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Characterization of fresh EMPIrE and SEMPER FIDELIS U(Mo)/Al fuel plates made with PVD-coated U(Mo) particles

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Abstract. The HERACLES group and the US-DOE work jointly to develop dispersed U(Mo)/Al as LEU fuel for conversion of high performance nuclear research reactors. Within this frame, two irradiation programs are in progress. In the first, EMPIrE, mini-plates are tested in the ATR reactor (USA) and in the second, SEMPER FIDELIS, full-size plates are irradiated in BR2 (Belgium). In both experiments, U(Mo)/Al plates with optimized microstructure are tested under high duty conditions. This paper focuses on analyses made at CEA Cadarache on seven fresh plates made of atomized particles, with or without Mo homogenization, and with ZrN coating. Five EMPIrE mini-plates and two SEMPER FIDELIS full-size plates were examined by optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). A particular attention is paid to the integrity of the ZrN coating (thickness, cracks...) and to the U(Mo) particles microstructure.

1 Introduction

The use of low-enriched uranium (LEU) nuclear fuels for research reactors (material testing reactors and neutron sources) is worldwide encouraged. A fuel core made of a dispersion of U(Mo) alloy (with 7–10 wt% Mo) particles within an Al matrix, colaminated between two aluminium alloy plates, constitutes one of the candidates for this type of fuel. Under aggressive irradiation conditions, the performances of U(Mo)/Al dispersed fuels are limited by an interaction process between U(Mo) particles and the Al matrix, which induces a significant swelling of the fuel plates [1]. A 1 μm thick ZrN layer can strongly decrease this interaction but, at high burn-up, a swelling acceleration is still observed. This behavior is attributed to a recrystallization mechanism of the fuel which induces both U(Mo) grain refinement and precipitation of large (micrometer sized) fission gas bubbles [2]. A way to delay this recrystallization and, thus, the associated swelling under irradiation, could consist in modifying the U(Mo) particle microstructure (which is an "as-solidified" microstructure, in powders produced by an atomization process), using homogenization thermal treatments, as pointed out in the frame of the KOMO-5 experiment [3].

Verifying the benefits of a homogenization heat treatment, followed by a ZrN coating of the particles, on the swelling behaviour of U(Mo)/Al dispersed fuel, is one of the main goals of the EMPIrE and SEMPER FIDELIS irradiation experiments [4,5]. Both in-pile tests are currently ongoing in the ATR (Idaho, USA) and BR-2 (Mol, Belgium) reactors, respectively.

This work is aimed to characterize fresh fuel plates from both experiments. We have chosen to focus on PVD-coated plates, made with atomized U(Mo) particles produced by KAERI. If only some powder batches were homogenized at 1000 °C for 1 hour, all of them were coated by PVD with ZrN in conditions similar to those used for SELENIUM experiment [6]. Both powder treatments (high temperature annealing and powder coating) were performed at SCK-CEN. Finally, plates were manufactured by CERCA using the conventional picture-frame technique.

2 Experimental details

2.1 Materials

Table 1 recaps the main characteristics of the seven plates examined here. They all correspond to off specifications plates, according to non-destructive examinations (the others being destined for irradiation). Four of them are

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Table 1. Main characteristics of EMPIrE and SEMPER FIDELIS plates.

Irradiation program	Plate designation	Mo homogenization heat treatment
EMPIrE (mini-plates)	EMP-711	No
	EMP-717	No
	EMP-803	Yes
	EMP-819	Yes
	EMP-828	Yes
SEMPER FIDELIS (full-size plates)	SF-202 (full designation: FIDJ0202)	Yes
	SF-402 (full designation: FIDJ0402)	No

