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Analysis of Thermal Evolution of $\text{Si}_2\text{U}_3/\text{Al}$ Calcined Miniplates

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Abstract

As part of a process called *cerus* for the conditioning of spent fuel elements from research reactors (which is about its immobilization in a sintered ceramic matrix of uranium oxide) were performed calcinations and sintering on an aluminum miniplate that representing a real plate from MTR fuel type, but containing natural Si_2U_3 instead of enriched. Product of heat treatments it results a complex multi-phase material, it was studied its behavior during and after heat treatments involved in the *cerus* process. There were performed differential thermal analysis (DTA) in air to 1250 °C, and X-ray diffraction at high temperature (700-1100 °C) to elucidate which compounds were generated during the calcination and sintering and the moment when these transformations occur, and as a result there were obtained complex alloys of Al-U, and the formation of oxides of aluminum and uranium. On the other hand, tests were carried out on compacted powder of calcined miniplates in a high temperature microscope (HSM) and dilatometry to know their linear and surface response to the heating and sintering in order to characterize their individual contributions to the final material, resulting in an important expansion of about 25% which was attributed to oxidants interactions and/or formation of uranium aluminides and silicides. Several intermetallic of Si-U and Al as well as the generation of oxides of aluminum and uranium were found.

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Waste conditioning, oxidation, spent nuclear fuel, heat treatments

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1. Introduction

The main objective of the management of spent fuels and radioactive wastes is to treat / modify them in order to protect the environment and human health today and in the future without that being a trouble for the coming generations. The immobilization has been the path chosen to conditioning radioactive wastes, spent fuel from power reactors and liquid wastes from nuclear industry.

With regard to spent fuel from research reactors MTR (Material Testing Reactor) type, they are within decay pools in the grounds of the reactors, waiting about 10 years for its cooling till the next step in its management, and as a result of this time underwater, it was founded some corrosion signs on the aluminum cladding of the plates fuel, generating an imminent and undesired release of radionuclides to the pool water.

The MTR type fuel elements have 19 to 21 aluminum plates slightly curved, placed in an aluminum frame, within each plate locates the Si_2U_3 fissile material enriched to ^{235}U 19.75%, resulting in a parallelepiped box; 16 of these elements are placed in the reactor core. In the Nuclear Materials Department in Bariloche Atomic Center (CAB) have been proposed methods of treatment for the conditioning of these spent MTR fuel plates consisting on their immobilization as sintered compacts so that they can be temporarily disposed in dry reservoirs while deciding about its final disposition.

The named *cerus* process [Spanish acronym for ceramization of radioactive elements in sintered uranium, Arboleda (2011)] consists of a series of simple physical procedures applied on a fuel miniplate like the real MTR described above but with natural U_3Si_2 and then isotopically diluted with U_3O_8 (natural-U) to reduce its nominal enrichment and later sintering the mixture to obtain a ceramic compact with suitable mechanical and chemical resistance.

2. Experimental procedure

As a substitute for a real fuel plate it was used a miniplate (MP) as shown in the scheme in Fig. 1 of reduced size respect to the real one; the MP was provided by the ECRI Department (Spanish acronym for Fuel Elements for Research Reactors) of Constituyentes Atomic Center to the Nuclear Materials Department in Bariloche Atomic Center. This MP is composed by a pair of 6061 aluminum sheets (96% Al - 1.2% Mg - 0.8% Si) covering tightly the U_3Si_2 fuel-plate (natural uranium, enrichment 0.711%). This MP was taken as representative material of the plate irradiated in order to study the response to the heat treatments involved in the *cerus* process. The plate mass contains about 55wt% of uranium silicide and 45wt% corresponds to aluminum which is partially in the meat (mixed with the silicide), although the largest percentage of Al is provided by the cladding.

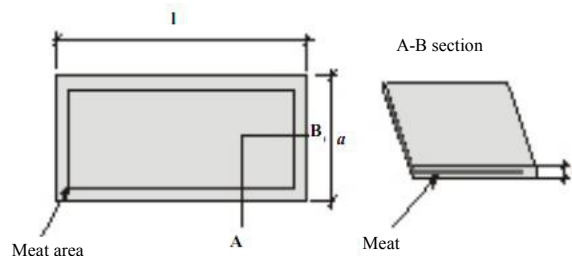


Fig. 1. Scheme of a miniplate

The distribution of the components in the meat was analyzed through EDS mapping using an Edax Genesis 2000 detector attached to a SEM FEG NovaNano 230 from FEI, these mappings are shown in Figure 2. Previous analysis of XRD showed the presence of an intermediate phase of AlU product of the interaction between the meat and the cladding.

