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POWDER PRODUCTION OF URANIUM– MOLYBDENUM - METAL ALLOYS APPLYING HYDRIDE - DEHYDRIDE METHODOLOGY

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ABSTRACT

U-Mo alloys are candidate materials for use as the fuel phase in high-density fuels. In order to manufacture dispersion fuel elements it is necessary to develop effective methodologies for powder production. Previous results using hydride-dehydride process (HD) shown advantages related to simplicity of process, low cost equipment and the ability to produce irregular shapes and a wide size range. In other hand, according to recent studies, Si, Ti and Zr seem to be beneficial to control the interaction between fuel particles and their surrounding matrix. Until today, there is no information about application of HD process in these modified UMo-Me systems. This paper presents the first results on the application of HD processing for powder production of UMo containing 1 wt% of these third elements. Taken into account the disadvantages of HD processing, a modified methodology for powder production based on HD processing for UMo-Me alloys is proposed. Using a sequence of steps closed by a final controlled passivation stage, is possible to assure a safe and useful product. According to first results, fragmentation of samples was possible in each system and the powder produced seems to be adequate for dispersion fuels.

1.- INTRODUCTION

PIE results recently published for UMo dispersion fuels [1] are in accordance with the latest results reported by CCHEN [2] related to out of pile tests that confirm the positive influence of small amounts of some third element added to UMo alloys, whose presence seem to be beneficial to control the interaction between fuel particles and their surrounding matrix [1]. Additionally, beneficial effect produced by silicon added to the aluminum matrix [3] appears as promissory solutions for interaction problem, apparently the efforts are well focused and the final solution is very near. Therefore, the following challenges will be in relation to the optimization of available powder production methodologies in order to meet international standard and adequate specifications for fuel manufacturing, as well as the optimization of fuel plates manufacturing processing.

The Chilean U-Mo fuel development program, launched five years ago, has been progressing in dispersion fuels using UMo powder made by means of mechanical crushing, although some preliminary results have been obtained using cryogenic milling and hydride - milling – dehydride (HMD) methodology applied to U - 7% wt Mo alloys [4]. Addition of small amounts of selected third elements into binary U-Mo alloys promotes an increasing in brittleness [5],

nevertheless this effect is not enough to improve the low efficiency of the mechanical grinding methods.

The atomization methods seem to be the best alternative for powder production, although a brief revision of bibliographical data allows knowing some disadvantages; the use of inert gas for fragmentation and fast solidification produces particles near to spherical shapes, which could to cause particle incrustation in thin Al cladding [5]. Due to this same reason, the particles could be easily segregate from the aluminum matrix powder during and after blending, besides, spherical particle dispersion generates levels of residual porosity in the aluminum matrix five times lower than those obtained using morphologies irregulars [6] what could to limit the reserve volume useful to contain fission gases and, as consequence, it would increases the undesirable swelling phenomenon.

According to several authors, an alternative interesting for powder production would be then the method of hydride-dehydride- HD, process that results very attractive considering the simplicity of the methodology, the low cost [7], low power consumption and simplicity of the equipment [5], In whole, all authors conclude that this process is an effective option to manufactures U-Mo irregular fuel powders with necessary shape, size, phases, chemical compositions [8], and crystalline structure. However, HD processing also have some disadvantages related to the oversize of the particles produced and his extremely pyrophoric characteristics (only should be handled in an inert atmosphere) [9]. Taken into account all these consideration and based on the information above mentioned, resulted a CCHEN's proposal to develop at laboratory-scale a suitable methodology for powder production based on HD processing for UMo-Me alloys using a well defined sequence of steps closed by a final controlled passivation stage capable to obtain a safe and useful product. Thus, this article presents the first results and discussion derived from application of HD process for UMo-Me powder production.