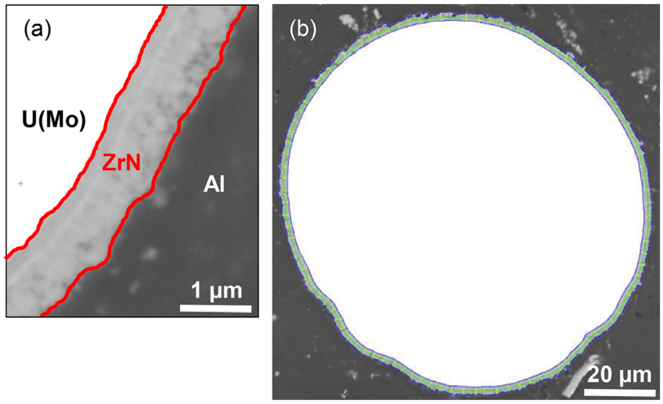

Fig. 1. Principle of ZrN coating thickness measurement, on BSE images: (a) detection of ZrN layer boundaries, (b) measurement of ZrN layer thickness at 100 locations around the particle.

made with heat treated particles (three mini-size plates and one full-size plate). The two types of plates considered here (EMPIrE and SEMPER-FIDELIS) are both cladded with AG3NE aluminium foils. Mini- and full-size plates were manufactured using close conditions.

A 9×28 mm^2 piece was taken from each plate at CERCA and sent to CEA Cadarache. There, two samples per piece, were cut and then mechanically polished:

– a 9×9 mm^2 square sample, polished parallel to the fuel-cladding interface, down to the middle part of the fuel zone, for X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) examinations,

– a 9 mm long cross-section, for optical microscopy (OM) and complementary SEM + EDS examinations, especially close to the fuel-cladding interface.

2.2 Characterization methods

OM examinations were performed with an Olympus DSX500 opto-digital microscope. SEM examinations were carried out mainly in backscattered electrons mode (BSE), with a FEI Nova Nano SEM 450, equipped with an Oxford Instruments EDS system. The mean Mo content in U(Mo) particles was determined by EDS, on 15 particles per plate [7].

The STREAM Olympus software was used to analyse BSE images in order to measure:

– the U(Mo) particles sphericity (defined as the squared ratio between the width and the length of a particle, excluding ZrN coating), on about 100 particles per plate, with a minimal diameter of 20 µm,

– the thickness of ZrN coating, on about 30 particles per plate.

In order to minimize the potential measurement error due to bias cutting effects, only particles with diameters larger than 70 µm were considered for ZrN thickness measurements. Those with significantly damaged coatings (partly delaminated and/or fragmented) were also disregarded. On each particle, ZrN layer boundaries were detected thanks to the grey level variations at the Al/ZrN and ZrN/U(Mo) interfaces (Fig. 1a). After that, the coating thickness was measured at 100 different locations regularly distributed around the particle (Fig. 1b). Statistical results presented in Section 3.3 are based on mean values obtained from each particle.

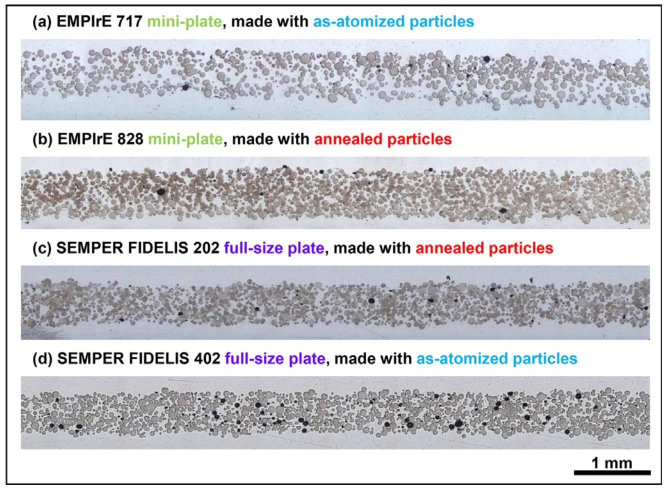

Fig. 2. OM macrographs of (a) EMP-717, (b) EMP-828, (c) SF-202, (d) SF-402 plates.

