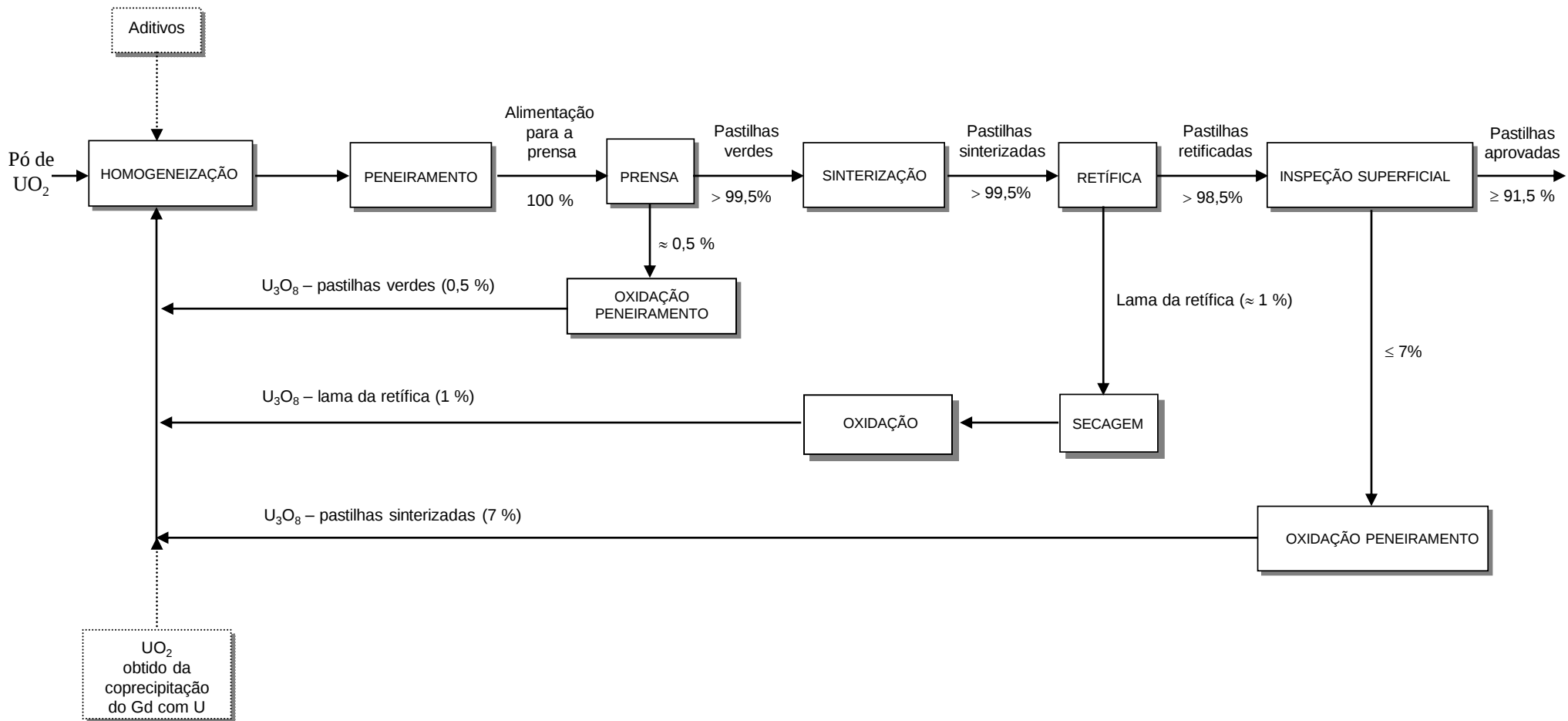
<i>Tipo</i>	<i>UO₂-Gd₂O₃</i>	<i>ZrB₂</i>	<i>UO₂-Er₂O₃</i>
Fabricantes	(a)	Westinghouse (USA)	Combustion Eng. Co. (USA)
Concentração	6-10% em peso	—	1-2,5% em peso
Diminuição na condutividade térmica	significativa	negligenciável	pequena
Redução na temperatura de fusão	significativa	negligenciável	pequena
Proporção de varetas por elemento combustível	3–6 %	30–40 %	20–30 %
Redução da massa de ²³⁵ U no elemento combustível	pequena	negligenciável	pequena
Velocidade de queima	alta	alta	média
Reatividade residual no final do ciclo de queima	pequena	negligenciável	significativa
Distribuição de potência na vareta de veneno queimável	boa	satisfatória (b)	boa
Pico de potência localizado	significativo	pequeno	pequeno
Controle do coeficiente de temperatura do moderador	bom	satisfatório	ótimo
Facilidade de fabricação	pequena variação na linha padrão	grande equipamento adicional	pequena variação na linha padrão
Reprocessabilidade do combustível como veneno queimável	boa	questionável	boa

(a) Franco-Belge de Fabrication du Combustible (França e Bélgica), Siemens AG (Alemanha), Fabricazione Nucleari (Itália), Japan Nuclear Fuel (Japão), Mitsubishi Nuclear Fuel & Nuclear Fuel Industries (Japão), Korean Nuclear Fuel Company (Coreia), Empresa Nacional del Uranio AS (Espanha), ASEA-ATOM (Suécia), British Nuclear Fuels BNFL (Inglaterra), TENEX-Novosibirsk-Ulbinskiy (Rússia/Kazaxistão), Babcock&Wilcox Fuel (USA), General Electric (USA) e Siemens Power (USA).

(b) Devido à rápida queima.

VENENO QUEIMÁVEL DE $\text{UO}_2\text{-Gd}_2\text{O}_3$:

O excesso de reatividade nos combustíveis novos de reatores BWR foi a causa do desenvolvimento deste tipo de controle, pois devido a concepção do projeto não se poderia usar boro solúvel e varetas de veneno queimável discreto. O uso de $\text{UO}_2\text{-Gd}_2\text{O}_3$ tornou-se rotina em todos os reatores BWR após a decisão da G. E. adota-lo no reator Dresden-2 no final dos anos 60. Com a crescente preocupação de otimizar o combustível nos PWR, a utilização deste tipo de combustível nos PWR passou a ser considerada. Com a experiência acumulada nos BWR e como os fabricantes de combustível para os BWR e PWR são os mesmos, os fabricantes colocaram o $\text{UO}_2\text{-Gd}_2\text{O}_3$ como opção natural para reatores PWR



Processo de obtenção de pastilhas de UO_2

OBJETIVO GERAL

Estudar a densificação de pastilhas de $\text{UO}_2\text{-Gd}_2\text{O}_3$ contendo 7 % Gd_2O_3 . Este teor de 7 % de Gd_2O_3 está fundamentado para a concepção do tipo de reator PWR - Angra 2

OBJETIVOS ESPECÍFICOS

- estudar a influência do aditivo Al(OH)_3 na densificação das pastilhas de $\text{UO}_2\text{-7\%Gd}_2\text{O}_3$
- _ estudar a influência do rejeito adicionado na forma de U_3O_8 na densificação das pastilhas de $\text{UO}_2\text{-7\%Gd}_2\text{O}_3$
- _ avaliar a evolução microestural das pastilhas em termos de poros e grãos
- relacionar o crescimento e/ou a diminuição dos grãos e dos poros com os aditivos U_3O_8 e Al(OH)_3
- modelo termodinâmico relacionado com os aditivos e a taxa de densificação

METODOLOGIA

Por meio de estudos preliminares foram estabelecidos os limites inferiores e superiores dos componentes da mistura, bem como a pressão de compactação, considerando as diferentes funções que material exerce no processamento do combustível.

Reciclo U_3O_8 obtido de pastilhas sinterizada

U_3O_8 obtido de pastilhas verdes

UO_2 coprecipitado (Gd coprecipitado com U)

% $\text{Al}(\text{OH})_3$	0,0 % Reciclo	3,0 % Reciclo	7,0 % Reciclo	10,0 % Reciclo
0,10	X	X	X	X
0,15	X	X	X	X
0,20	X	X	X	X
0,25	X	X	X	X
0,30	X	X	X	X

PRINCIPAIS CONDIÇÕES DE PROCESSO

- temperatura de sinterização: 1750 °C
- tempo de sinterização: 4 horas
- atmosfera fixa e redutora de hidrogênio
- teor de Gd_2O_3 nas pastilhas: 7 %
- pressão de compactação: 4,0 tf/cm²

STUDIES ON THE SINTERING BEHAVIOUR OF THE $\text{UO}_2\text{-Gd}_2\text{O}_3$ NUCLEAR FUEL



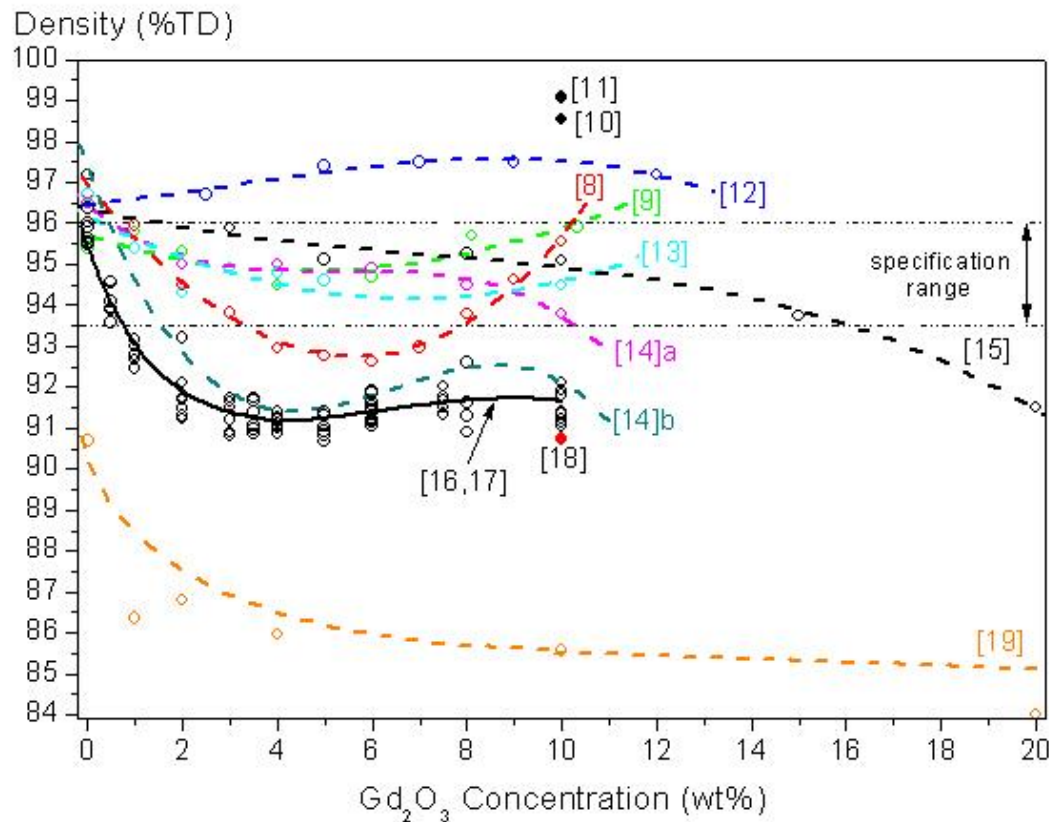
Michelangelo Durazzo
Humberto Gracher Riella

The incorporation of gadolinium directly into nuclear power reactor fuel is important from the point of reactivity compensation and adjustment of power distribution enabling thus longer fuel cycles and optimized fuel utilization.

The incorporation of Gd_2O_3 powder directly into the UO_2 powder by dry mechanical blending is the most attractive process because of its simplicity.

Processing by this method leads to difficulties while obtaining sintered pellets with the minimum required density. This is due to the deleterious effect of the Gd_2O_3 on the traditional UO_2 sintering behaviour.

The purpose of this work is to investigate the possible causes for explaining the bad sintering behaviour of the UO_2 - Gd_2O_3 fuel prepared by the dry mechanical blending method.