2. EXPERIMENTAL PROCEDURES

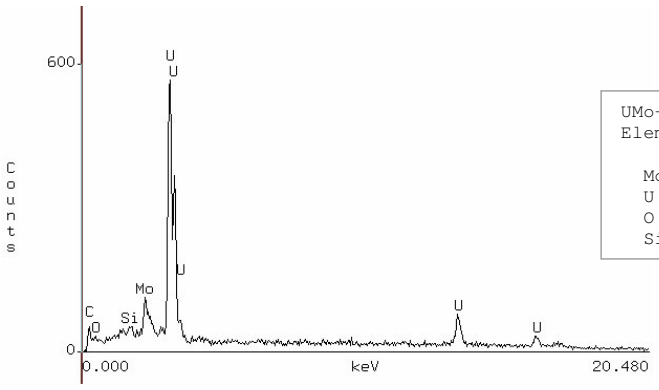
The samples for hydride-dehydride (HD) tests were extracted from ingots obtained through induction melting and poured under inert atmosphere (Argon) into closed graphite mould. Small pieces of ingots (50 – 100 g) were used for density measurements using immersion methodology. Before fragmentation tests, the samples were chemically cleaned using a dilute acid solution. With the purpose of avoid uncontrolled oxidizing reaction (pyrophoric characteristics) and excessive oxidation of samples, the fragmentation treatment was designed taken into account reducing the time intervals between stages and maintaining the furnace chamber always closed until the last stage was finished. The hydriding annealing was carried out to temperatures in the range of decomposition of metastable γ-phase and soaking times depending on sample mass, using hydrogen flow and keeping the pressure slightly upper than atmospheric level. After the hydriding step is completed and sample is cooled, the hydrogen is drawn off by heating the hydrided fragments under vacuum (700 °C, 2h, and secondary vacuum). In this stage occurs uranium hydrides decomposition and the hydrogen slowly dissociates from the particles leaving only the UMo-Me alloy in powdered form. After cooling the samples, a homogenization vacuum annealing was applied in order to recover the metastable γ-phase of initial state, followed by an argon flow quenching (200°C/min). The final stage was passivation at room temperature, it consists in keep the

samples under vacuum and gradually to admit air into furnace chamber (secondary vacuum: 48h – rough vacuum: 48h - natural vacuum leaking: 48h). After these six days the samples were extracted from chamber, canned and stored in glove boxes. The fragments produced for each composition were characterized by means of SEM with EDS, XRD and total hydrogen measurements.

3. RESULTS AND DISCUSSION

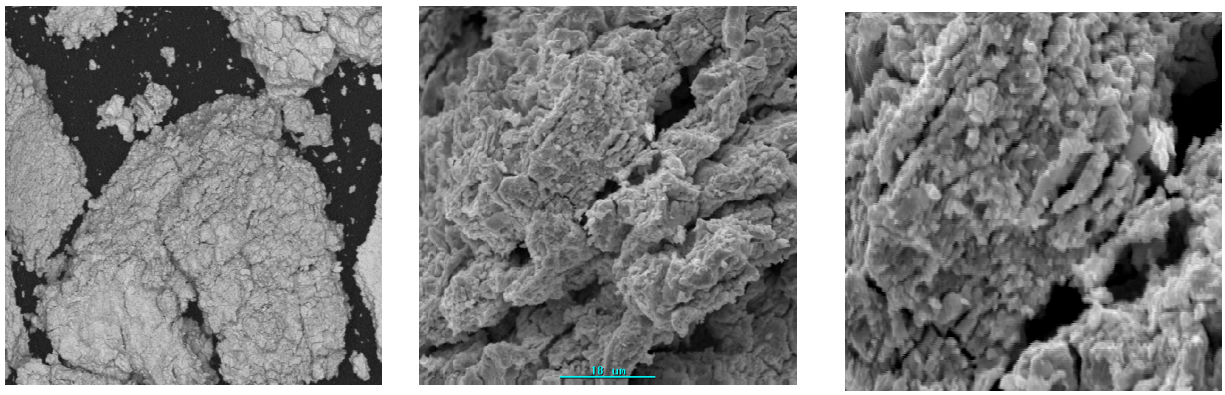
Alloy composition	Density (g/cm^3)	Uranium Density (gU/cm^3)
U + 10% wt Mo	17,14	15,43
U + 7% wt Mo	17,45	16,23
U + 7% wt Mo + 1% wt Si	16,58	15,25
U + 7% wt Mo + 1% wt Ti	16,68	15,35
U + 7% wt Mo + 1% wt Zr	16,97	15,61

Table 1.- Experimental density and calculated uranium density of UMo and UMo-Me alloys.



