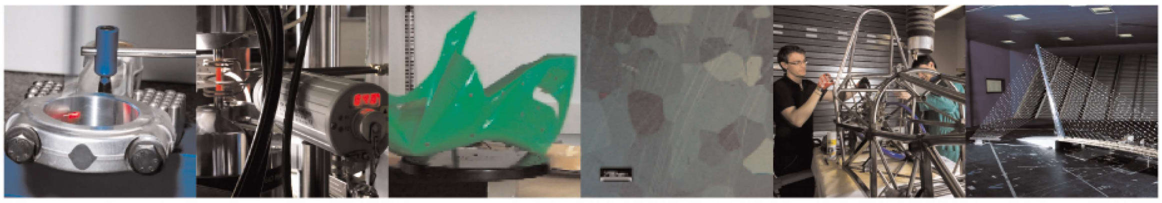

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DEMO radioactive wastes: decarburization, recycling and reuse by additive manufacturing

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Recycling is a real indicator of whether any nuclear industry is taking seriously about reducing its radioactive waste volume. Hence, manufacturing components starting from recycled activated material originated by DEMO reactor, with the relative manufacturing techniques, might be an important factor to support the environmental sustainability of fusion radioactive waste management. Accordingly, in this work the feasibility of recycling materials from decommissioned nuclear plants are presented.

In the initial part, the powder production from activated steels AISI 316L(N) and EUROFER and their use by Additive Manufacturing (AM) technologies is investigated as studied during EUROfusion Consortium funded activities. Chemical-physical parameters of this processed materials have been defined, together with the viability, of producing metal powders with an industrial VIGA (Vacuum Induction Gas Atomizer) facility. Experimental activities have been performed, aiming at powder production by VIGA and its characterization. A preliminary analysis of processing of these powders via selective laser melting (SLM) has been carried out. Additional results are presented for the experiments carried out on the decarburization of AISI 316L(N) and EUROFER and experiments on the pollution of solid lithium orthosilicate breeder (Li_4SiO_4) coming from the refractory material, by simulating the thermal process of Li_4SiO_4 production or recycling, assessing the impact of platinum, zirconia, graphite and mullite on the quality of Li_4SiO_4 and on the feasibility of removing radioactive impurities.

1. Introduction

A small fraction of carbon present in neutron irradiated steels is due to the 14C isotope whose generation is largely due to the following transmutation reaction

$^{14}N\ (n, p)\ ^{14}C$

Other reaction generating ^{14}C is:

$^{13}C\ (n, \gamma)\ ^{14}C$

but it is negligible considering the low isotopic abundance of ^{13}C (1.1%).

Therefore, the ^{14}C level in an irradiated steel does not depend from its carbon concentration. Anyhow, the interest for removing ^{14}C is dictated by fact that is one of the key nuclides for defining acceptance criteria for shallow-land disposal repositories for low-level radioactive waste. For tritium there would be the same concern, but its recovery, which must take place soon after its removal from the DEMO fusion reactor, is a must for economic reasons and management whatever route will be taken, recycling or disposal. Hence, decarburization might be postponed for a few tens of years waiting to have all the elements for a cost-benefit analysis between recycling or disposal.

Literature data from previous fundamental analysis have been used to define the process parameters both for decarburization (ref. [1]) and to produce powders for the preparation of AM samples (ref. [2]). The thermodynamic analysis (ref. [3]) showed that in a decarburization process of EUROFER steel, at temperature of 1700 °C and pressure of 1 mbar absolute, a minimum value of 1.15 ppm of carbon concentration, starting from an initial value of 1200 ppm [1], can be obtained without oxidation of other steel components. The minimum C concentration without slag, at 1700 °C and 1 mbar, in the decarburization of AISI 316L is 5.2 ppm.

To perform decarburazation tests non-activated materials were used, as their behavior during melting, powder production and assessments of new products by SLM technique is the same whether they were activated or not.