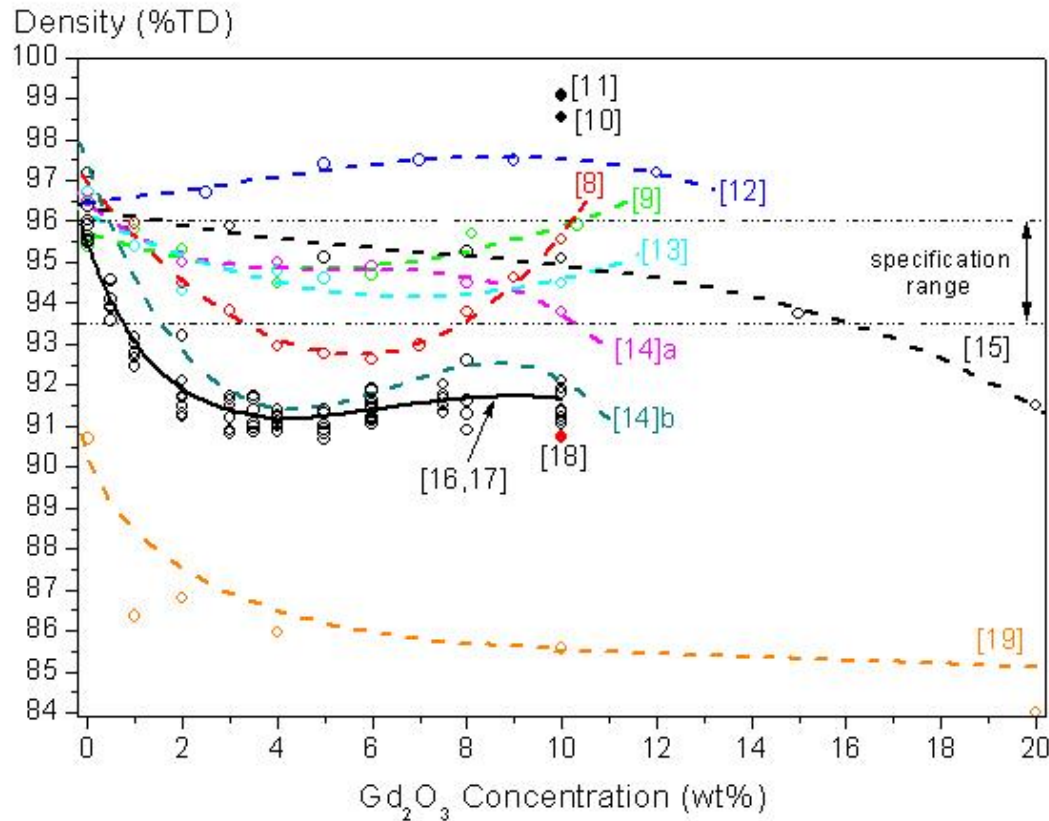


Ref.	Sintering Cycle	UO ₂ BET Surface (m ² /g)	Sintering Atmosphere	Method for Mixed Powder Preparation
[9]	1750°C/4h	n.i.	Ar/8% H_2 / H_2O	co-precip.
[10]	1650°C/4h	n.i.	N_2 /8% H_2 / H_2O	co-precip.
[11]	1750°C/4h	n.i.	25% N_2 /75% H_2	co-milling
[12]	1750°C/6h	3.50	H_2 / H_2O	co-milling
[13]	1620°C/3h	1.60	pure H_2	co-milling
[14]a	1700°C/2h	4.37	pure H_2	co-milling
[14]b	1700°C/2h	6.65	pure H_2	co-milling
[8]	1750°C/2h	n.i.	pure H_2	dry blend
[15]	1700°C/2h	3.10	pure H_2	dry blend
[16,17]	1650°C/3h	5.6	pure H_2	dry blend
[18]	1680°C/4h	5.0	pure H_2	dry blend
[19]	1650°C/4h	n.i.	N_2 /6% H_2	dry blend

n.i. – not informed

UO₂-Gd₂O₃ Sintered Densities

(from literature)



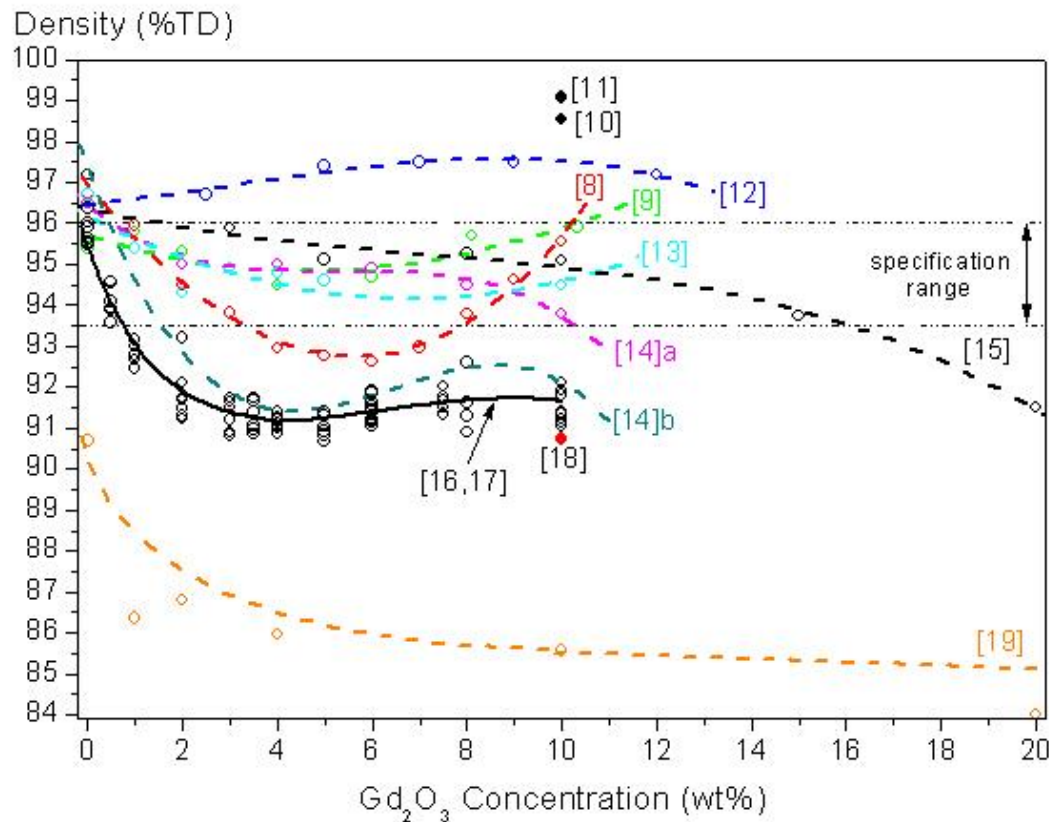
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we can see a wide range of sintered densities

varying from 85%TD to 98% TD

Why?

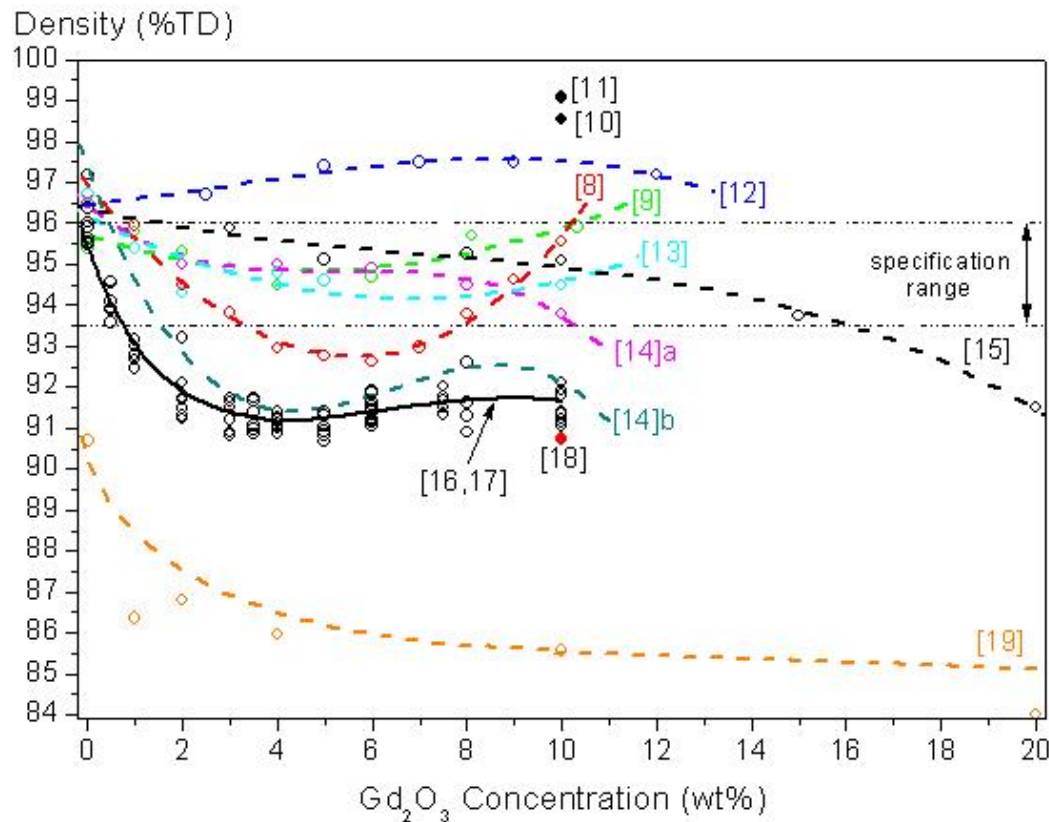


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We can observe 3 groups:

- Coprecipitation ➡ very good sintering densities
- Comilling ➡ good sintering densities (most)
- Mechanical Mixture ➡ bad sintering densities (most)