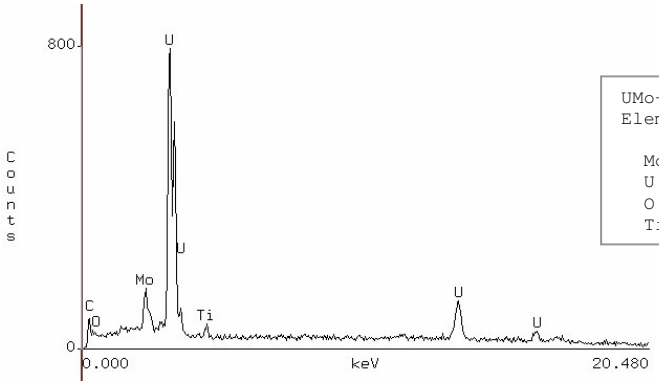
UMo-Si HD EDS analysis area scanning 200x

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0509	1.415	14.12	7.21	+/- 0.62
U -M	0.8558	1.066	72.03	91.23	+/- 2.24
O -K	0.0013	5.303	7.99	0.68	+/- 0.81
Si-K	0.0038	2.319	5.87	0.88	+/- 0.14



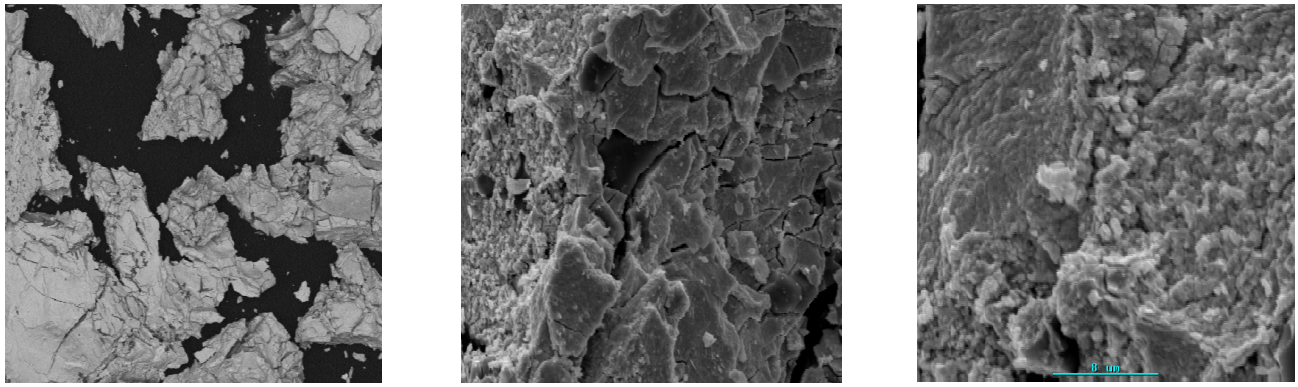
200X **2000X** **5000X**

Figure 1.- EDS quantitative analysis applied in 200X area scanning and SEM micrographs of U-7wt% Mo + 1% Si powders produced by HD processing.



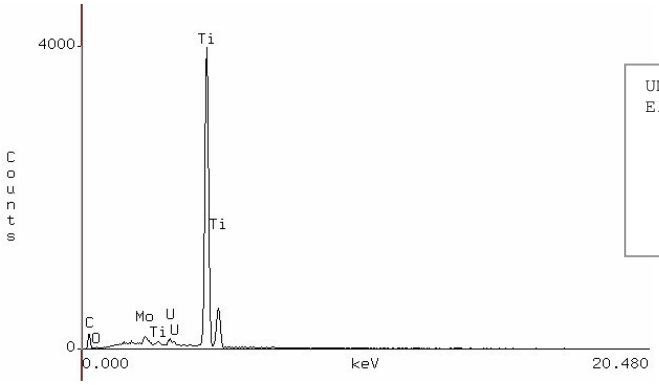
UMo-Ti HD EDS analysis area scanning 5000x

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0542	1.400	15.15	7.59	+/- 0.51
U -M	0.8488	1.063	72.55	90.19	+/- 1.93
O -K	0.0008	5.412	5.15	0.43	+/- 0.74
Ti-K	0.0107	1.674	7.15	1.79	+/- 0.17