3 Results

3.1 Macrographs

Figure 2 gathers four representative macrographs, obtained by OM on cross-sections from two EMPIrE and two SEMPER FIDELIS plates, each couple of plates comprising one plate made with heat treated particles. At this scale, the only noticeable difference is that EMPIrE mini-plates seem to present a more heterogeneous

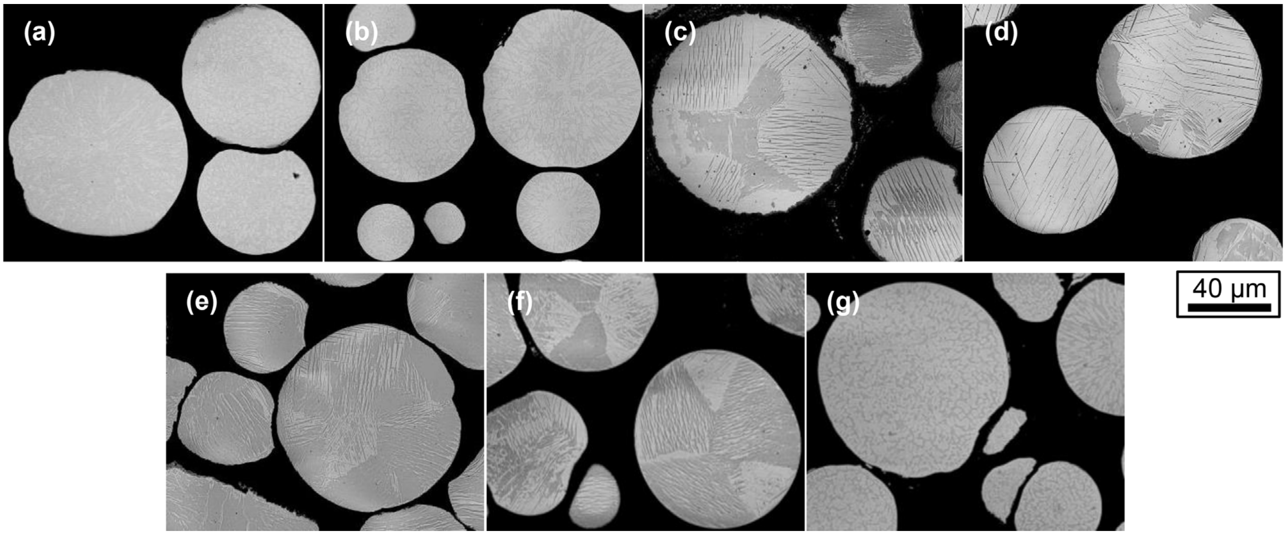

Fig. 3. U(Mo) particles microstructure, observed by SEM (BSE mode) in (a) EMP-711, (b) EMP-717, (c) EMP-803, (d) EMP-819, (e) EMP-828, (f) SF-202, (g) SF-402 plates.

distribution of U(Mo) particles within the fuel core (in accordance with less demanding manufacturing specifications concerning its homogeneity).

3.2 U(Mo) particles characteristics

Figure 3 shows SEM micrographs taken on each plate, in imaging conditions allowing grains visualization within U(Mo) particles. As expected, the three plates made with as-atomized particles exhibit typical columnar and/or cellular solidification microstructures (Fig. 3a,b,g). The four other ones are characterized by large grains which reach a size of the order of several tens of microns, as expected after a 1000 °C 1 h annealing [7,8]. In some cases, single crystalline particles are encountered (see for example Fig. 3d: particle on the left hand side). Grains are more or less difficult to distinguish, since they almost systematically contain lamellas with darker contrasts. Such features were already observed in certain particles from heat treated KOMO-5 powder batches and were interpreted as Widmanstätten microstructures which could appear depending on the cooling rate conditions [7]. They were also present in certain particles from heat treated EMPIrE powder batches (even if this point was not illustrated in [7]), but to a lower extend than in the EMPIrE plates. Batch to batch variabilities linked to cooling conditions after homogenization and/or an incidence of the thermal history during plates manufacturing could explain why these lamellas are numerous in plates made with heat treated U(Mo) particles. XRD analyzes are in progress and should give clues about the origin of these features.