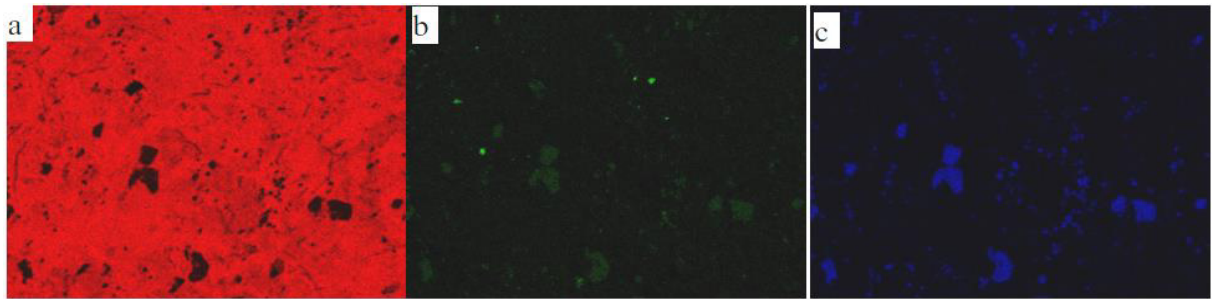


Fig 2. EDS mapping of the components in the meat (a) Al; (b) Si; (c) U.

Table 1 shows descriptive data for the MP and its components, composition was analyzed by EDS; the dimensions are proportional to a standard MTR fuel plate.

Table 1. Characteristics of a miniplate.

Mass (g)	26.4		
Dimensions (cm)	Length:11	Width:5	Thickness:0.05
Content	Al(%wt)	Si(%wt)	U(%wt)
Meat	38.66	7.31	54.02
Cladding	96	0.8	--
Maximum density (g cm^{-3}) of U inside the meat	4.8		

MP was cut in ~ 5 mm pieces and these were calcined at 750°C during 5 h to embrittle the aluminum, we noticed that at this temperature the aluminum is partially melted, but due to the interaction with the meat (as discussed later) after the heat treatment result fragile and deformed pieces, Fig. 3 shows a photo of cut MP after the first calcination. Then, the calcined MP was grounded in a mill ring. The obtained fine powder was calcined again aiming at complete oxidation.



Fig 3. First calcined miniplate to 750°C (5h).

After the heat treatments, the weight increase due to oxidation was about 0.5%. This calcined powder was mixed with a given amount of natural U_3O_8 such as the nominal enrichment was reduced from about 9.5% (for real fuels) to 1%, and then pressed into pellets, these were sintered in air at 1200°C . This work focuses on the process of calcining and sintering MP separately and its behavior during the forming of the final sintered waste-block.

Studies of the thermal behavior of MP powders were conducted by dilatometric measurements using a vertical differential dilatometer Theta Dilatronics II-SDP at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ under O_2 flow and atmospheric pressure, for which were prepared small pressed pellets of 6 mm in diameter and 3 mm high.

DTA differential thermal analyzes were carried out in a Q600/2690 SDT Universal VIIIATA apparatus and under N_2 flow at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. On the other hand, in a high temperature microscope (hot stage microscope) HSM assembled in the laboratory of Nuclear Materials Department, it was analyzed the area variation of the shadow for a sample (initial height of 5 mm) made of compacted calcined MP-powders conveniently illuminated, during heating (at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air). Studies through XRD at high temperature were performed in a Philips Panalytical X'pert MRD/MPD 7-axis, the X-ray source was $\text{CuK}\alpha = 0.154056\text{ nm}$ (acceleration voltage 40 kV and current of 40 mA) in the Functional Materials group (University of Saarland, Germany). Analyzes were performed between 700 and 1100 $^{\circ}\text{C}$ and the diffractograms were recorded every 30 $^{\circ}\text{C}$.