200X **2000X** **5000X**

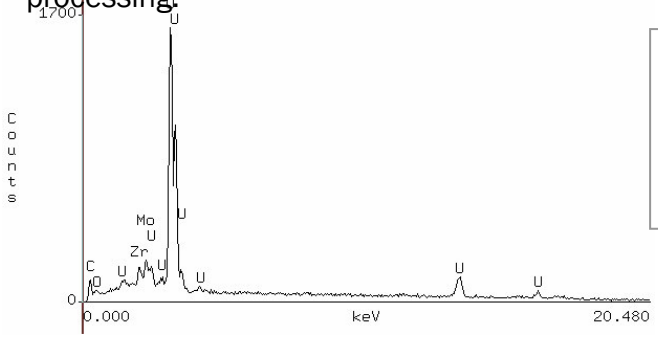
Figure 2.- EDS quantitative analysis applied in 5000X area scanning and SEM micrographs of U-7wt% Mo + 1% Ti powders produced by HD processing.



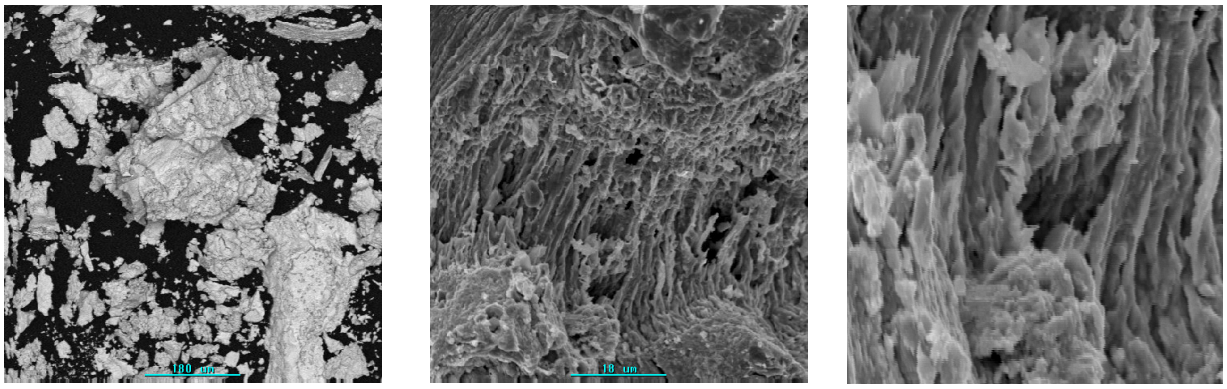
UMo-Ti HD EDS analysis Ti rich dark particle 2000x

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0306	1.150	1.83	3.52	+/- 0.28
U -M	0.0514	0.915	0.99	4.70	+/- 0.58
O -K	0.0005	14.035	2.13	0.68	+/- 0.88
Ti-K	0.8620	1.057	95.05	91.10	+/- 0.57
Total			100.00	100.00	

Figure 3.- EDS quantitative analysis applied at dark particle (Ti rich) located at center of 2000X micrograph (spotted scanning) of U-7wt% Mo + 1% Ti powders produced through HD processing.

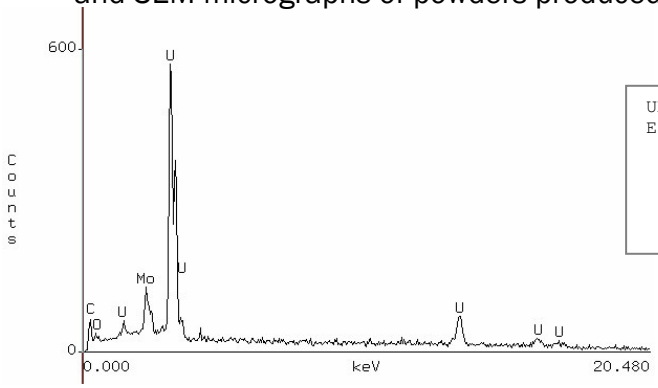


UMo-Zr HD EDS analysis area 5000x					
Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0293	1.446	8.00	4.24	+/- 0.25
U -M	0.8605	1.060	69.45	91.20	+/- 1.34
O -K	0.0027	5.270	16.34	1.44	+/- 0.43
Zr-L	0.0190	1.639	6.20	3.12	+/- 0.22
Total			100.00	100.00	