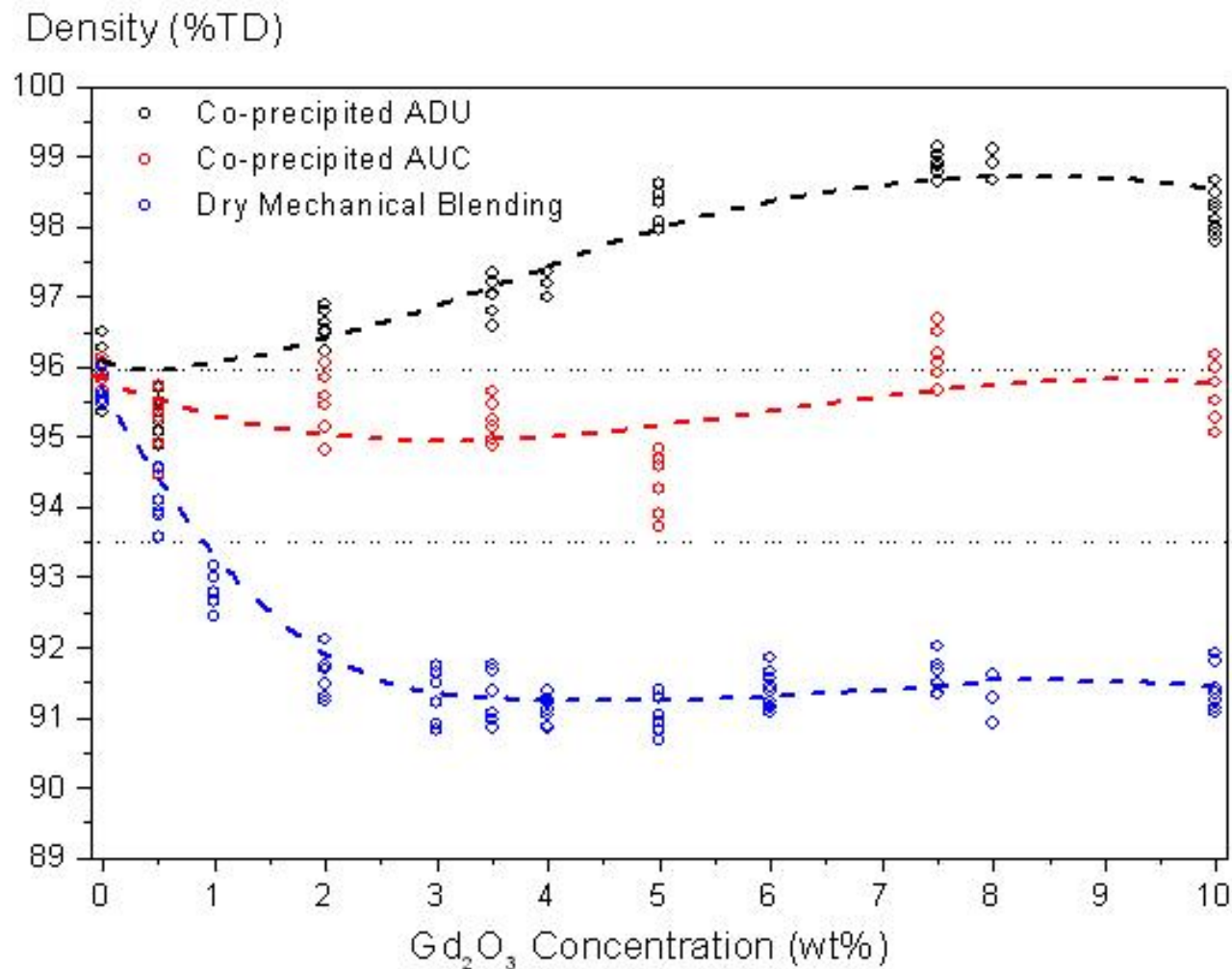


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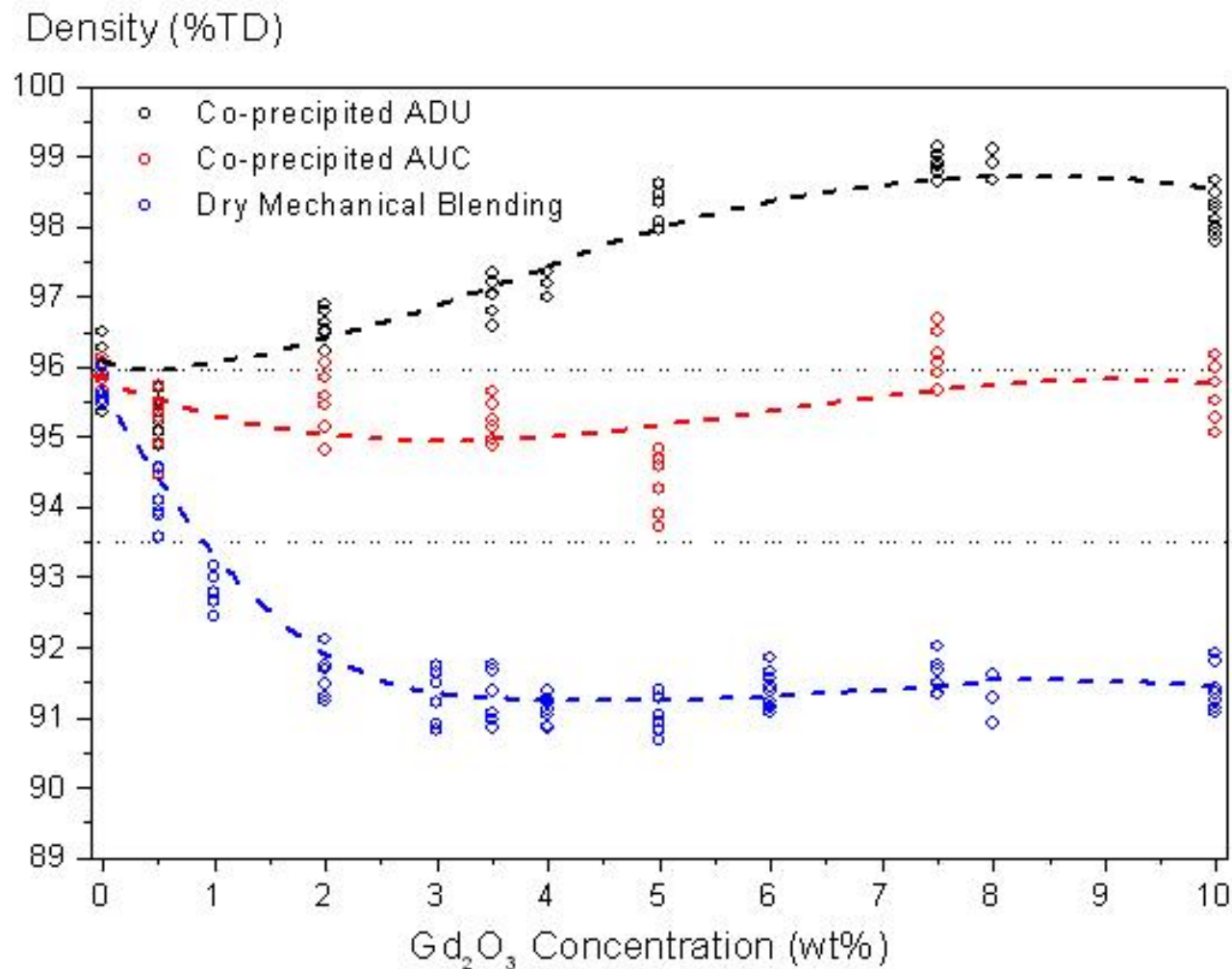
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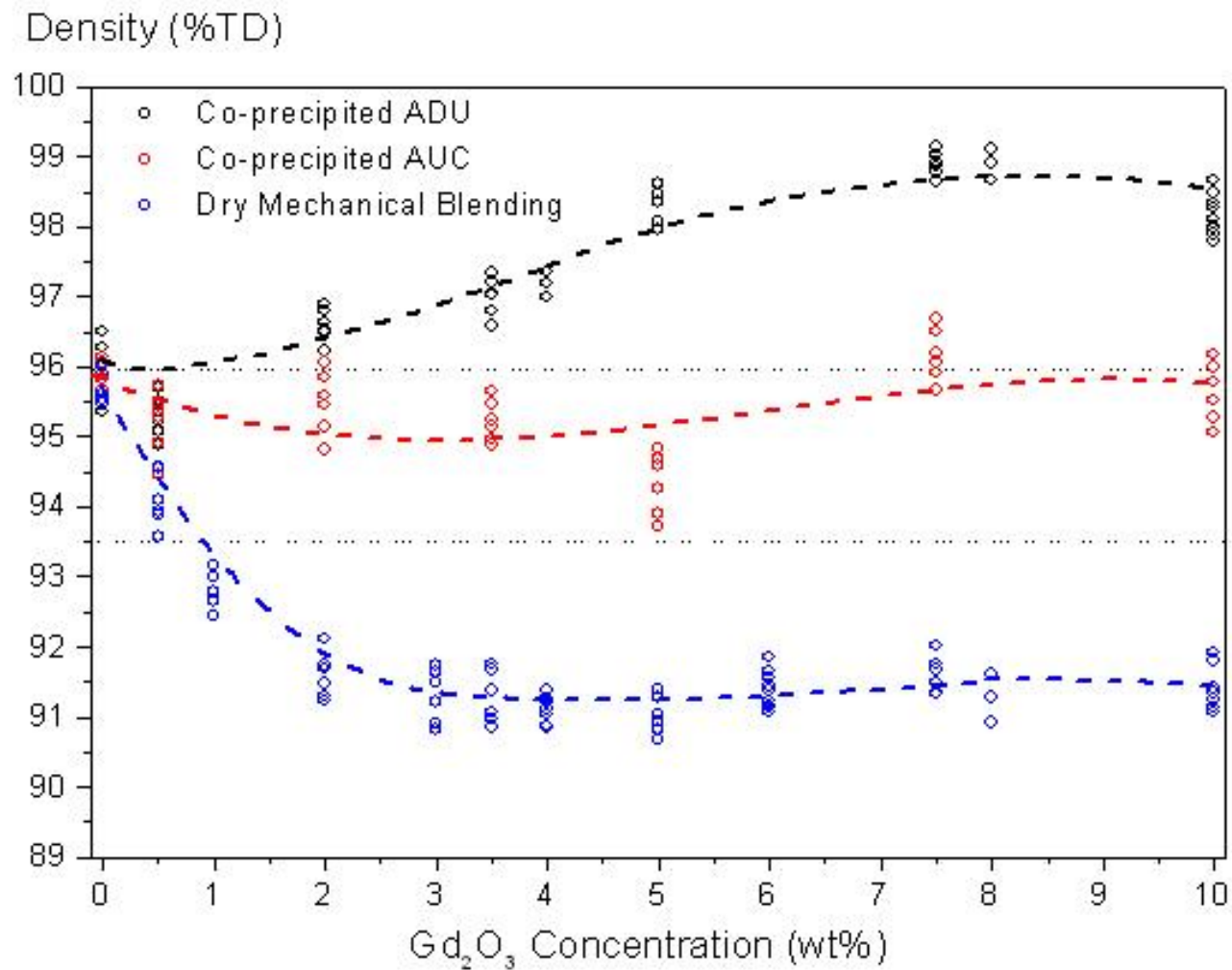


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Coprecipitation ➡ very good sintering densities

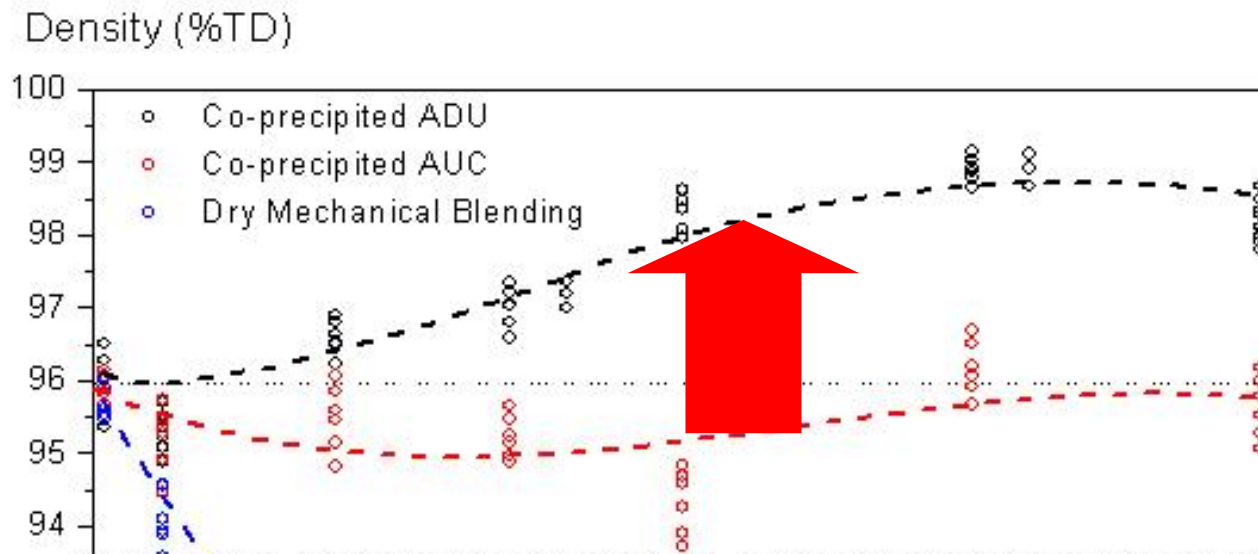
Comilling ➡ good sintering densities (most)

Mechanical Mixture ➡ bad sintering densities (most)



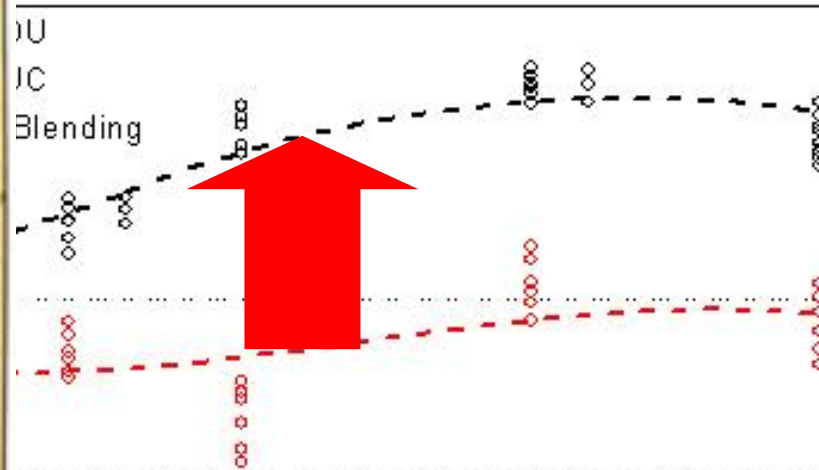
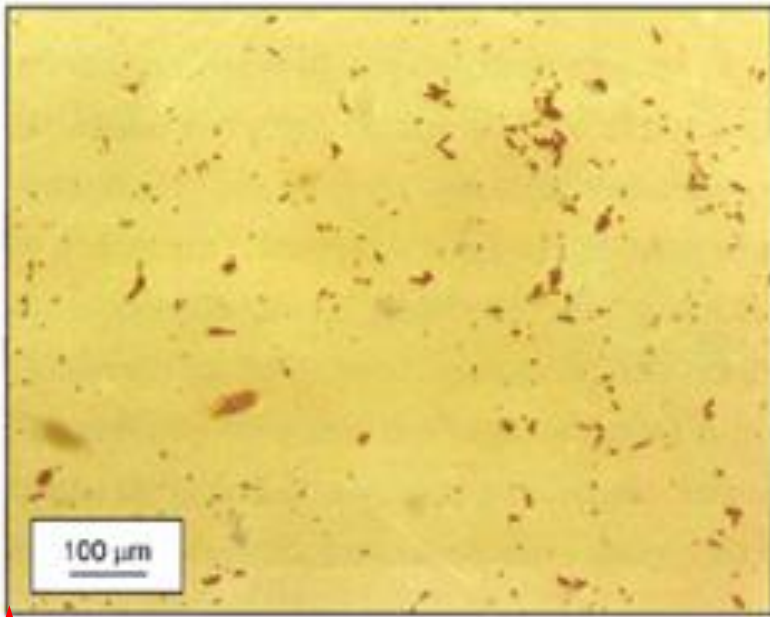
What is different ?

The level of homogeneity in the Gd_2O_3 distribution into the fuel .



ADU Coprecipitation  ***Atomic Level***

Most of the Gd_2O_3 powder originally added to the UO_2 powder is present in the mixed powder as solid solution. After reduction, most of the gadolinium has already been incorporated in the UO_2 FCC lattice (fluorite type). The Gd_2O_3 is homogenized in an atomic level.