From the XRD data the relevant expansions starting at 600 $^{\circ}\text{C}$ were obtained, also, there was significant increase in mass as well as phase changes during heating. It was aimed at identifying the generated phases and changes in volume to design and improve the overall process and get compact cerus with improved properties. U-Si system is characterized by the existence of several intermetallic compounds like Si_3U , Si_2U , $\text{Si}_{1.88}\text{U}$, Si_5U_3 , SiU , SiU_3 and Si_2U_3 as suggested in studies of Berche et al. (2009) and the phase diagram of Fig. 4.

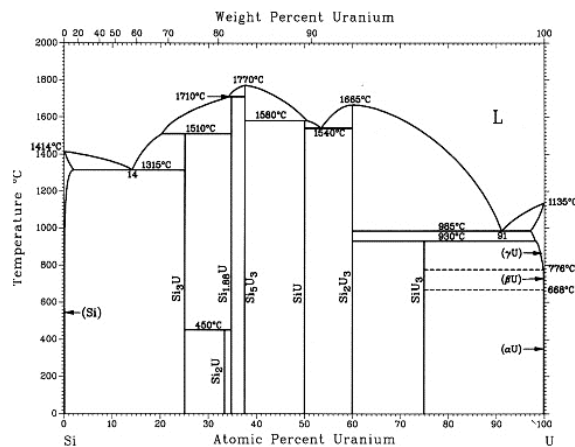


Fig 4. Phase diagram Berche et al. (2009).

3. Results and Discussion

3.1. First calcination

It was noted a significant expansion in dilatometric and HSM data around 600 $^{\circ}\text{C}$, this expansion was about 12% for samples diluted vitrocerus process natural U_3O_8 and having 10% VG98 borosilicate glass added as a binder, this expansion was independent of measuring atmosphere as reported in reference Arboleda (2012). Densification starts shortly before the 1000 $^{\circ}\text{C}$ and sintering is completed at about 1150 $^{\circ}\text{C}$. This previous swelling is not convenient in the final material that it must to be a dense and tough compact.

Differential thermal analysis in Fig. 5 shows a curve with marked reactions, beginning with an endothermic peak around 620 $^{\circ}\text{C}$, which denotes aluminum melting followed by an endothermic peak at 850 $^{\circ}\text{C}$, which produced reactions between uranium oxides and aluminum, as suggested by Adams et al. (2011), it is clear that the system does not reach the equilibrium during the treatments. From XRD analysis this can be attributed to the formation of intermetallic compounds as well as incomplete oxidations, this corresponds to the volume changes and expansion data measured with the dilatometer.

It is also notorious a mass-increase in the thermogravimetric curve in Fig. 6 with an isotherm at 900 °C (1h) , which amounted to an overall increase of 12.7%.

Furthermore, it should be noted that the plates also present significant swelling during the burn-up stage in the reactor (during its use as fuel) as reported by Adams et al. (2011).

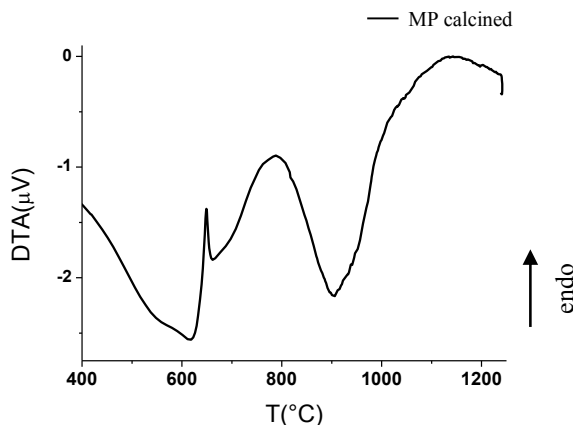


Fig 5. DTA graph for powders of calcined MP.

In the diagram Al-Si-U according to Dwight (1982), between 700-800 °C there is a rather large liquid phase region rich in aluminum, the authors recommend treating MTR type fuel plates like those of uranium aluminum alloys Al-Si-U and expect the response should be quite similar to the calcinations data.