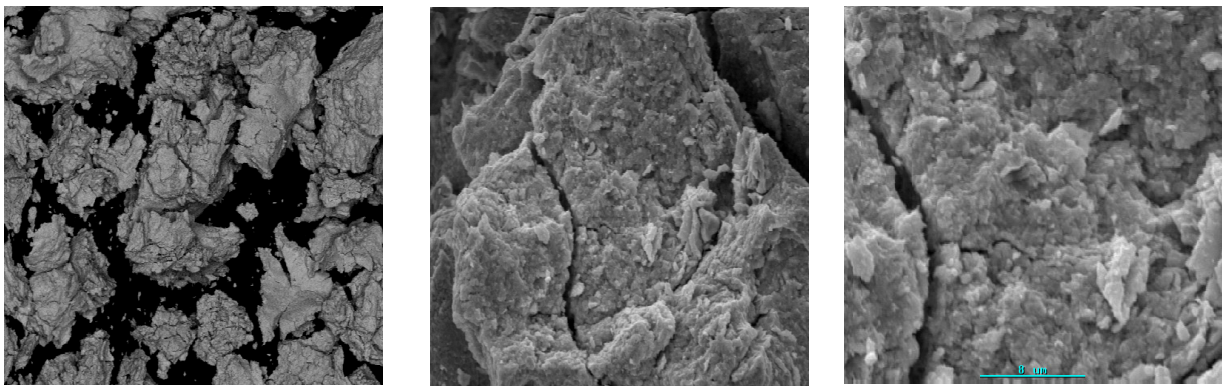


200X **2000X** **5000X**

Figure 4.- EDS quantitative analysis applied at 5000X area scanning of U-7wt% Mo + 1% Zr and SEM micrographs of powders produced through HD processing.

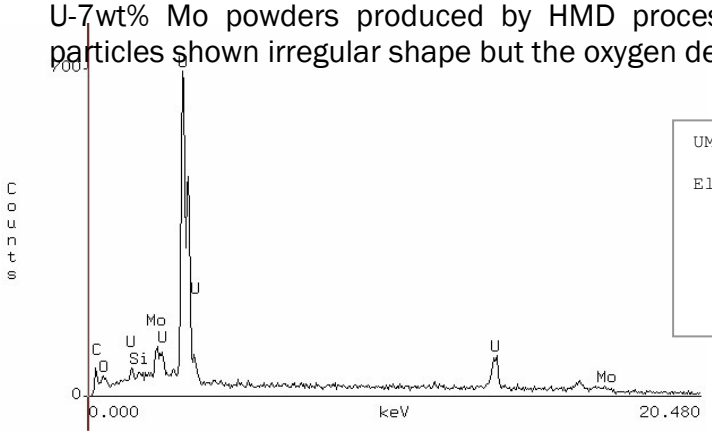


UMo-HMD EDS analysis area scanning 200x					
Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0575	1.407	14.09	8.09	+/- 0.65
U -M	0.8364	1.073	62.98	89.71	+/- 2.24
O -K	0.0041	5.348	22.93	2.20	+/- 0.86
Total			100.00	100.00	