Table 2 recaps the results of sphericity measurements on U(Mo) particles, by image analysis, and of EDS semi-quantitative measurements of Mo content in these particles, for the seven studied plates.

Table 2. Sphericity and Mo content of U(Mo) particles.

Plate designation	Mean sphericity	Mean Mo content (wt%)
EMP-711	0.90	6.2
EMP-717	0.85	6.2
EMP-803	0.76	6.5
EMP-819	0.85	6.3
EMP-828	0.73	6.3
SF-202	0.71	6.3
SF-402	0.71	6.3

Circularity measurements were already performed on several PVD-coated EMPIrE powder batches [9]. They tended to evidence a deformation of originally round atomized particles, which was probably linked to their swirling in the coating reactor, and did not seem to vary significantly with their metallurgical state.

However, in EMPIrE plates, except for EMP-819 (probably because of sampling effects), the sphericity of particles seems to be related to this state: it is close to 0.9, for as-atomized particles, while this value is only about 0.75 in heat treated ones. These results tend to show that homogenization leads to a softening of U(Mo) particles, linked to grain growth, which favors their deformation during rolling. This difference of shape between annealed and as-atomized particles is not observed in the case of SEMPER FIDELIS plates, which are both characterized by a 0.71 mean sphericity value. This value suggests that the full-size plates rolling conditions led to a slightly greater deformation of U(Mo) particles, whatever their mechanical properties, compared to mini-plates.

Mean particle Mo content is almost the same in all plates, i.e. about 6.3 wt% (standard deviation: 0.2 wt%). This amount is fully consistent with those measured, with

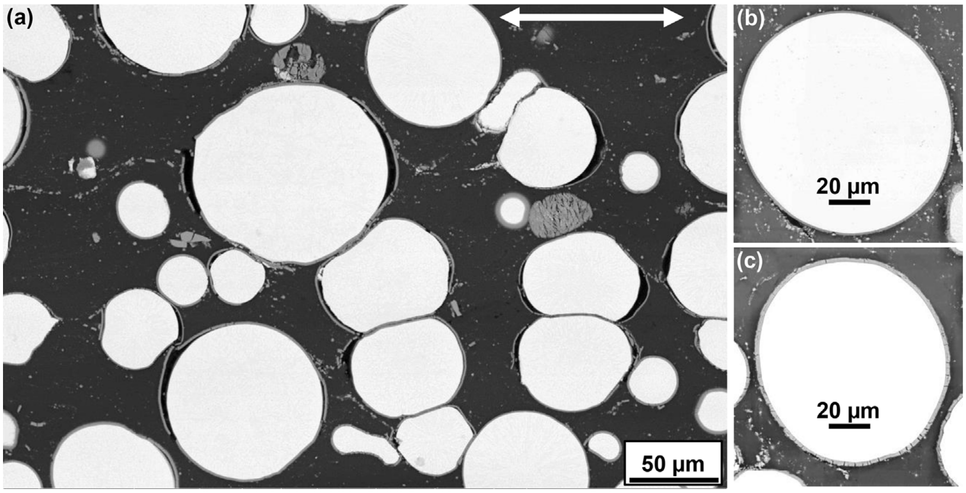

Fig. 4. SEM micrographs taken on (a) EMP-717 (cross-section), (b) SF-202, (c) EMP-819 plates.