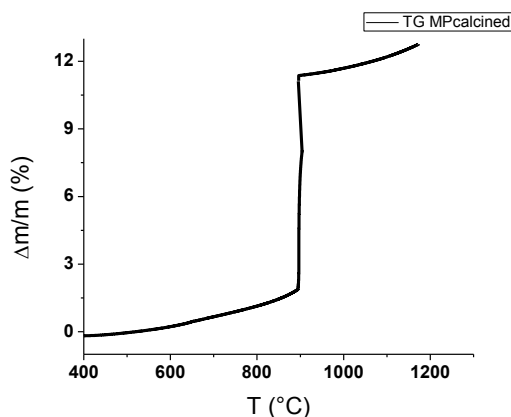
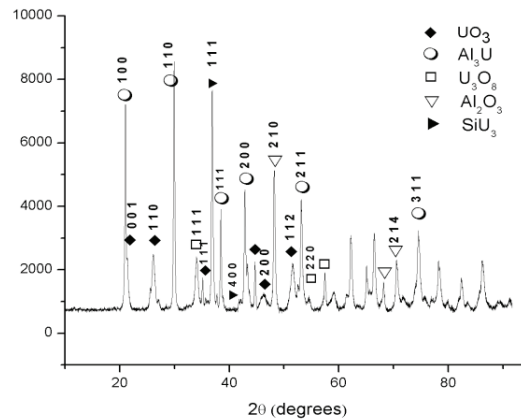


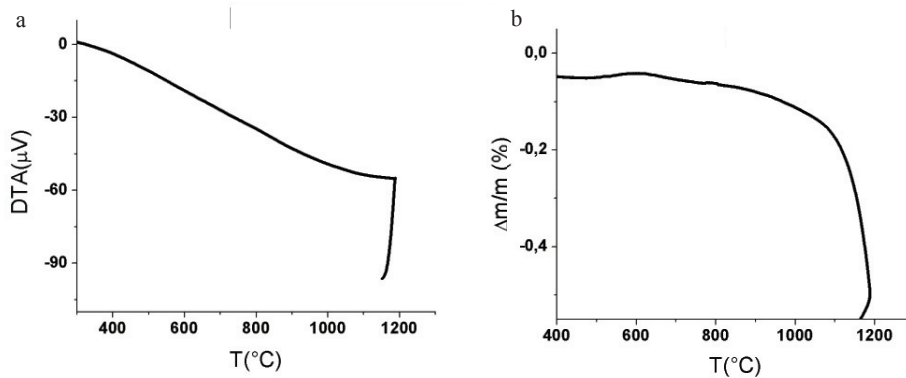
Fig 6. Termogravimetric graph for powders of calcined MP to 750 °C (5 h).

However, it has been found that above 800 °C the reactions continue and they interfere in the poor densification of calcined MP compact. The generation of intermetallic compounds of different structures during the transformation from U_3Si_2 to U_3Si (this last one having a lower density) and also the oxidation that took place, is confirmed by XRD analysis, the corresponding diffractogram carried out at 700 °C is shown in Fig. 7, which indicates the formation of UO_3 , U_3O_8 , Al_3U , Al_2O_3 and SiU_3 . In the work by Marin et al. (1996) for temperatures above 609 °C the precipitated phase identified by XRD corresponds to $U(Al, Si)_3$.



3.2. Second calcination

Aiming at finding stability conditions, besides the MP-calcination at 750 °C for 5 h, it was conducted a further calcination at 950 °C during 2 h. New differential thermal analysis and thermogravimetry measurements for MP calcined at 950 °C for 2 h in air are shown in Fig. 8. At this time, no mass gain is detected but instead a decrease of about 0.5% was found at 1100 °C, the temperature at which higher density is obtained; on the other hand the differential thermal analysis graph did not show significant transformations.



However, the dilatometric analysis after the second calcination treatment (Fig. 9) revealed again a swelling of about 5% of the initial length, this expansion begins also at 650 °C and it was found that the compact starts the densification just before the 1000 °C, but not enough to reach its maximum densification due to limitations of dilatometric equipment.

On the other hand, new high temperature microscopy and dilatometry measurements in O₂ up to 1080 °C, showed that due to the new cycle on the same pellet of MP discussed above, the material did not present the swelling previously experienced, reducing from 25% to 2% the increase in area at 800 °C -respect to the first calcination- there was a further reduction in the area of 3% overall.