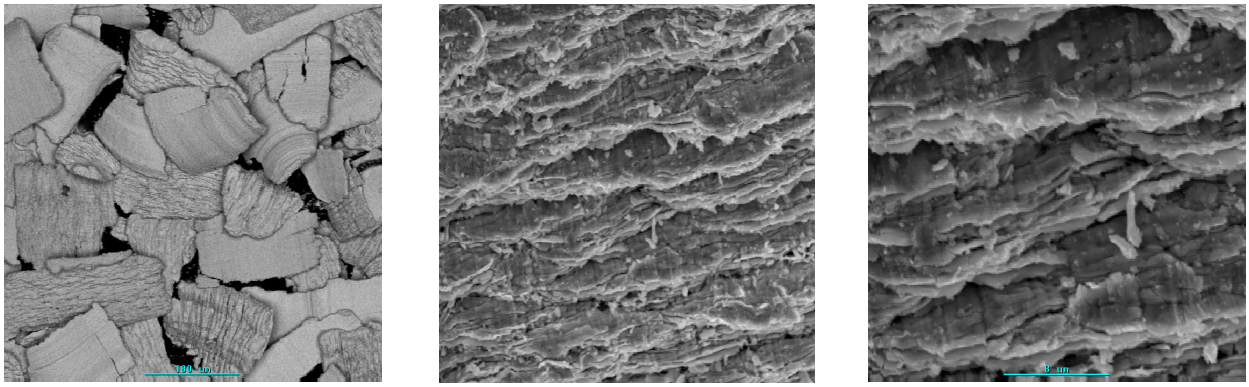
200X 2000X 5000X

Figure 5.- EDS quantitative analysis applied in 200X area scanning and SEM micrographs of U-7wt% Mo powders produced by HMD processing (2005) [10]. As in HD powder, the particles shown irregular shape but the oxygen detected is considerably greater.



UMo-Si Ground Powder EDS analysis area scanning 200x

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Mo-L	0.0333	1.426	8.75	4.75	+/- 0.37
U -M	0.8905	1.045	69.06	93.02	+/- 2.03
O -K	0.0033	5.201	19.00	1.72	+/- 0.77
Si-K	0.0022	2.358	3.20	0.51	+/- 0.12
Total			100.00	100.00	



200X 2000X 5000X

Figure 6.- EDS quantitative analysis applied at 200X area scanning and SEM micrographs of of U-7wt% Mo + 1% Si powders produced through mechanical grinding processing. Particles exhibits shavings shape, shown plastic deformation typical of ductile fracture mechanism. The oxygen level is higher than the same alloy comminuted by HD processing (Figure 1)

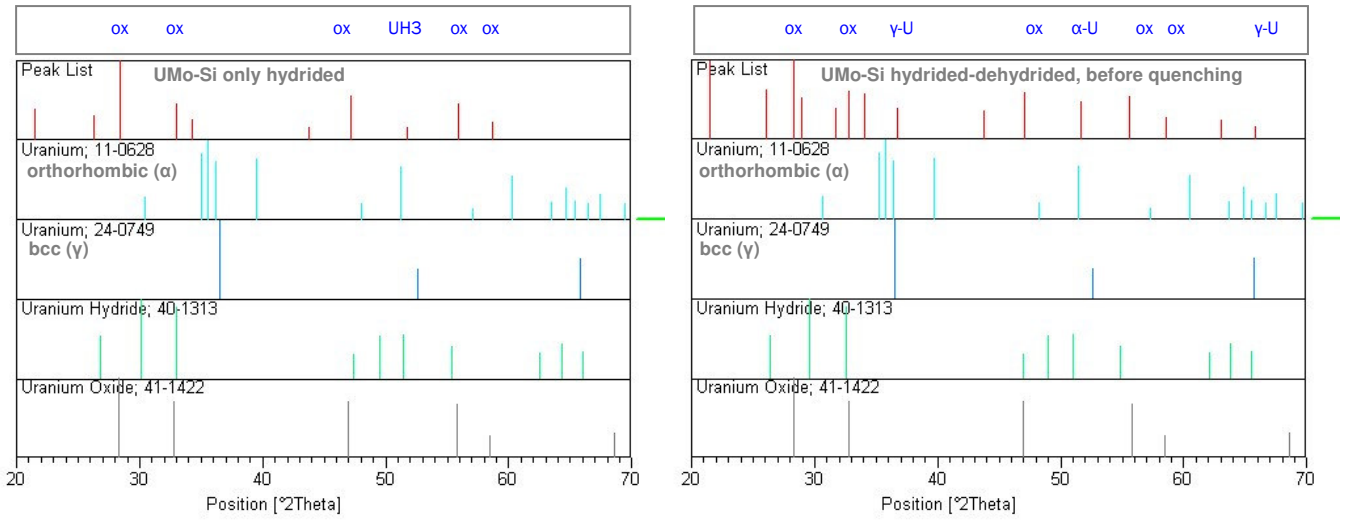


Figure 7.- Comparison of XRD patterns for UMo–Si powders produced through HD processing.(left) after hydride stage and (right) after dehydride stage (before quenching). UH_3 compound appear only in after hydride specimen, meanwhile α and γ phases were detected in after dehydride sample.