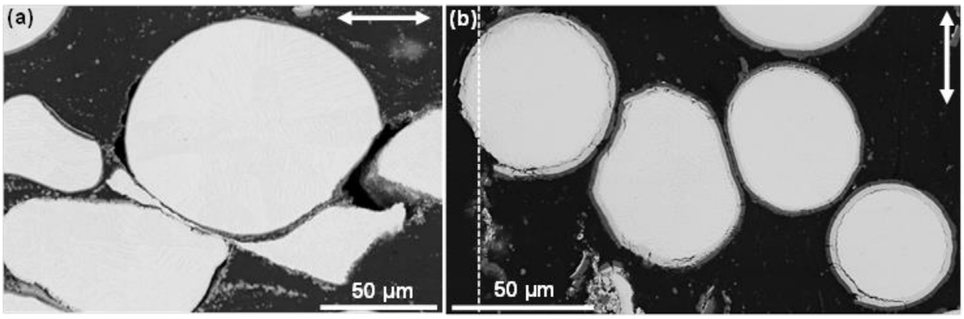

Fig. 5. SEM micrographs taken on cross-sections of (a) EMP-828, (b) EMP-819 plates (white arrows: rolling direction – dashed line: approximate location of fuel-cladding interface).

the same EDS equipment and the same analysis procedure, in several EMPIrE powder batches [7]. It is underestimated, compared to the content given by KAERI (7 wt%), very probably because of a systematic error due to virtual standards implemented in the EDS software.

3.3 ZrN coating characteristics

3.3.1 General features

3.3.1.1 Damaged coatings

In all studied plates, the ZrN coating around U(Mo) particles appears to be damaged, whereas few cracks could be evidenced on corresponding powders. It is difficult to determine precisely a representative amount of defective coatings, since it can largely vary from place to place, in a same sample, depending in particular on the local density of particles. In any case, there are never more than 50% of the particles exhibiting a perfectly continuous and adherent coating. This ratio can even fall below 30%, in certain cases, especially close to the fuel-cladding interface.

Figures 4 and 5 illustrate common degradation modes for ZrN coatings. The first one consists in an obvious delamination of the coating, around certain particles, in a preferential direction which is parallel to the rolling one. Figure 4a corresponds to an area where this phenomenon is particularly clear (the rolling direction is indicated by the white arrow). It is accompanied by the formation of a void between the ZrN layer (which remains unexpectedly “stuck” on the matrix) and the particle, this void reaching frequently several microns in thickness. This type of damage was mainly observed in EMPIrE mini-plates, manufactured with non-annealed U(Mo) particles (i.e. EMP-711 and EMP-717 plates). This suggests that rolling conditions of mini-plates, combined with relatively hard (i.e. poorly deformable) as-atomized particles could contribute to such coating delamination.

The second degradation mode is directly linked to the ZrN thickness. As it will be quantified in the next section, this thickness can vary by a factor two, from a particle to another one, and its mean value can also vary by the same order of magnitude, in the set of studied plates. Figures 4b and c compare two particles coated by respectively a one and a two microns thick layer. The second one undoubtedly presents more radial cracks. This cracking is very probably due to deformation incompatibilities between the coating and its substrate, during plate manufacturing and in particular during temperature transients as proposed in literature [10].

When particles are significantly deformed and/or in direct contact, as illustrated by Figure 5a, the ZrN coating frequently peels off or breaks down into small pieces, which