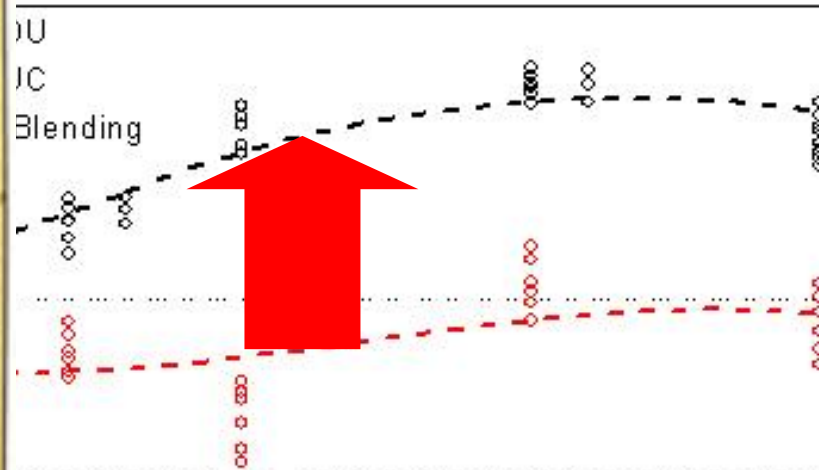
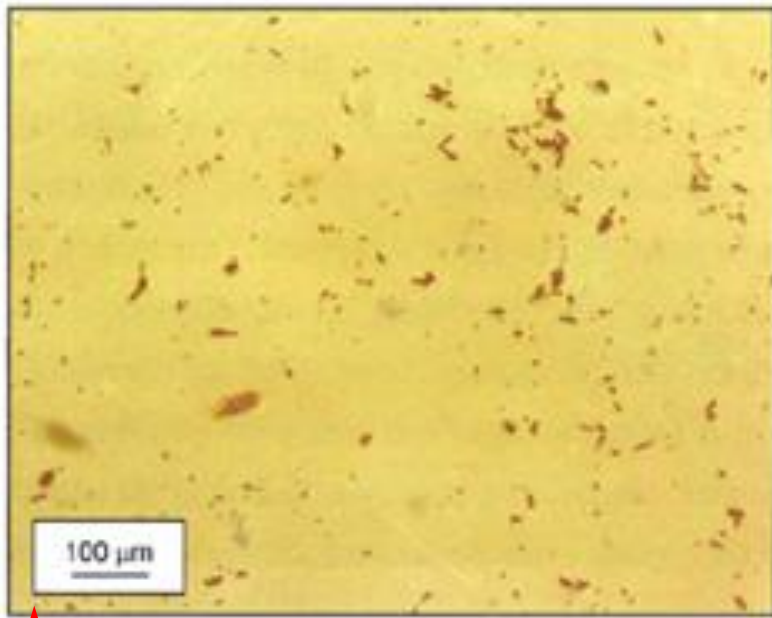


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Light yellow – solid solution
Brown – Gd rich (U,Gd) phases
Blue – free UO_2

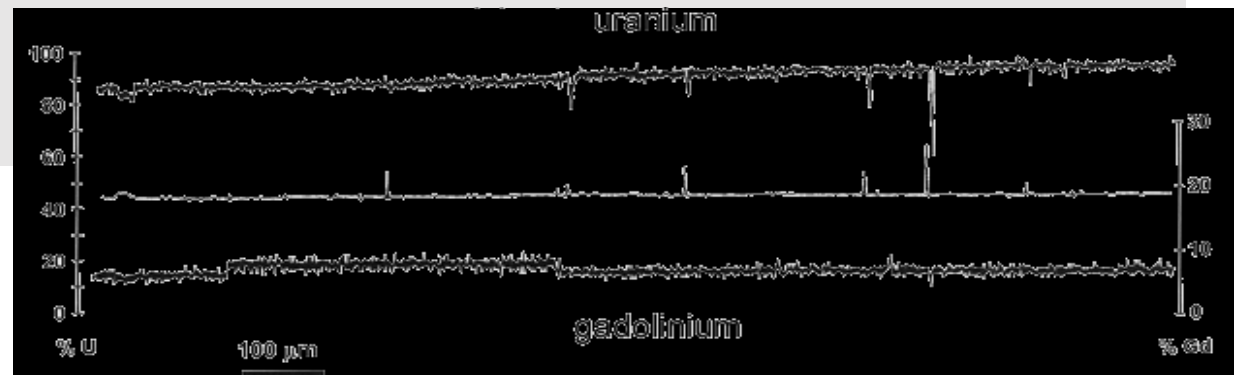
We have a very good homogeneity, as we can see in the micrograph and microprobe analysis

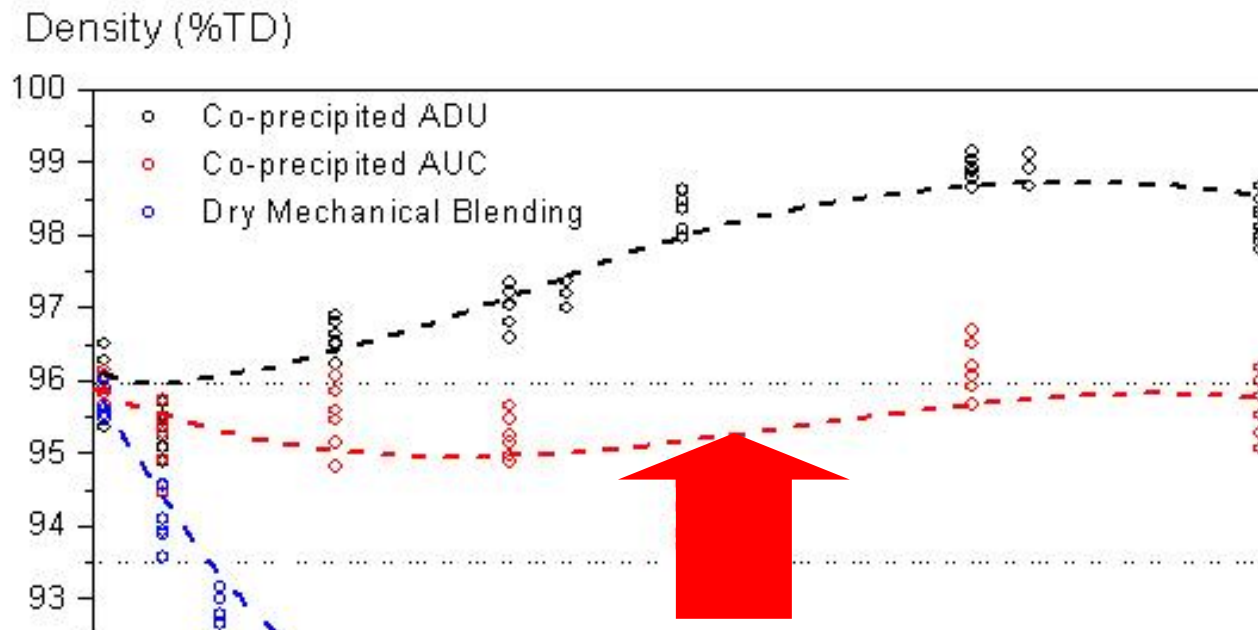


ADU Coprecipitation → Atomic Level

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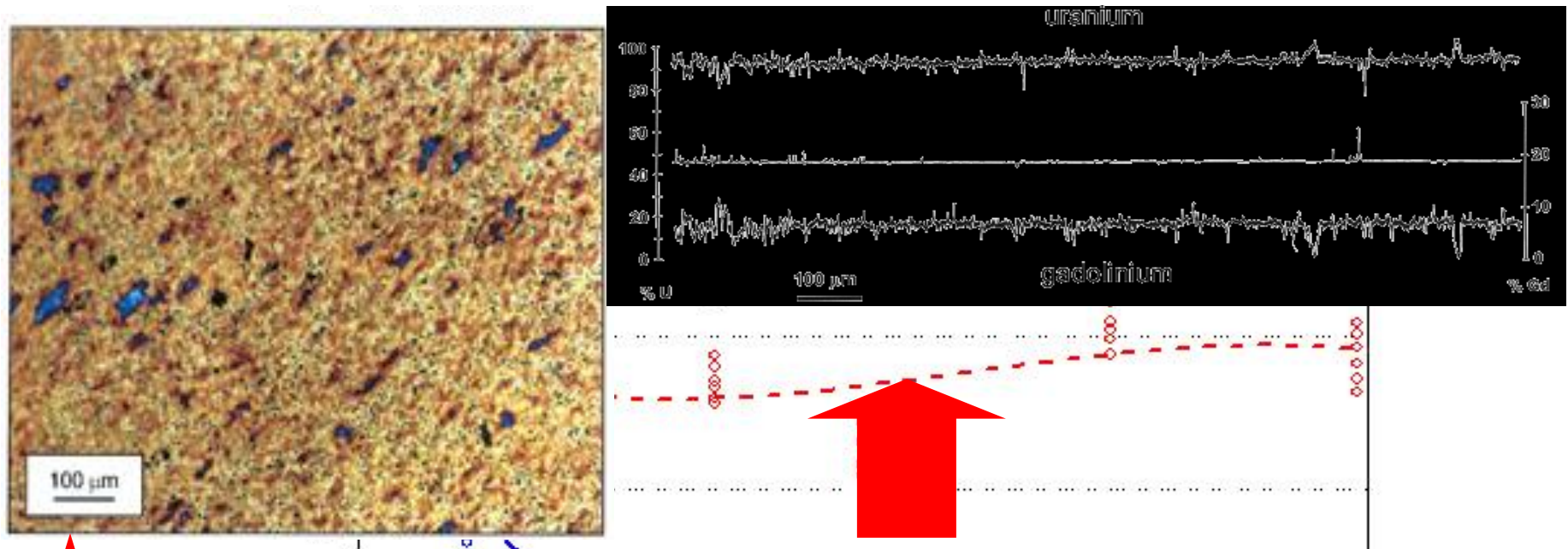
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AUC Coprecipitation  **Microscopic Level**

Some Gd₂O₃ powder originally added is present in the mixed powder as a solid solution and some of it remain as free BCC Gd₂O₃. Probably, the coprecipitation did not occur and a fractionating precipitation is probable to have been occurred. In this case the homogenization is done in the liquid phase and a good homogeneity is achieved, in a microscopic level.