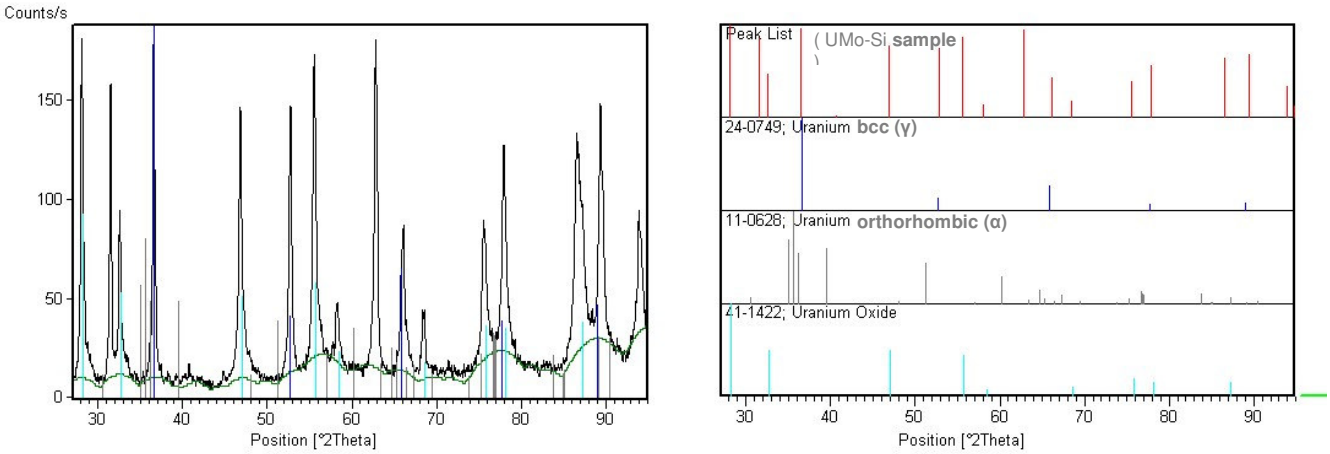


Figure 8.- XRD pattern for UMo–Si powders produced through HD processing after quenching and passivation state. α-phase was not detected. Oxides and γ-phase seems to be the most relevant micro-constituents.

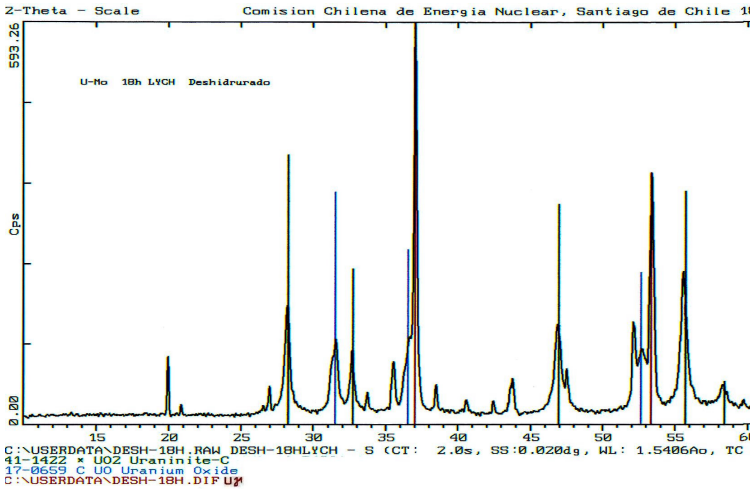


Figure 9.- XRD pattern of powders produced through HMD processing (2005) [10] starting with cold rolling and crushing state U-7%wt Mo alloy. Unidentified peaks 2θ=35,6° and 2θ=52° seem to indicate presence of α-Phase.