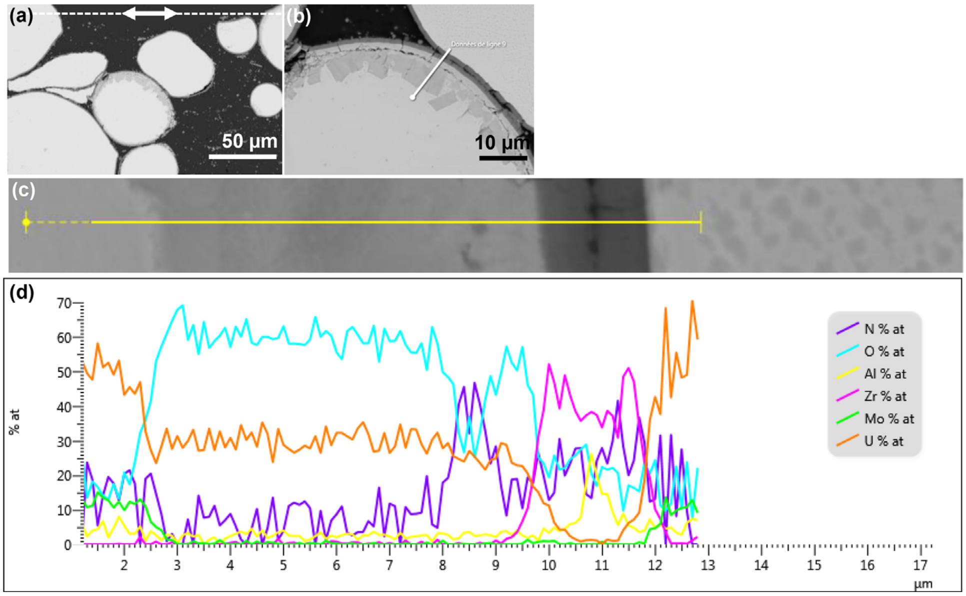

Fig. 6. SEM/EDS analysis of an oxidized U(Mo) particle in SF-202 plate (a) general view (white arrow: rolling direction – dashed line: approximate position of fuel-cladding interface), (b) and (c) location of the analysis line, (d) EDS profiles along the yellow line drawn in (c).

can be dispersed in the aluminium matrix. U(Mo) particle distribution heterogeneity, in the fuel core, thus strongly influences the ZrN layers physical state.

3.3.1.2 Oxidized particles

Another factor has a large influence on the mechanical stability of ZrN coatings: the presence of a brittle, highly circumferentially cracked oxidized layer, on the surface of some U(Mo) particles, below the coating, considerably reduces the adhesion of the ZrN layer. Such oxidized particles are preferentially observed close to the interface with the cladding, in all plates, as illustrated by Figures 5b and 6, but some can also be encountered in the middle of the fuel core, in certain plates, as it will be discussed later.

EDS profiles presented in Figure 6d show that the two analyzed ZrN coatings are partly oxidized: their oxidation probably occurred during the storage of the coated powder before plate manufacturing, as proposed in [10]. In Figure 6d, two ZrN layers which cover two different particles can be seen: in the following, we will focus on the U(Mo) particle located on the left hand side. Two sub-layers are found between the U(Mo) core and its coating: the outer sub-layer contains both nitrogen and oxygen, whereas the inner, which is thicker, mainly corresponds to an oxide (with a composition close to UO_2).

Severely oxidized particles, such as that presented in Figure 6, were already encountered in annealed EMPIrE powders. This allows concluding that their oxidation took place during their heat treatment. That is the reason why such particles can be found in the middle part of the fuel core, in plates made with homogenized U(Mo) particles. Their density varies from plate to plate and is particularly high in the EMPIrE 803 one, in accordance with observations previously carried out on the powder batch used to manufacture it. As already stated, oxidized particles are also present in all plates, close to the fuel-cladding interface, one side of the plate being sometimes more affected than the other side. This localization indicates that they probably oxidized during the plate hot rolling. The fraction of oxidized particles in the plates evolves basically as follows (from plates with numerous oxidized particles to ones with very few ones): EMPIrE mini-plates made with homogenized U(Mo) particles (EMP-803, EMP-819, EMP-828) > EMPIrE mini-plates made with as-atomized particles (EMP-711, EMP-717) > SEMPER FIDELIS plate made with homogenized particles (SF-202) > SEMPER FIDELIS plate made with as-atomized ones (SF-402). In the most oxidized plates, small UO_2 fragments, sometimes still partially coated with ZrN, can be locally dispersed in the matrix, especially close to the cladding. The white arrow, in Figure 7c, points such a fragment.

Finally, it is interesting to remind that, before plate fabrication, PVD-coated U(Mo) batches also comprise large ZrN flakes and much smaller spherical ZrN particles (Fig. 7a). The fraction of flakes and spherules can vary, from a powder batch to the other and, thus, from a plate to the other too. In the seven studied plates, it remains relatively low and comparable. ZrN spherules often agglomerate onto U(Mo) particles (Fig. 7b), whereas ZrN flakes are found broken into pieces in the Al matrix (Fig. 7c). ZrN fragments and spherules tend to form layers, roughly parallel to the rolling direction, especially close to the cladding interface (Fig. 7d).