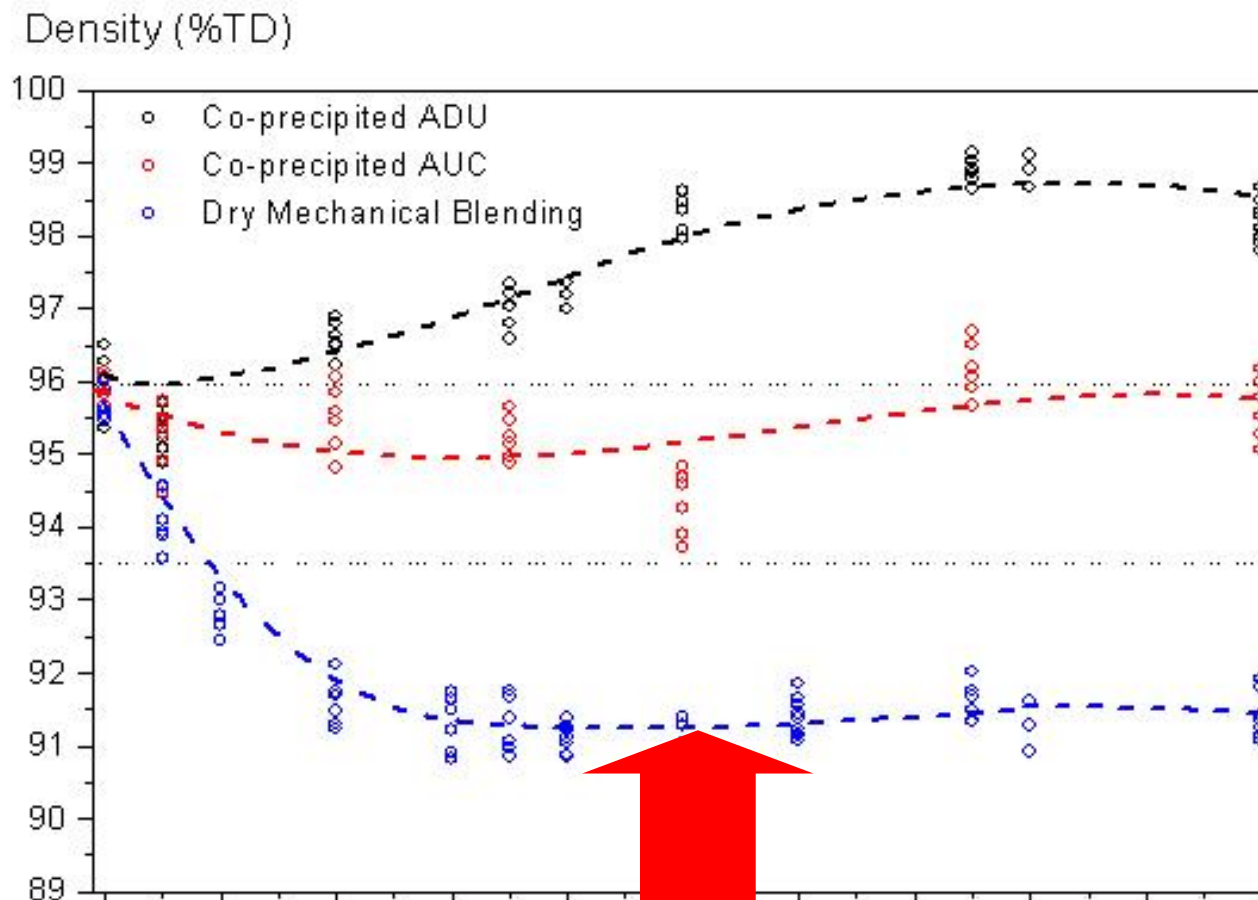


AUC Coprecipitation **Microscopic Level**

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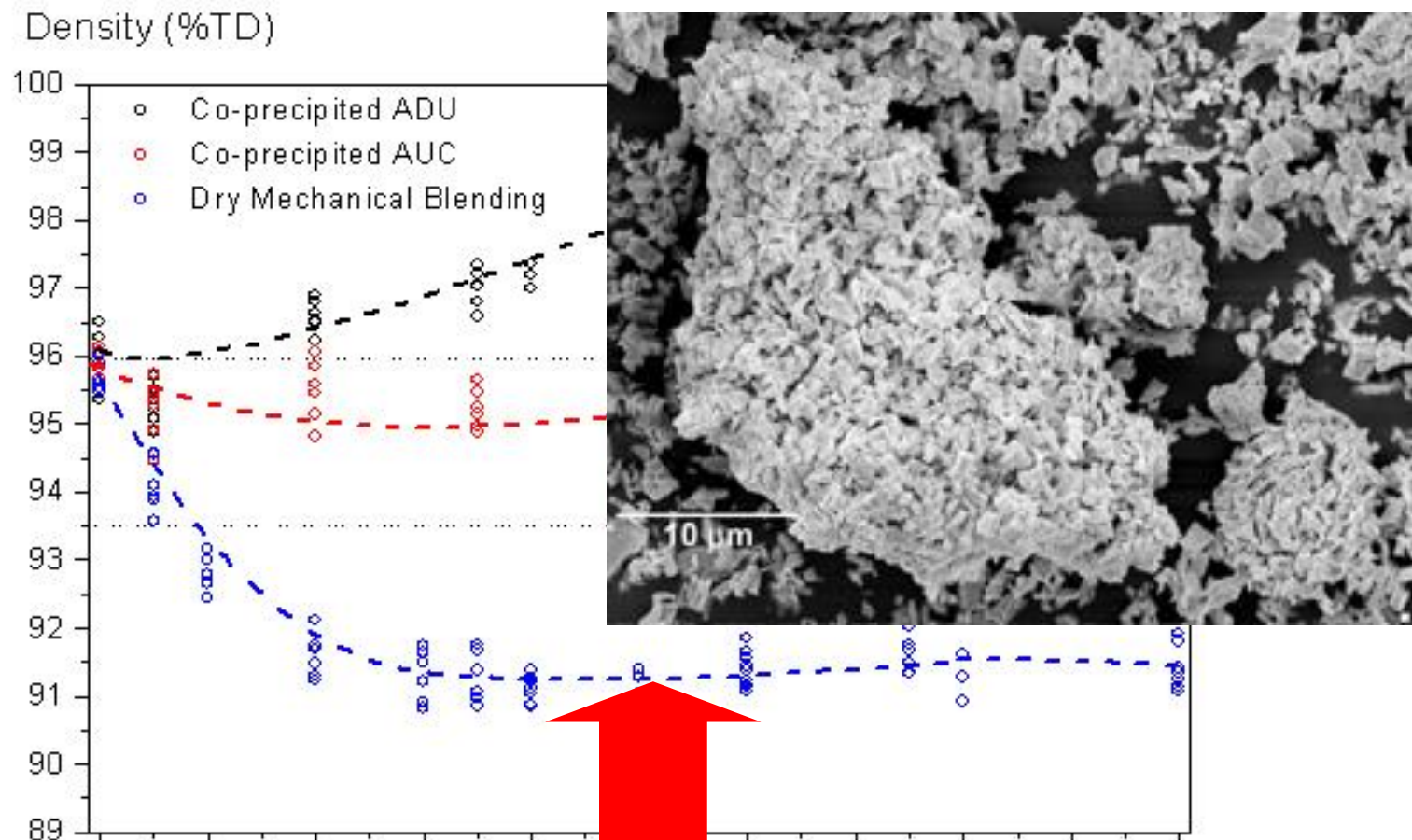
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We have a good homogeneity, but in a level lower than the one observed in ADU coprecipitation



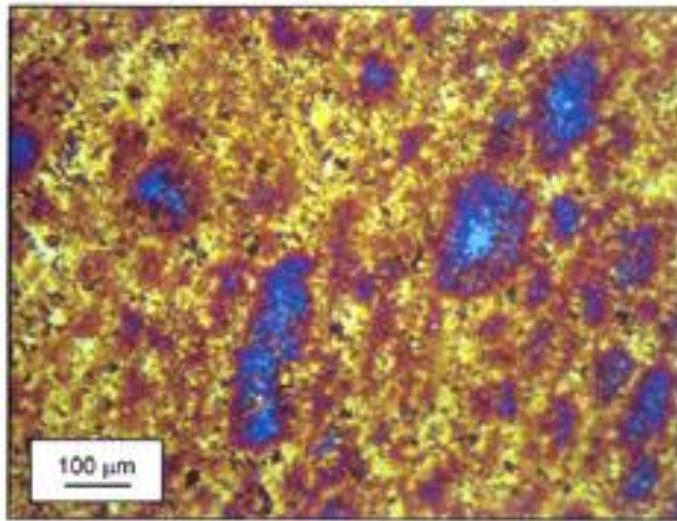
Dry Mechanical Mixture  ***Macroscopic Level***

In this case, all the Gd_2O_3 powder originally added is present in the mixed powder as free BCC Gd_2O_3 . The worst homogeneity is achieved and the Gd_2O_3 is present as a dispersion of agglomerates within the UO_2 powder. The high tendency of the Gd_2O_3 powder to agglomerate was observed (see SEM micrograph).

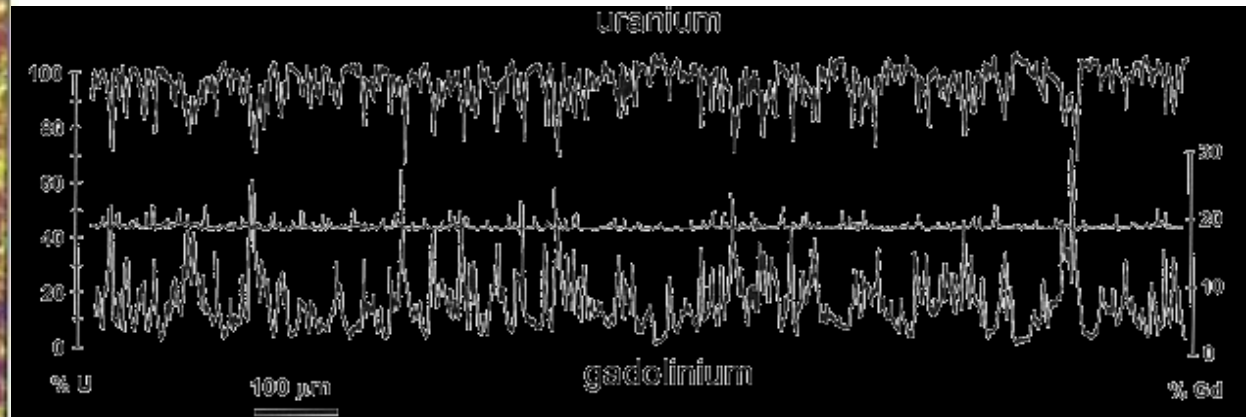


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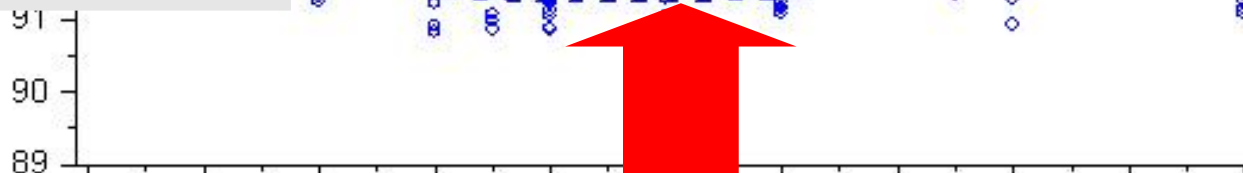
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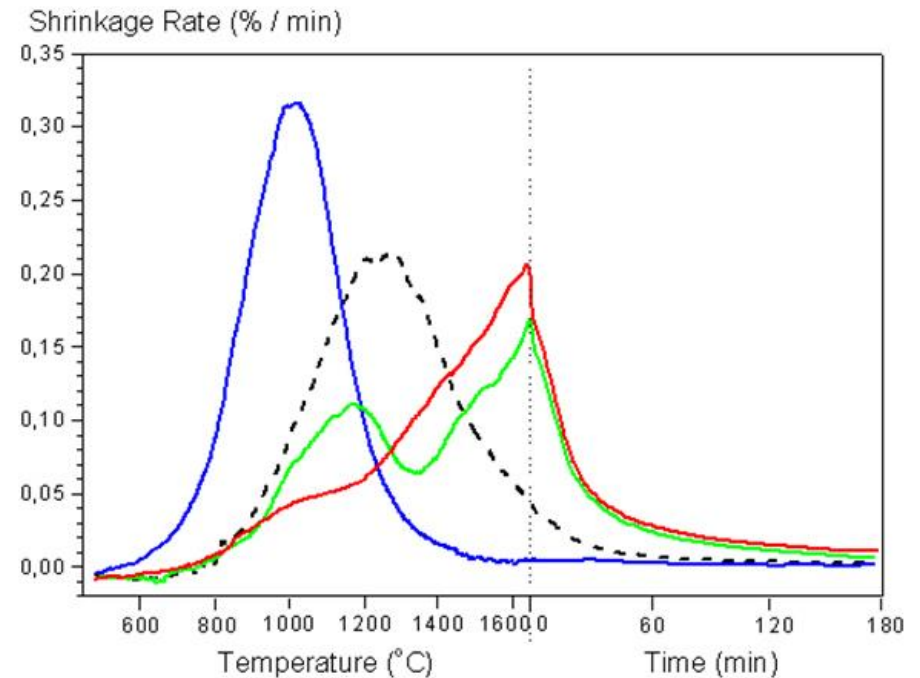
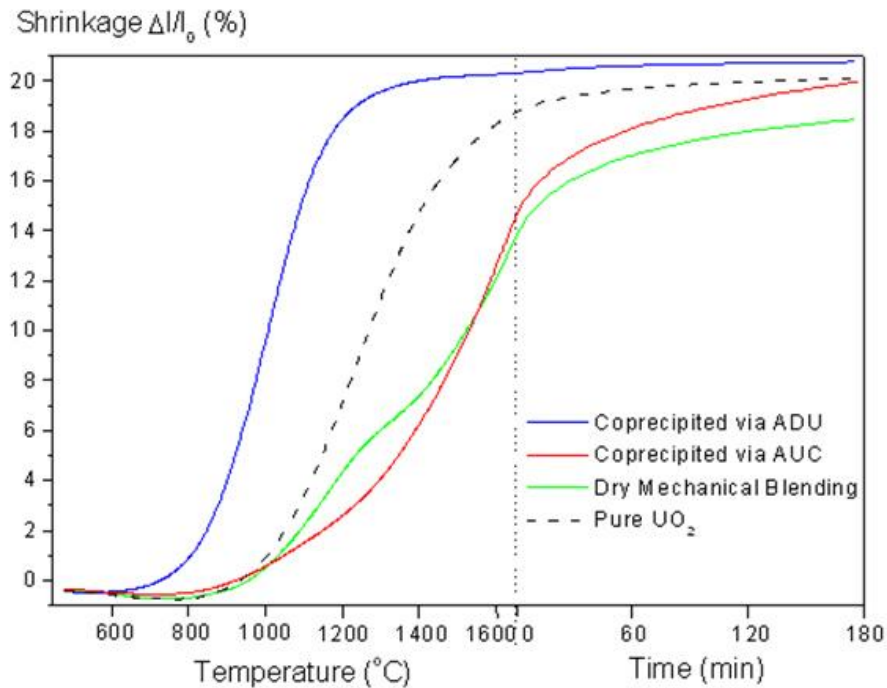