The general strategy followed is:

- the composition of EUROFER and AISI 316L(N) used for the ingots production was calculated from related FISPACT analyses simulating decay after irradiation in DEMO,
- two ingots (70 kg each) made by EUROFER and AISI 316L(N) were produced by Vacuum Induction Melting (VIM) facilities at RINA-CSM facilities with the defined chemical composition,
- decarburization of the alloy after melting (by VIM) and chemical characterization of the obtained ingot,
- powder production (by VIGA plant) and characterization (composition and size distribution),
- fabrication of specimens by SLM technique, their characterization (density, hardness test, roughness measurement and SEM analysis).

2. Metal powder production

The metal components recycling has been studied by means of the innovative metal powder production chain, developing specific metallic materials with tailored performance. Non-activated EUROFER and AISI 316L(N) ingots with equivalent chemical compositions have been obtained for the preparation of metal powders

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through the Vacuum Induction Gas Atomiser (VIGA) process (see Fig.1).

EUROFER Composition (Wt%)		AISI 316L(N) Composition (Wt%)	
C	0.12	Fe	bal
N	0.032	C	0.03
O	0.0034	N	0.097
Si	0.092	O	0.0042
S	0.0045	Cr	17.80
P	<0.006	Ni	12,57
Cr	9.10	Mo	2.63
Mn	0.49	Cu	0.32
Ni	0.016	Mn	1.87
Cu	0.0076	Ti	0.1
Mo /Al e Ti	<0.01	Co	0.05
Zr / Sn / Sb e B	<0.001	P	0.025
Ta	0.12		
W	1.08		
V	0.15		

Fig. 1 EUROFER VIM ingot pictures and ICP-MS analysis of EUROFER and AISI 316L(N) ingots

Ingots have a chemical composition, analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), close to the average composition of the HCPB WCLL and HCPB models irradiated components, simulated by FISPACT. After the ingot production in the VIM plant, powder production was made in the VIGA plant at RINA-CSM. (Fig. 2).

Fig. 2 RINA -CSM VIM (left) and VIGA (right) plant

Selective laser melting (SLM) is a powder bed fusion technique where the particle sizes (d) are typically between 15–65 µm. Hence, after separation of large and fine fractions produced by the plant, not adequate for powder metallurgy technologies, the remaining fraction (about 50% of the melted steel) has been sieved to collect the powder of interest for AM, at granulometry in the range of 15–65 µm. About 8 % of the EUROFER powder has been discarded, due to a granulometry higher than 65 µm and no Eurofer powders was lower than 15 µm. In the case of AISI 316 L(N), ~3 % of particles are below 15 µm and ~5 % is > 65 µm. Therefore, both samples have about 92 % of powders suitable for AM process (see Table. 1).

Table 1. EUROFER, AISI 316L(N) particle size distributions

Granulometric parameters (cumulative volume %)	EUROFER	AISI 316L(N)
Dv(10) µm	18.703	18.344
Dv(50) µm	33.786	31.656
Dv(90) µm	64.841	57.181

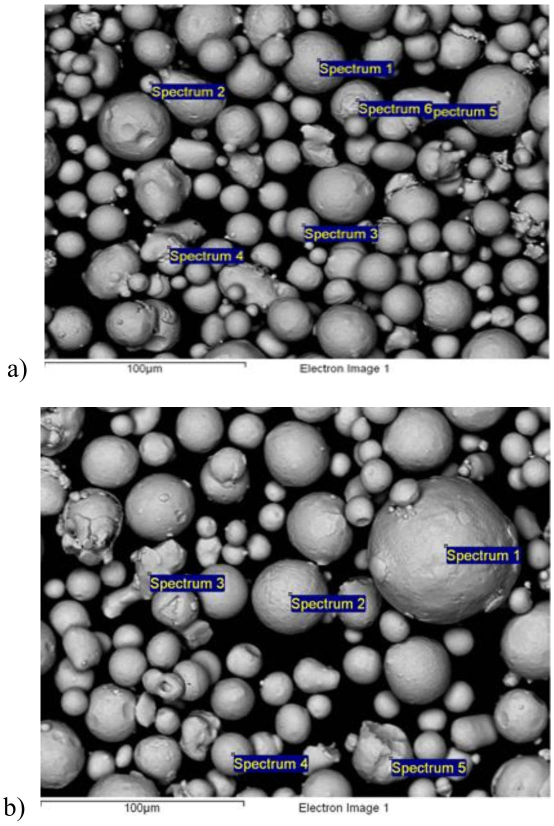

Fig. 3 SEM-EDS analysis of selected alloys a) EUROFER; b) AISI 316L(N)