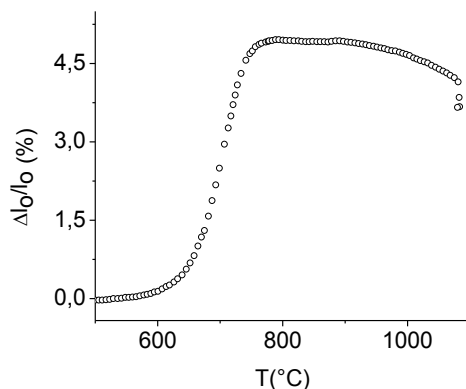


Fig 9. Dilatometry curve for MP calcined 950 °C

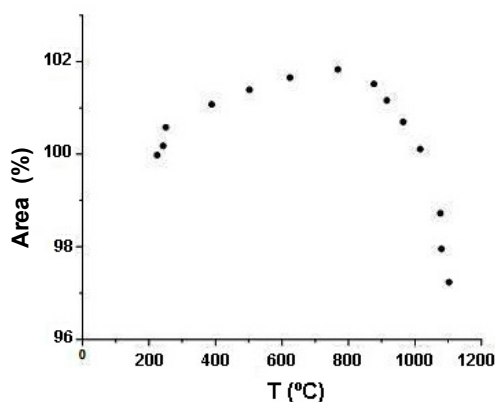


Fig 10. Hot stage microscopy curve for change in area of resintered MP.

In this instance the phases identified through the program X'Pert Highscore correspond to oxides of uranium and aluminum as U_3O_8 (01-074-0562), UO_3 (00-045-0857) and Al_2O_3 (01-075-1862) and as silicides of uranium Si_2U_3 (01-080-1374) and Si_2U (00-013-0545), these compounds would exhibit more stability and have a density higher than the phases generated at the first calcinations.

This material will be mixed with natural or depleted U -in order to decrease the residual enrichment- and a small percentage of borosilicate glass -to promote the sintering of this mixture- and achieve a final material with the shape of cylindrical compacts.

Nevertheless, studies by Dwight et al. (1982) indicates that the transformations in the system of MP induced by heating are quite slow, and the suggested treatments to complete certain transformations comprising several days. Considering this, we must define which treatments will be carried out and if it is worth doing prolonged processes due to the vision of implementing this method on a larger scale in hot cells for conditioning real irradiated fuel plates.

4. Conclusions

The effect of heat treatments on a miniplate that mimic a spent fuel plate from MTR research reactor was studied, registering significant swelling attributed to structural changes due to the generation of intermetallic compounds U-Si and Al oxides, U and Si.

The system Al-Si-U is quite unstable and it was difficult to identify the phases generated during heat treatments involve in the proposed process *cerus*. Several publications consulted also make note of ambiguity / complexity of this material and also prolonged treatments are necessary to achieve the stability

The expansion of the system is inconvenient due to the application that is sought, so new treatments were performed to achieve partial stability. It has been proposed a prolonged calcination at 950 °C to achieve compounds with denser structures.

For pellets of MP powders after resintering, the final maximum densification achieved was about 3% respect to its initial length.

Acknowledgements

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References

- Arboleda, P.A., 2011. Acondicionamiento de elementos combustibles irradiados de reactores de investigación”; Master’s degree thesis Instituto Balseiro. Bariloche. Director: Rodríguez, D.S., Co: Prado, M.O.
- Arboleda, P.A., Rodríguez, D.S., González Oliver, C.J.R., 2012. Study of Thermal Evolution of Uranium Oxides Sintered in the Vitrocerus Process; *Procedia Materials Science* 1, 535-542.
- Arboleda, P.A., Rodríguez, D.S., Prado, M.O., 2012. Vitrocerus: An Alternative for Processing MTR Spent Fuel from Research Reactors. *Materials Research Society Symposia Proceedings* 1475, 203-208.
- Berche, A., et al., 2009. Thermodynamic study of the U–Si system. *Journal of Nuclear Materials* 389, 101–107.
- Adams, T.M., Duncan, A.J., 2001. Development of a Treatment Technology for Diluting Highly Enriched Al-Based DOE Spent Nuclear Fuel: Principles and Practices; WSRC-MS-2001-00575. Conference GLOBAL. Paris.
- Dwight, A. E., 1982. A study of the uranium-aluminum-silicon system. In: “Technical Report to Argonne National Lab”. IL. W-31-109-ENG-38.
- Bethune, B., 1969. Structural Transformation in U_3Si . *Journal of Nuclear Materials* 31 197-202.
- Marín, J., et al., 1996. Synthesis and clad interaction study of U_3Si_2 powders dispersed in an aluminum matrix. *Journal of Nuclear Materials* 228, 61-67.