RESULTS AND DISCUSSION (continuation)

The sequence design of HD process proposed in this article has allowed improving in safety conditions very necessary in thermal treatments that involve hydrogen under pressure. This simple experimental design allows developing and completion of thermal treatments giving enough time to the occurrence of physical, chemical and micro structural transformations. The passivation of powders takes place in final stage; meanwhile the controlled atmosphere keeping during the intermediate stages allows controlling the pyrophoric reaction, diminishing the risk for materials, equipment and operators. With the purpose of achieving equilibrium between pyrophoric characteristics control and oxidation of particles, especially in smaller size, further work is planned for optimizing the passivation stage.

According to first experimental results, their applicability of HD processing in UMo-Me alloys was demonstrated in terms of capability for produces fragmentation of solid samples. The particles generated have irregular shape and SEM images shown to wide range of size. The finest with about 20 μm meanwhile coarser particles reached sizes of 1 or 2 mm. Oversize of particles constitutes a disadvantage of HD processing; nevertheless, SEM images of particles shown an extraordinary embrittlement of material evidenced by particles plenty of micro cracking. Thus, the size of coarser particles could be easily reduced using any mechanical grinding method.

EDS quantitative analyses reveals important levels of oxygen which would be part of thin uranium oxide layers in the particle's surface formed, probably, during passivation stage. These oxide layers seem to be beneficial since it could act as a barrier to the inter-diffusion of fuel/matrix, hindering the interaction between fuel particles and Al matrix.

Crystalline phases present in samples were not clearly detected through XRD analyses, due, probably, to the oxide coating of particles or broadening of peaks caused by presence of fine sub-grains or high levels of stress. Anyway, XRD pattern detect the presence of α-phase after dehydriding stage and γ-phase as predominant micro-constituent for quenching condition. It means that HD processing retains, on the whole, the initial metastable microstructure of UMo-Me alloys.

In comparison with HD powders, mechanical grinding particles (X Figures) exhibits form of shavings, probably with high residual stress due to high levels of cold deformation, previous analyses also detect surface contamination with iron from tool steel (HSS) and/or cobalt from rotating knifes [4].

Total hydrogen content analyses reveals high content after hydride step (774 ppm). At the end of process (after quenching), the remaining hydrogen founded was only 58 ppm, slightly upper to mechanic grinding powder (not hydrided) which measured level was 41 ppm. The few presence of uranium hydride (UH_3) in XRD patterns of hydrided sample (only $2\theta = 52°$

peak appear clearly), could evidence amorphicity of compound and/or its amount is under detection limit. Thus, after dehydride stage, the hydrogen contents decreases at levels near to those originally contained in alloys before HD processing. Whatever, the hydrogen contents for dehydrided and after quenching samples were lower those maximum acceptable levels recommended for dispersion fuel material (200 ppm for U_3Si_2 LEU fuel).

HD processing, in comparison with HMD [10] had shown some advantages in terms of simplicity and safety of processing. Since the HMD hydriding processing at low temperature (in γ-phase) it doesn't produce complete fragmentation, except for the material in special condition of cold rolling and crushing, in HMD process, is necessary to apply mechanical crushing operation to hydrided product, stage that involves risk of superficial contamination and spontaneous oxidation (pyrophoricity). Finally, in the framework of CCHEN's UMo fuel development program, the next stages should be dispersion miniplates manufacturing using UMo-Me powders produced by HD processing and it's comparison with miniplates manufactured using ground powders.

4. CONCLUSIONS

According to first experimental results, their applicability of HD processing in UMo-Me alloys was demonstrated in terms of capability for produces fragmentation of solid samples.

The sequence design of HD process proposed in this article has allowed improving in safety conditions very necessary in thermal treatments that involve hydrogen under pressure.

XRD analyses detect the presence of γ and α phases after hydriding-dehydriding sample. However, only γ-phase is the predominant micro-constituent for quenching condition. It means that HD processing retains, on the whole, the initial metastable single-phase microstructure of UMo-Me alloys.

HD hydriding processing, in comparison with HMD hydriding process previously reported, had shown some advantages in terms of simplicity and safety for materials, equipment and operators.

Finally, the hydrogen contents for dehydrided and after quenching samples were lower those maximum acceptable levels recommended for dispersion fuel material (200 ppm for U_3Si_2 LEU fuel).

5. ACKNOWLEDGMENTS

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