3. Selective laser melting of the produced powders for component refabrication

There are several technologies for metal Additive Manufacturing (AM). Depending on the route to achieve the final part they can be divided in "direct" and "indirect" processes:

- In the "direct" processes the metal powder is completely melted and then solidified to form the final components. "Direct" metal AM technologies include "Selective Laser Melting" (SLM), "Laser Metal Deposition" (LMD) and "Electron Beam Melting" (EBM).
- In the "indirect" processes a binder is used to join the particles of metal powder together and post processing is necessary to achieve the target density.

For the components refabrication with the produced powders, the SLM technicque has been selected as it has the great potential on the future production of components with various and even complicated shapes and better suitable for remote handling.

Although the conventional powder metallurgical processes can provide economic solutions, it is important to explore new and interesting sectors of applications.

Particles lower than 15 micrometers cause low flowability during the SLM process due to aggregation phenomena that obstacle the preparation of homogeneous layer. On the contrary, particles higher than 65 micrometers can be reason of inhomogeneity of powder bed, will require a too high energy for local melting and are too big for the extrusion nozzle of the "machine" (and/or other parts of the equipment).

Direct technologies can produce denser parts because they do not need debinding and sintering phases. Hence components with high mechanical resistance can be obtained in a straightforward manner considering the future metal AM applications.

The first step in AM technology is the production of powders. The metallic powder is produced from melted alloy, which is poured inside a so called "atomization" chamber, where a gas jet impact on the liquid stream forming small droplets of liquid metal, which rapidly solidify forming the desired powder. Final step of refining, densification, thermo-mechanical treatment can be applied to give the target properties.

An industrial SLM system with 200 W laser power was used for assessing the processability of the produced powders (Renishaw AM250, Stone, UK). The SLM system was fitted with a reduced build platform (RBV) system allowing to process small quantities of powder (<5 kg). The powders were processed under constant Ar flow with the initial O_2 less than 1000 ppm. The preliminary analysis assessed the flowability of the powder and consolidation of the material with the laser beam as a function of the main process parameters namely laser power, point and hatch distance, pulse duration, and the focal point [4]. Experiments were executed on the two materials varying the main process parameters involved in the SLM process with a PW laser within an energy density range of 20-160 J/mm^3.

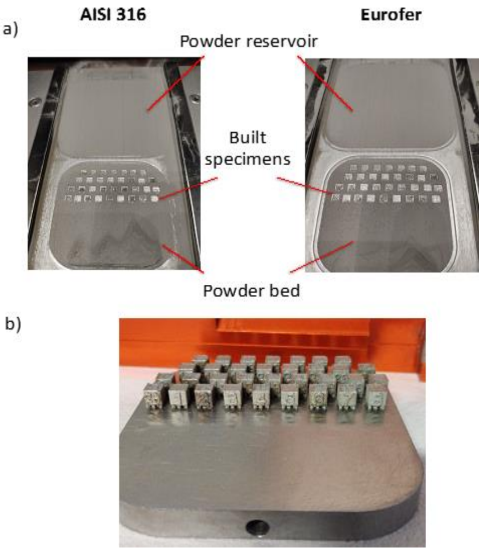

Fig. 4. The regular powder bed formed during SLM of AISI 316L(N) and EUROFER. b) Freestanding samples.

Fig 4.a shows the powder bed regularity of the two materials. During the initial trials 33 specimens with different process parameters could be consolidated with each material. Fig 4.b shows the AISI 316L(N) specimens produced on the build platform. The images confirm that freestanding components without macro defects. The initial results showed the feasibility of producing freestanding high density (99.5%) small specimens with both EUROFER and AISI 316L(N). Further investigations to characterize the material properties are ongoing.