3.3.2 Thickness measurements

Table 3 summarizes the ZrN coating thicknesses measured on the seven studied plates, with the method previously illustrated in Figure 1. In all cases, mean values range from 1 to 2 µm, the thinnest layer being found in the SF-202 plate and the thickest in the EMP-819 mini-plate. Standard deviations are of the same order of magnitude for each sample.

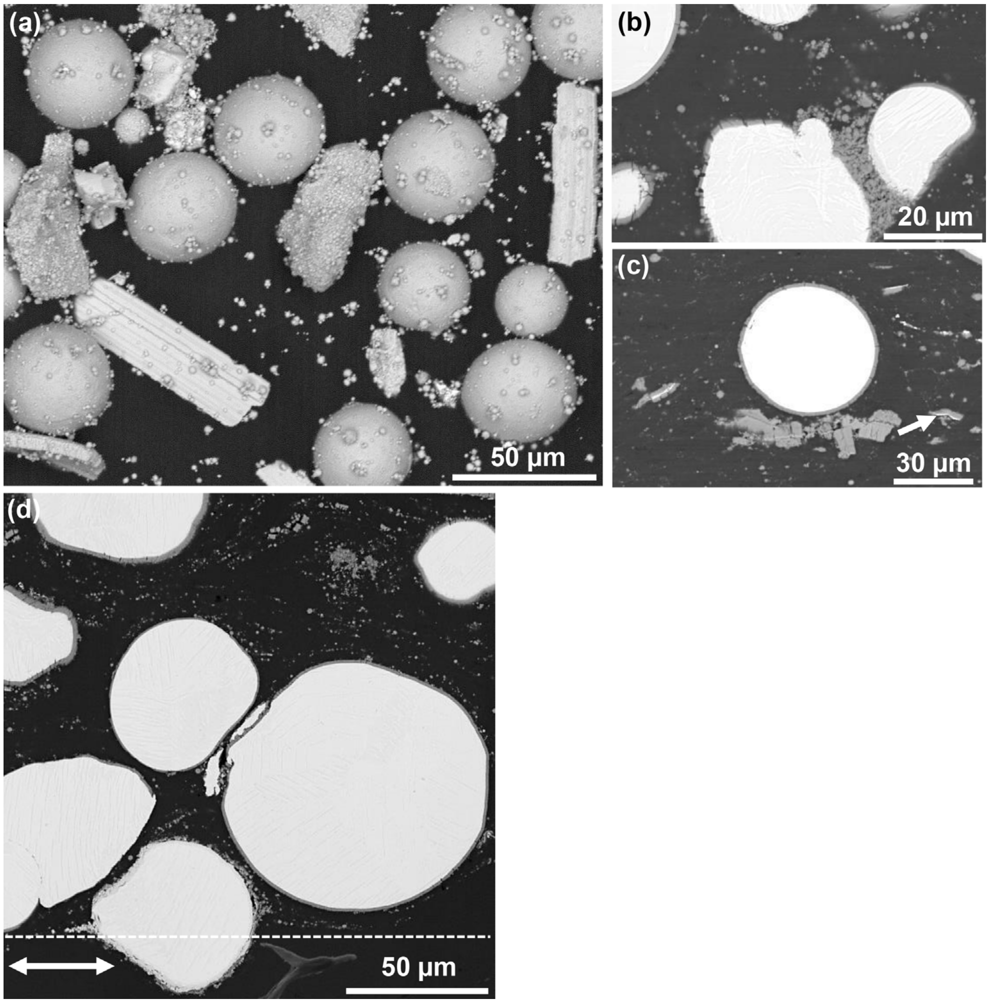

Fig. 7. SEM micrographs taken on: (a) a PVD-coated powder from one EMPIrE batch, (b) SF-202 plate, (c) EMP-819 plate, (d) EMP-828 plate (white arrow: rolling direction – dashed line: approximate position of fuel-cladding interface).