In this case we have a bad homogeneity



Dry Mechanical Mixture  **Macroscopic Level**

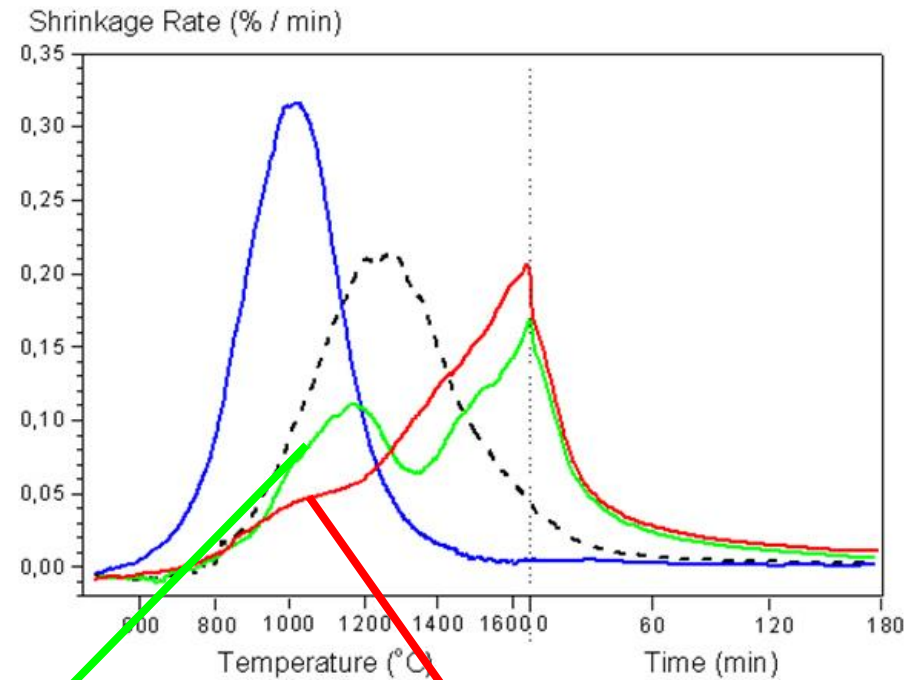
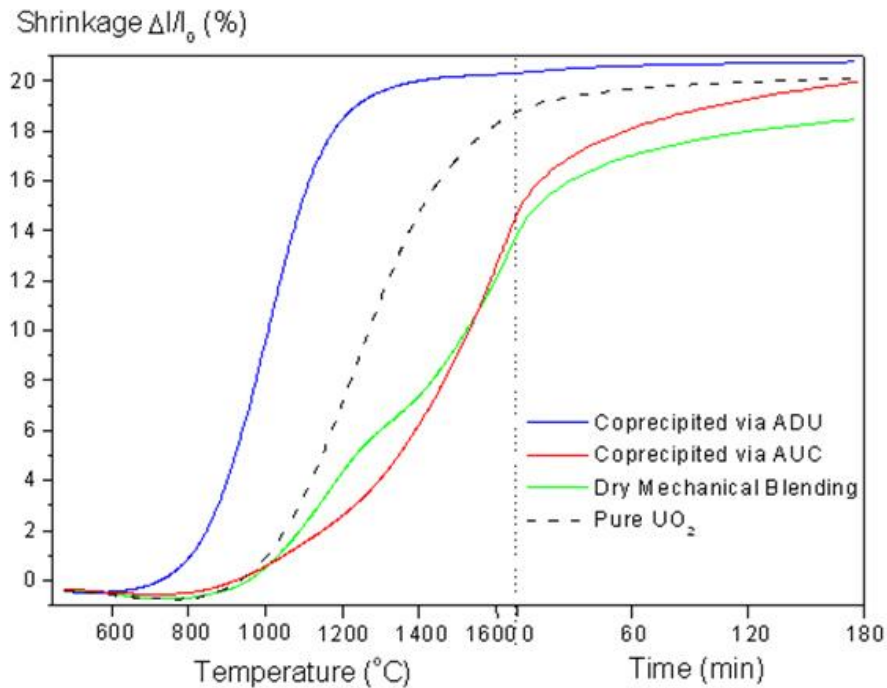
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3 homogeneity levels  3 densification levels

Depending on the homogenization level, the shrinkage is delayed (1100-1400 C) and the final density is lowered (sintering blockage).

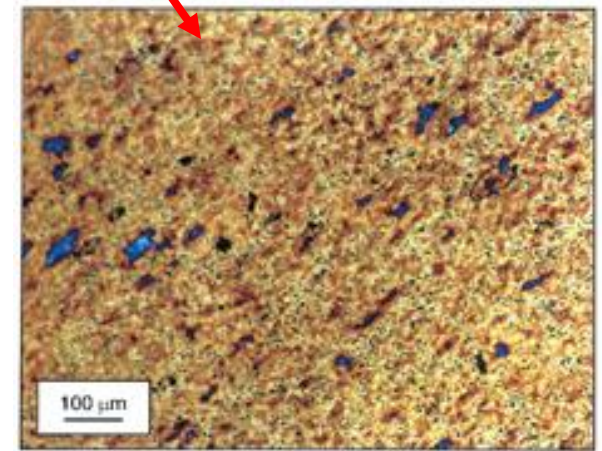
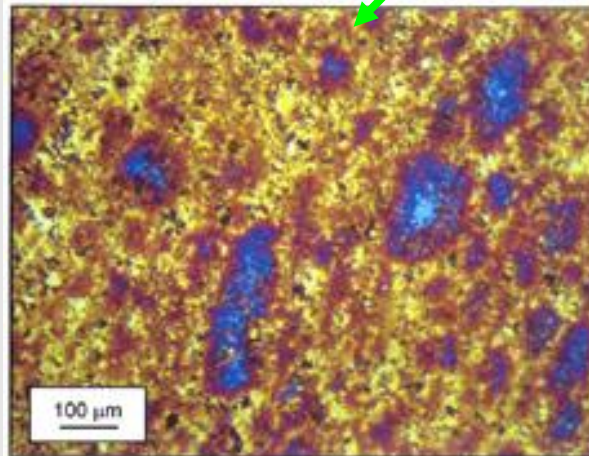
***The first hypothesis was the “diffusion barrier formation”, proposed by:
Manzel and Dörr (Am.Ceram.Soc.Bull 59, n.6,p. 601, 1980)
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(brownish areas in micrographies around blue pure UO_2 areas)***

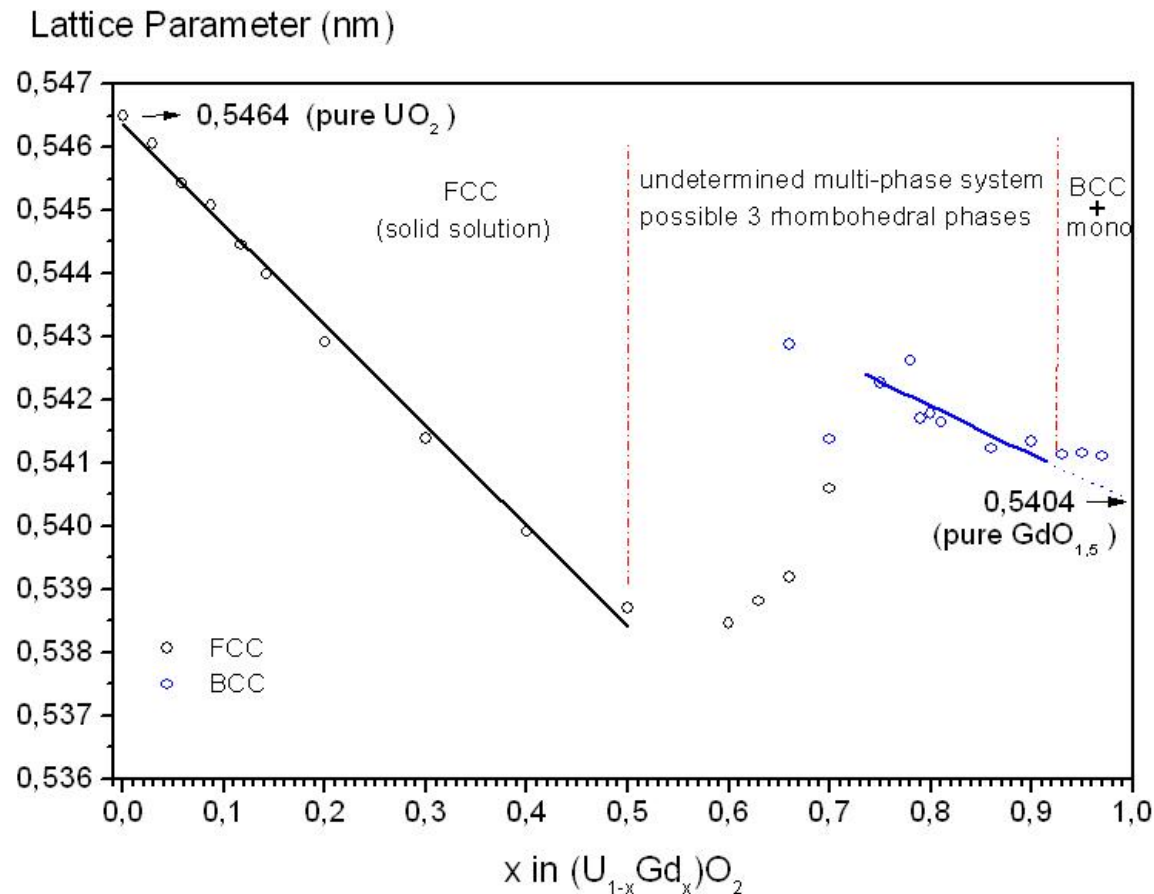


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Depending on the homogenization level, the shrinkage is delayed (1100-1400 C) and the final density is lowered (sintering blockage). The first hypothesis was the “diffusion barrier formation”, proposed by: Manzel and Dörr (Am.Ceram.Soc.Bull 59, n.6, p. 601, 1980).

Assmann, Peehs and Roepenack (J.N.M 153, p. 115, 1988) (brownish areas in micrographies around blue pure UO_2 areas)

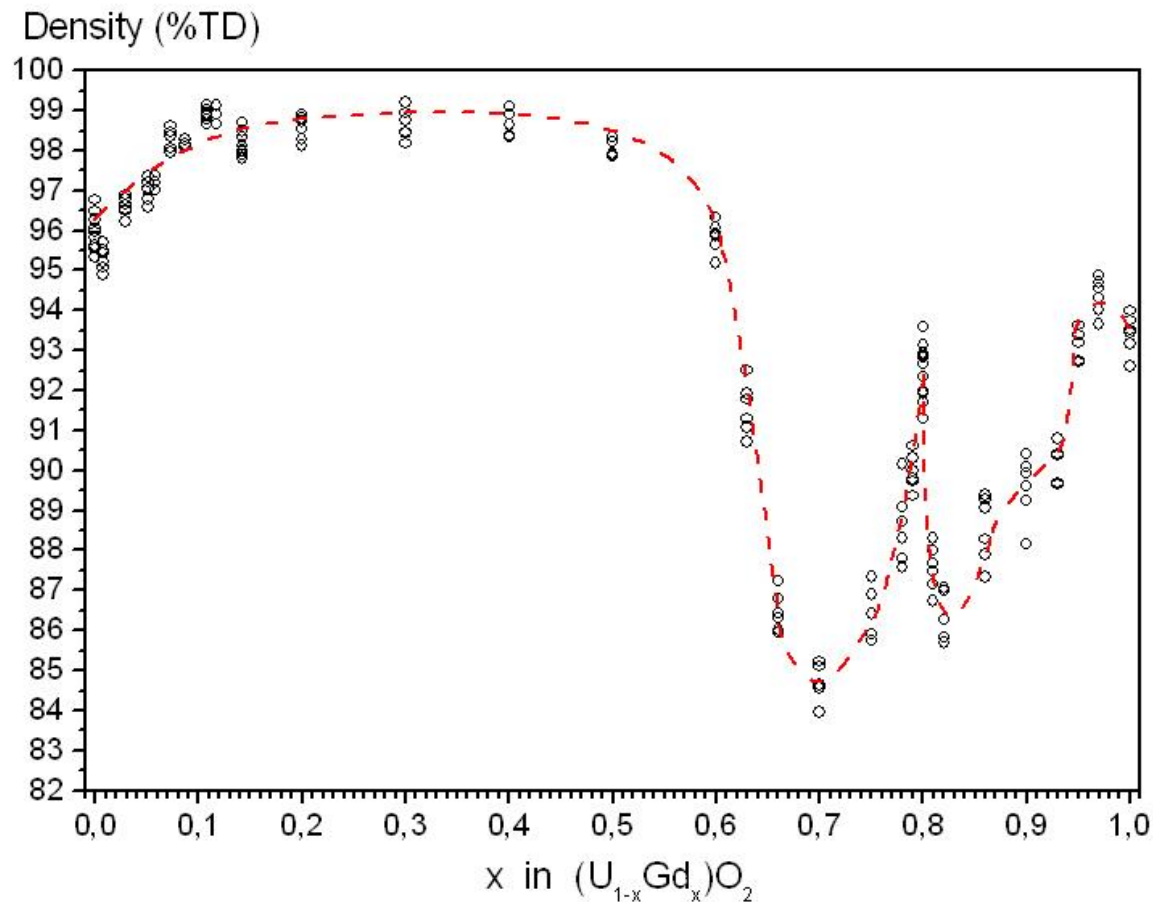




Variation of the fluorite lattice parameter with dissolved gadolinium content.

Linear decrease of lattice parameter below 50 at% Gd, which indicates single fluorite phase. Above 50 at% Gd new phases different from fluorite are formed (maybe 3). Probably these phases are isostructural to the rhombohedral phases observed in the RE-O, U-Y-O and U-La-O systems (UGd₆O₁₂)

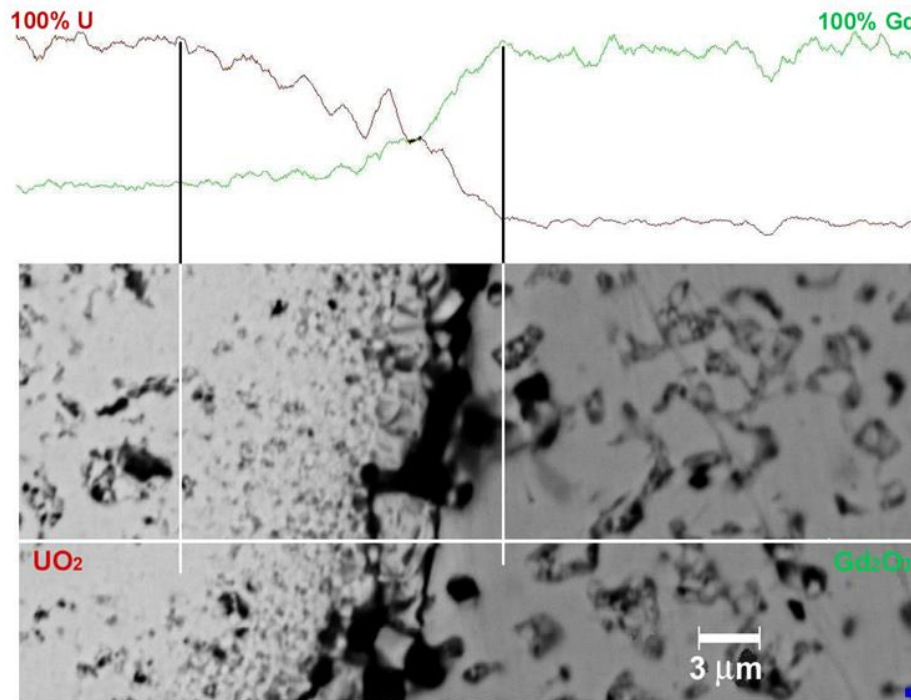
The presence of these phases causes the densification decrease.