4. ^{14}C decarburization of EUROFER and AISI 316L(N)

Decarburization might be considered an alternative to recycling, as it is aimed to comply with reference acceptance limits for low-level waste in shallow land repositories. Alternatively, however, the decarburization together with the removal of tritium can be considered a preparatory process pending a final decision regarding the recycling or not of the component / material which can be deferred for a few decades depending on the technical and economic framework for fusion materials supply for blanket and divertor construction. These thermal processes that include the remelting allow the recovery of tritium, a better characterization of the material to be recycled or disposed of a reduction of space for interim storage or final disposal.

Pending a more comprehensive analysis some preliminary results are provided herewith. To analyze the decarburization kinetic of both Eurofer and AISI 316L(N) alloys, the tests were performed in a Balzers induction furnace (see Fig. 5).

Fig. 5. Balzer Induction furnace

The decarburization process tests have been designed and performed in a regime where no oxygen oversaturation is achieved (see Fig.6), obtaining selective oxidation of carbon, without formation of other species.

Steel ingots of 3.5-6.3 kg were melted injecting O_2 gas, as oxidizing agent, at the lowest possible flux (<5-10 l/h) under argon cover atmosphere to minimize slag formation and flooding issues. Oxygen was inflated in the metal bath by a porous septum (see Fig. 6) with alumina shaft specifically made (for better O_2 blowing and hence greater mixing in the metal bath), or by a canula.

The quantity of gas blown has been calculated in view of improving C capture.

Fig. 6. EUROFER, AISI 316L(N) decarburized ingot and porous septum with alumina shaft

Fig. 7. Decarburization phase

Decarburization efficiency obtained is up to 99 % for both EUROFER and AISI 316L(N). These results indicate that the practical O_2 volume to obtain decarburization with efficiency close to 100% is 1.5 times the theoretical volume for EUROFER and about 2.0 times the theoretical volume for AISI 316L(N) calculated previously [1]. These are to be considered limits for decarburization without slag formation. Larger O_2 volume causes oxidation of other species in steel.

A value of 99% decarburization efficiency (EFF) corresponds to a decontamination factor (DF) of 100, which means a reduction of two order of magnitude of the ^{14}C specific activity which must be considered practically constant for several centuries. EFF is given by the quantity of C captured divided the initial quantity of C, i.e. [(Cin- Cfin) / Cin] while the decontamination factor DF is Cin/Cfin. The relation of the two parameters cited is shown in the following equation:

$$EFF = (1- 1/DF) \times 100\ (\%)$$

Taking reference values of ^{14}C specific activities for EUROFER components of DEMO WCLL and HCPB blankets (from FISPACT activation calculations), DF for decarburization of 100 would reduce ^{14}C levels up to few tens of kBq/kg which is well below acceptance criteria for some EU Low Level Waste (LLW) repositories. For AISI 316L(N), it would be sufficient to reduce the carbon content to ~10 ppm to fully comply with the acceptance criteria for such LLW repositories with a reduced secondary waste production, similar to that of Eurofer (3% in mass).

The difference between EUROFER and AISI 316L(N) is justified by the fact that in the case of AISI 316L(N), a minimum amount of chromium is inevitably oxidised together with carbon.

To better define the decarburization kinetic of both EUROFER and AISI 316L(N) alloys (see in Fig. 7 decarburized ingots), several decarburization trials, with different times and different oxygen flow rates, were performed. The details of the reference decarburization process parameters with extensive analysis on process efficiency, duration, flow regimes, Ar cover pressure and degassing (see Fig. 8) have just been completed and will be presented in a next Technical Report to EUROfusion.

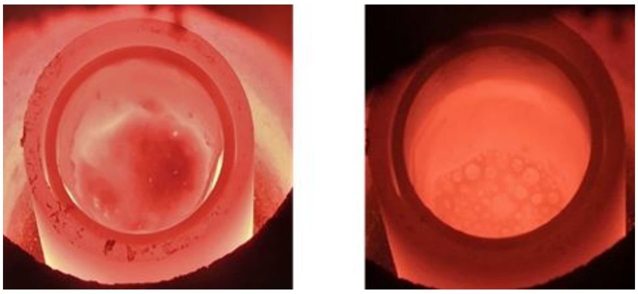

Fig. 8. Melting - Degassing phase during the test.