Table 3. ZrN coating thickness measurements.

	ZrN coating thickness (μm)			
Plate designation	Minimum thickness	Maximum thickness	Mean thickness	Standard deviation
EMP-711	0.80	1.74	1.19	0.22
EMP-717	0.94	2.02	1.37	0.26
EMP-803	1.05	2.16	1.53	0.29
EMP-819	1.59	2.52	1.98	0.23
EMP-828	1.03	2.01	1.36	0.24
SF-202	0.68	1.40	1.06	0.20
SF-402	1.11	2.35	1.71	0.33

4 Conclusion

In this study, five mini-plates, from EMPIrE test matrix, and two full-size plates, from SEMPER FIDELIS one, were examined by OM, SEM and EDS. All of them were made with atomized U(Mo) particles (from KAERI), homogenized or not at 1000 °C, and PVD-coated with a ZrN layer.

OM macrographs showed that the fuel core thickness and the distribution of U(Mo) particles within it were more irregular in EMPIrE mini-plates. U(Mo) particles microstructure was similar in both types of plates and corresponded either to a fine solidification microstructure, for plates made with as-atomized particles, or to relatively large equiaxed grains containing lamellas, for plates made with annealed powder.

In EMPIrE plates, the sphericity of particles seemed to be related to their metallurgical state (as-atomized or annealed). This difference was not observed in the case of SEMPER FIDELIS plates, which were both characterized by a lower particle mean sphericity value, suggesting that the full-size plates rolling conditions led to a slightly greater deformation of U(Mo) particles, whatever their mechanical properties, compared to mini-plates. Mean particle Mo content, measured by EDS, was almost the same in all plates.

In all studied plates, coated particles often exhibited damaged ZrN layers. The following main types of defects were identified: (i) a delamination of the coating, around certain particles, in a preferential direction parallel to the rolling one, (ii) the development of radial cracks in ZrN especially in the thicker layers, (iii) multiple cracks in the coating on significantly deformed particles or on those in direct contact, and (iv) a considerable reduction of the adhesion of the ZrN layer when an underlying oxidized layer was present at the surface of U(Mo) particles, as often observed close to the fuel-cladding interface.

All of these damages were difficult to quantify. Delaminations occurred preferentially in plates made with as-atomized particles, and seemed to be more marked in EMPIrE ones. Radial cracks were closely related to ZrN thickness, which varied between nearly 1 and 2 μm in both sets of plates. Damages linked to contacts were high in all plates. Finally, those linked to the powder oxidation were more numerous in plates made with homogenized particles (as heat treatment at 1000 °C induced the oxidation of some particles), and especially in EMPIrE ones.

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Author contribution statement

Both EMPIrE and SEMPER FIDELIS in-pile irradiation tests are international experiments, involving several partners. I. Glagolenko and D.D. Keiser, from INL (USA), participated more particularly in the design and implementation of the EMPIrE irradiation. S. Van den Berghe and A. Leenaers, from SCK-CEN (Belgium), worked on these two experiments. They supervised the heat treatment and PVD-coating of U(Mo) particles at SCK-CEN (Belgium) and their shipment to Framatome-CERCA (France), where the fuel plates were manufactured, under the responsibility of B. Stepnik, J. Allenou and F. Vanni. After the manufacturing, all authors were involved in the definition of a characterization plan, which included the choice of EMPIrE mini-plates and SEMPER FIDELIS full-size plates to analyze. B. Stepnik, J. Allenou and F. Vanni contributed to the sample cutting and shipment to CEA/Cadarache (France), where they were prepared and examined. X. Iltis coordinated the examinations and processed the experimental data. X. Iltis and H. Palancher analyzed the results and wrote the manuscript, with critical feedback of all authors.

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