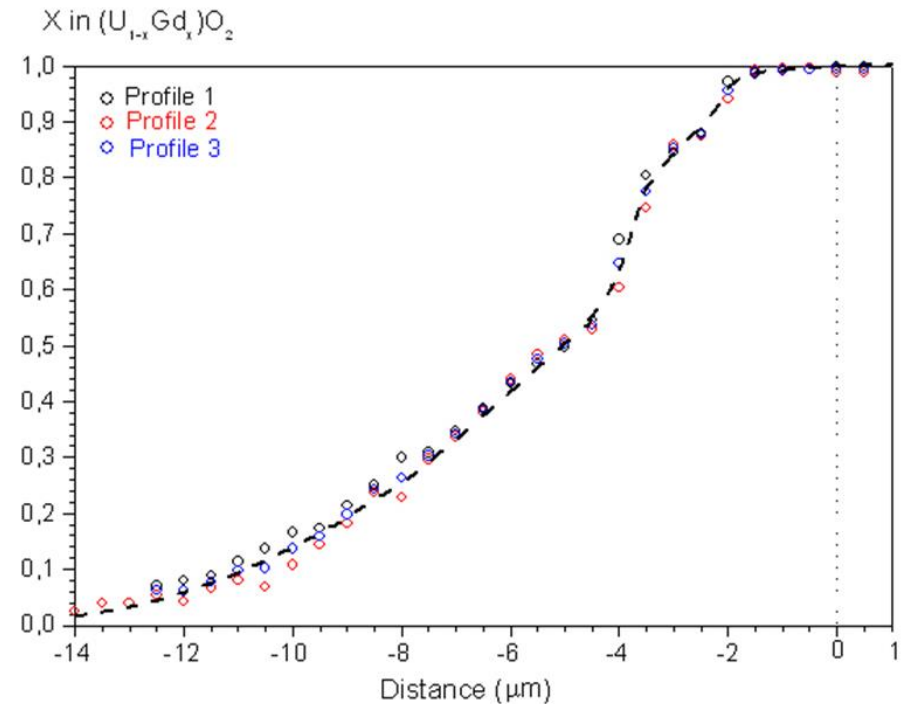
Effect of the gadolinium concentration on the sintered density of (U,Gd)O₂ pellets prepared by co-precipitation (solid solution)

The presence of these phases causes the densification decrease.

Above 50 at% Gd (final of single fluorite phase field), the densification decrease abruptly. At about 80 at% Gd there is an increase in the sintered density, followed by another decrease. This observation indicates more than one U-Gd-O phases different from fluorite.



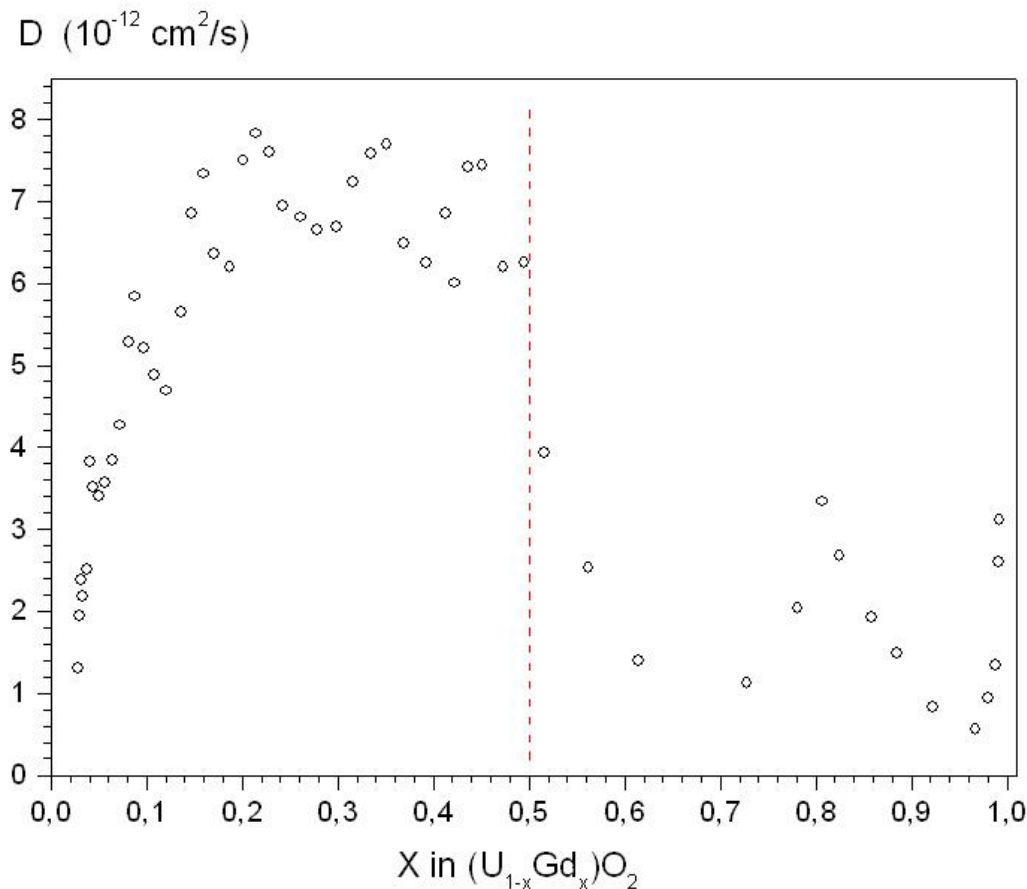
Scanning electron micrograph illustrating the UO₂/Gd₂O₃ interface.



Gadolinium concentration profile across the UO₂/Gd₂O₃ interface.

Why the presence of these phases causes the densification decrease?

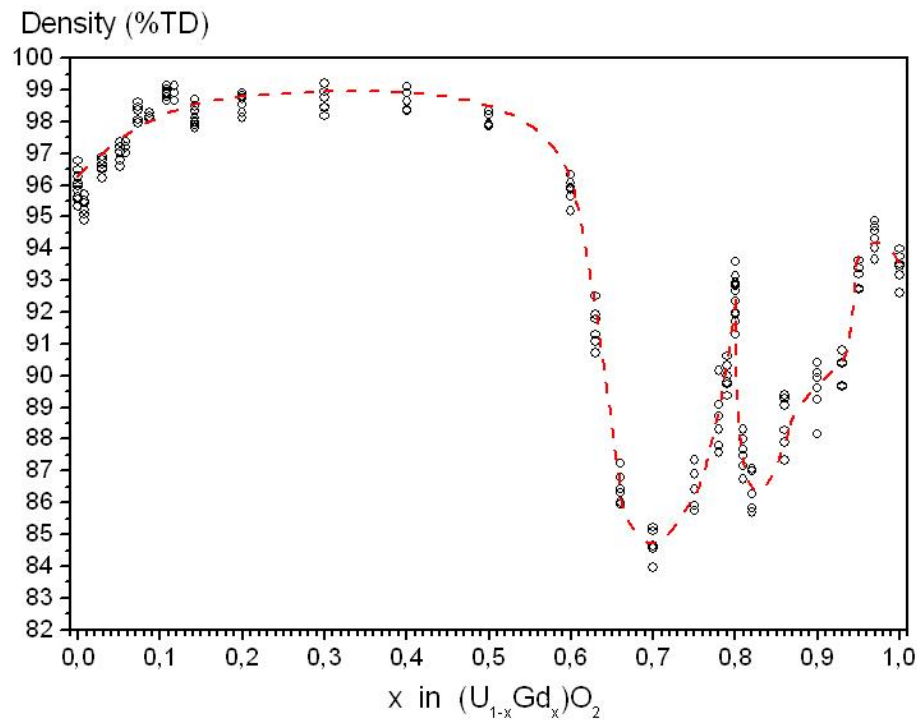
From the interpenetration curves, the interdiffusion coefficients are determined by applying a graphic methodology for the solution of the second Fick's law (the Matano's Method).



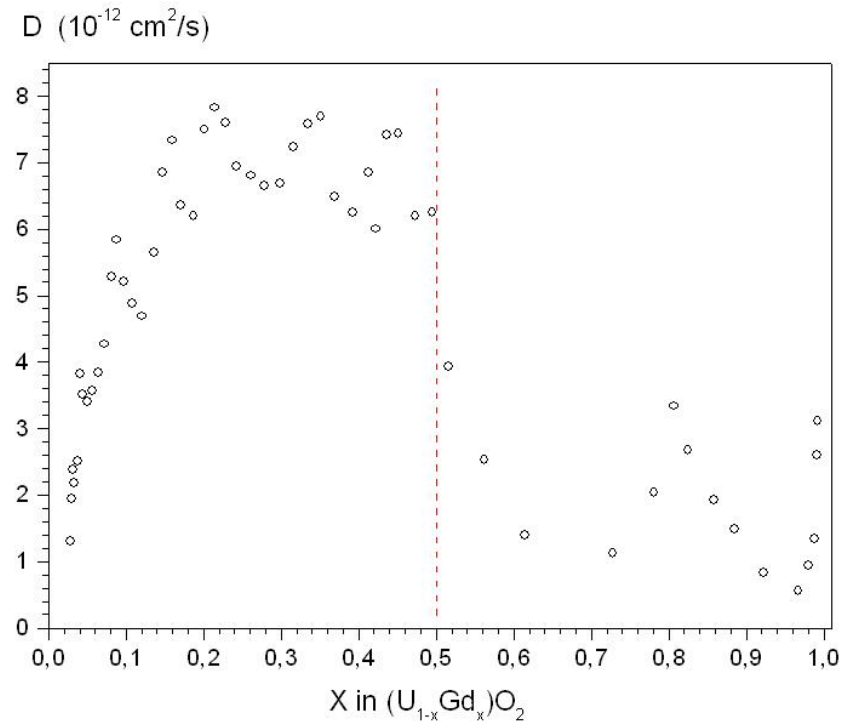
Interdiffusion coefficient as a function of the molar fraction of gadolinium.

Why the presence of these phases causes the densification decrease?

Above 50 at% Gd the interdiffusion coefficient decreases abruptly, as observed for the densification. Like the densities curve, at about 80 at% Gd there is an increase in the interdiffusion coefficient, followed by another decrease. The shape of both densification and diffusion coefficient curves are very similar.



Sintered densities



Interdiffusion coefficient

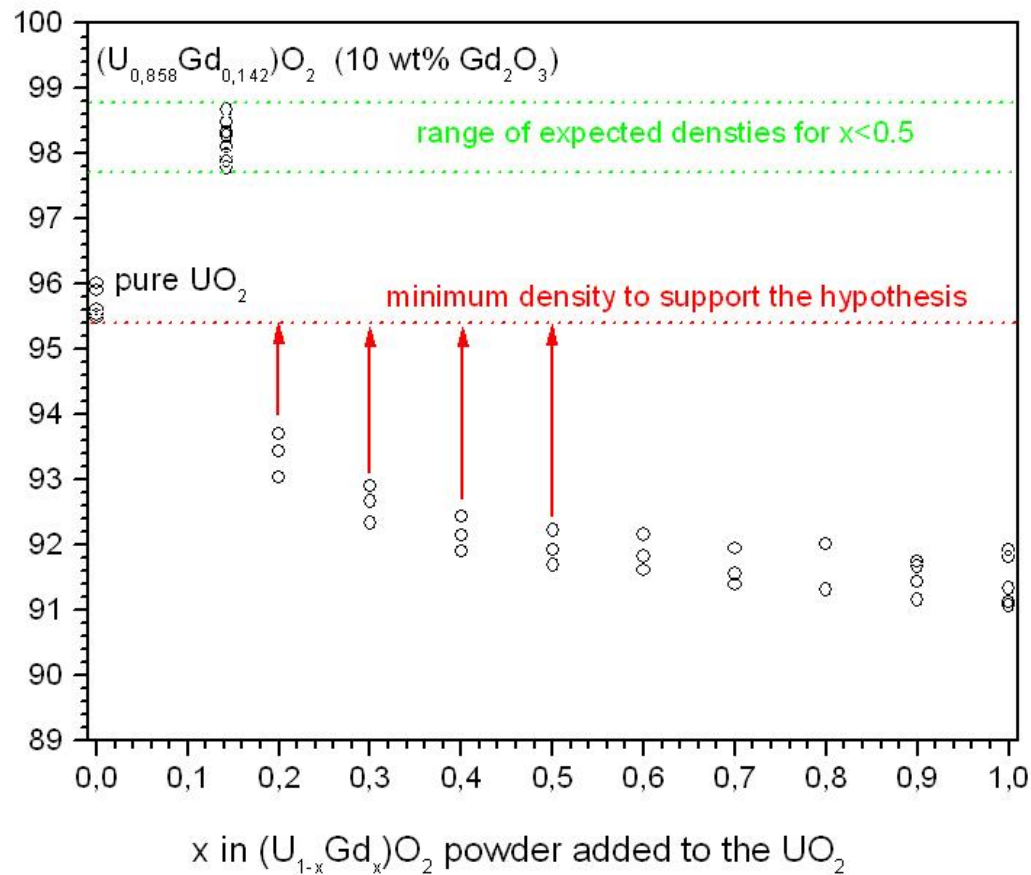
Why the presence of these phases causes the densification decrease?