The main results about O_2 flow rate to perform deep decarburization (EFF >99 %) without slag can be summarized as follows: 4.3 l/(kg·h) for the EUROFER and about 1.9 l/(kg·h) for AISI 316L(N).

The corresponding kinetic parameters are: 0.18 1/min for EUROFER and 0.23 1/min for AISI 316L(N).

5. Li_4SiO_4 pebbles recycling for ^6Li refurbishment and impurity minimization

The fabrication of lithium orthosilicate pebbles is described in many works such as in [5] and [6]. The process analyzed aims to reduce the usage of highly costly ^6Li enriched materials and the quantity of radioactive waste to dispose. Various pebble compositions have been reported in literature.

In a pure Li_4SiO_4 (with only Li, Si and O) the activated element after irradiation is 26Al [7]. The addition of SiO_2 and calcium fluoride (CaF_2) to Li_4SiO_4 in a high temperature melting process, decrease the concentration of Al_2O_3 in the melt, forming gaseous Aluminum fluoride radioactive species and gaseous compounds containing Li, without anyway being decisive, and with serious problems for collecting, recover and confining the species. Melting test was carried out under vacuum in an induction furnace adding CaF2 (Al:F=3) [3] (see Fig. 8). This test also evaluated the effectiveness of Al removal as AlF3 gas, simulating the removal of activated Al from the melted bath (see Table 2).

Table 2. Efficiency of Al removal as gas (AlF3)

Samples of the mixture Li_4SiO_4-Li_4TiO_4+Al_2O_3+CaF_2	Al (%)
After 1st melting (to mix Al_2O_3+CaF_2 in the silicate)	0.19
After re-melting under vacuum	0.16

From a theoretical point of view, the addition of SiO_2 and calcium fluoride (CaF_2) to Li_4SiO_4 in a high temperature melting process, decrease the concentration of Al_2O_3 in the melt, forming gaseous aluminum fluoride. To explore this possibility, melting test was carried out under vacuum in an induction furnace adding CaF_2 (Al:F = 3). This test demonstrated the occurrence of Al volatilization, without being decisive, because the final Al concentration was far from the theoretical value, which is of the order of tens of ppm. This test cannot be considered a decisive proof of the feasibility of the Al removal by a degassing operation. However, it cannot be excluded that this option might be investigated in a deeper way in future activities.

6. Conclusions

The air flow rates required to achieve deep decarburization are normally achievable in industrial practice. The experimental tests confirmed the feasibility of decarburization of both EUROFER and AISI 316L(N) without slag formation, in agreement with the thermodynamic calculations. EUROFER and AISI 316L(N) ingots have been produced by VIM technology with a chemical composition close to the reference for DEMO (HCPB and WCLL models) irradiated blanket components at shutdown. These ingots have been used to produce powders for additive manufacturing after thorough characterization in terms of composition and dimension distribution.

First Selective Laser Melting (SLM) freestanding components were produced without macro defects using EUROFER powder. The results show that the overall processability EUROFER and AISI 316L(N) materials are comparable to the alloy more conventionally processed by SLM (e.g. AISI 316 and 18Ni300) [8]. The good processability is owed to the correct chemical composition, correct powder size distribution and the choice of the process parameters. Further investigations to characterize the material properties are undergoing. These first results encourage the continuation of research activities in the field of manufacturing of structural components and not for fusion reactors by AM using powders generated from recycled activated materials.

^{14}C decarburization tests show results in line with theoretical thermodynamics modelling up to 99 % decontamination efficiency both for EUROFER and AISI 316L(N). The decarburization efficiency gained seems to be enough to reduce the ^{14}C below the reference limit levels (for acceptance) in some EU LLW disposal facilities. Melting test results for Li_4SiO_4 pebbles recycling indicates that a fraction of the aluminum was removed with the gas, but is far from the theoretical value, which is of the order of tens of ppm. Other degassing tests might be performed in future activities scanning other process parameters.

Acknowledgments

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