Above 50 at% Gd the interdiffusion coefficient decreases abruptly, as observed for the densification. Like the densification curve, at about 80 at% Gd there is an increase in the interdiffusion coefficient, followed by another decrease. The shapes of both densification and diffusion coefficient curves are very similar.

All these observations would confirm the “diffusion barrier” hypothesis.

Let's to test this hypothesis!

Sintered Density (%TD)

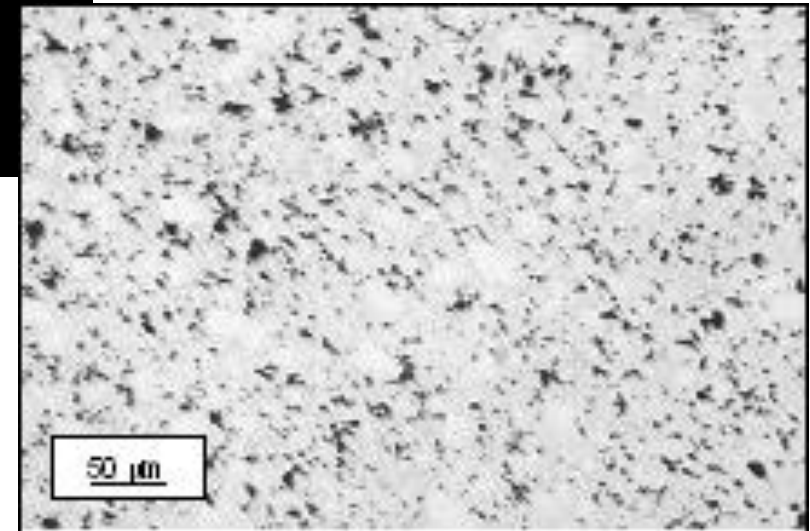
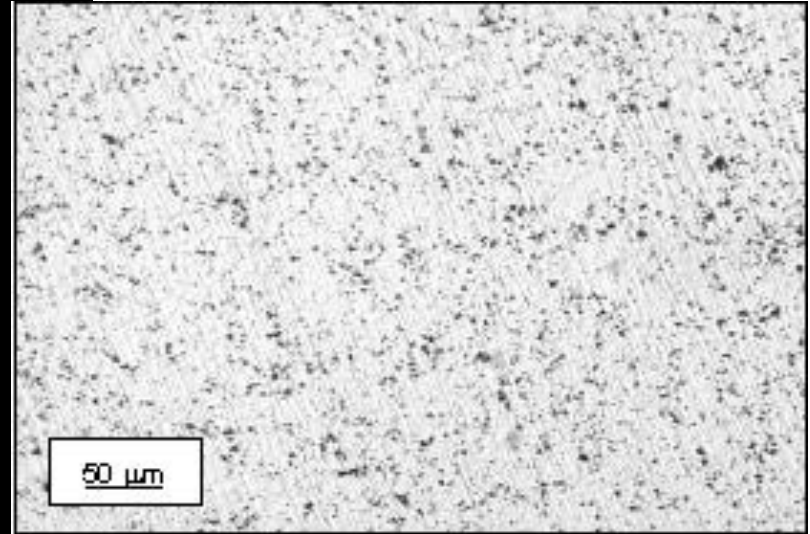
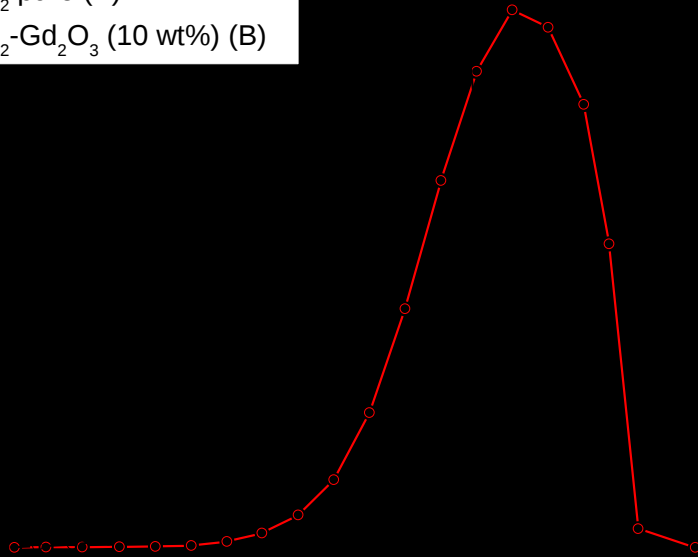


ADU coprecipitated powder (good Gd homogeneity and good sintering) was added to the UO_2 powder by mechanical mixture. The final composition was always equivalent to 10 wt% Gd_2O_3 .

In this way, when the added $(\text{U}_{1-x}\text{Gd}_x)$ coprecipitated powder has $x < 0.5$ (below the value to form possible low diffusivity phases), the final densities must be in the range observed for the coprecipitated 10 wt% Gd_2O_3 powder (above 97.5 % TD).

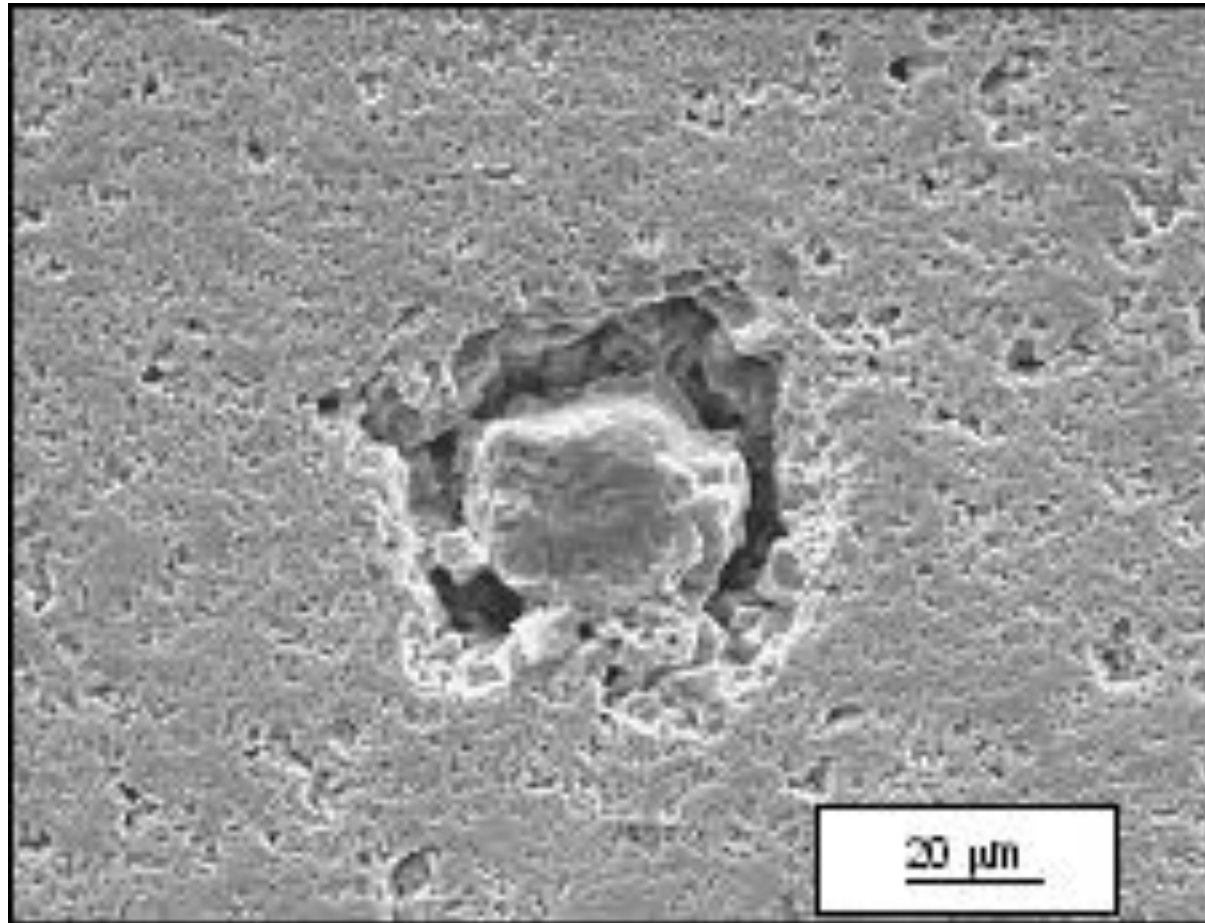
The Diffusion Barrier Hypothesis was not confirmed!

—○— UO_2 pure (A)
—○— $\text{UO}_2\text{-Gd}_2\text{O}_3$ (10 wt%) (B)

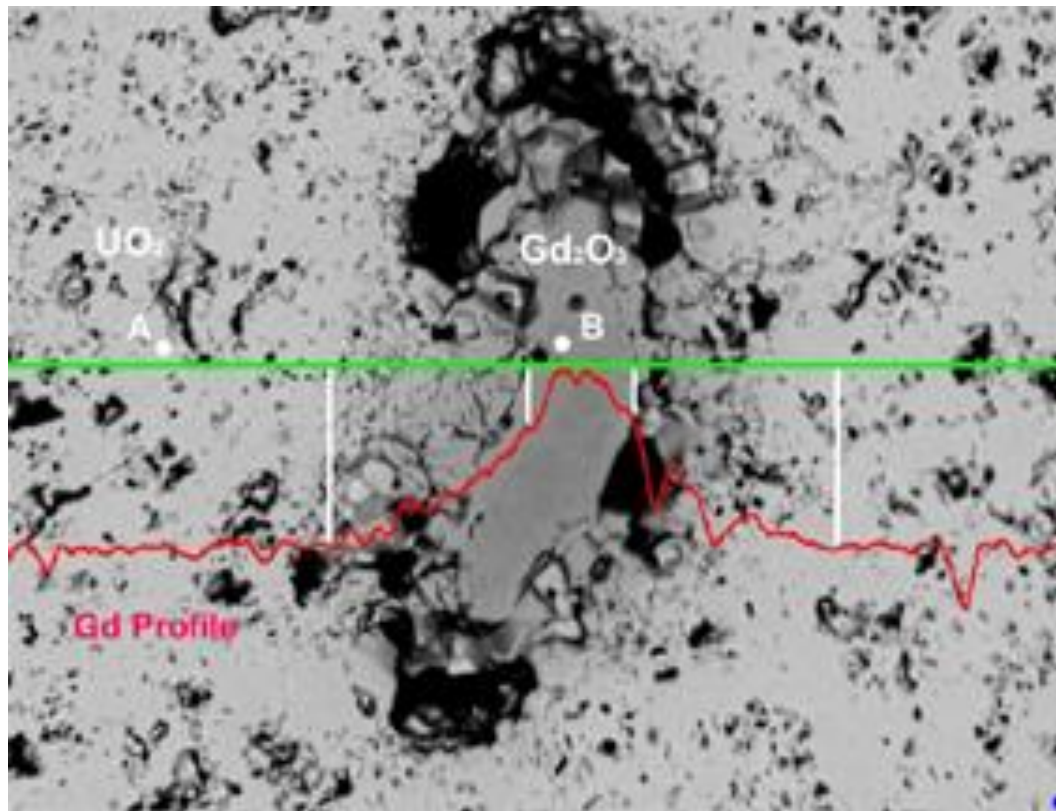


The Gd_2O_3 powder showed agglomerates with $\approx 30\ \mu\text{m}$ and the micrographies (sintered $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets) showed pores larger than the pores observed for pure UO_2 .

The curve of pore diameter distribution is shifted in the direction of larger diameters.



There was observed pores around big Gd₂O₃ agglomerates.



There is an unbalancing diffusion (material transport) between UO_2 and Gd_2O_3 . The Gd diffuses preferentially into the fluorite lattice of UO_2 .

When the diffusion process starts (1200 C), Gd from agglomerates diffuses preferentially into the UO_2 matrix, leaving back pores (Kirkendall Effect). These pores are difficult to be eliminated in the further sintering process, once they were formed at high temperature.

This is the “Pore Formation Hypothesis”

CONCLUSIONS

The presence of phases different from the fluorite structure of UO_2 was indirectly detected. These phases have low diffusivity and occur when the molar fraction of gadolinium surpasses the value of 0.5.

Despite this experimental evidence, the hypothesis more frequently proposed to explain the sintering behaviour of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel was not proven experimentally in this work. The hypothesis is based on the formation of a diffusion barrier around the Gd_2O_3 agglomerates due to the formation of the gadolinium rich phases with low diffusivity. The blockage in the sintering does happen even when the molar fraction of gadolinium added as $(\text{U,Gd})\text{O}_2$ solid solution is smaller than 0.5, when the system is monophasic with fluorite type crystal structure and has high diffusivity.

Another hypothesis is under investigation, which is based on the formation of stable pores during sintering due to the significant difference in the interdiffusion coefficients of the gadolinium into UO_2 and of the uranium into Gd_2O_3 (Kirkendall effect).