Proof-of-Principle of Recycling of Off-spec Scalmalloy® in Molten Salt

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The aim of this work is to evaluate a feasible mean for recycling off-spec Al-Mg-Sc alloy (Scalmalloy®), a distinctive lightweight alloy used in additive manufacturing processes. The first attempts are carried out to define a safe procedure due to its dangerousness and to obtain a first view of the agglomeration of powders. The experiments were conducted in molten equimolar KCl–NaCl plus 2 % of CaF_2 at 750 °C, following the established approach in aluminium recycling industry. Furthermore, the distribution of major alloying elements is analyzed in the solid phases through ICP-OES chemical analysis. The results show that the metal yield is above 85 %, magnesium distributes preferably to gas phase during melting and scandium distributes to both metal and slag phase.

Keywords:

Scalmalloy – Recycling – AM powders – Molten salts

Proof-of-Principle of Recycling von Off-Spec Scallmalloy® in geschmolzenem Salz

Das Ziel dieser Arbeit ist es, ein praktikables Verfahren zum Recycling von Al-Mg-Sc (Scalmalloy®)-Legierungspulvern zu evaluieren, einer charakteristischen Leichtmetalllegierung, die in additiven Fertigungsprozessen verwendet wird. Es werden erste Versuche unternommen, um ein sicheres Verfahren aufgrund seiner Explosivität zu definieren sowie einen ersten Einblick in die Agglomeration der Pulver zu erhalten. Die Experimente wurden in Salzschmelzen aus äquimolarem KCl–NaCl plus 2 % CaF_2 bei 750 °C durchgeführt, in Anlehnung an die in der Aluminium-Recyclingindustrie etablierte Vorgehensweise. Zusätzlich wird die Verteilung der wichtigsten Legierungselemente in den Festphasen mittels chemischer ICP-OES-Analyse untersucht. Die Ergebnisse zeigen, dass die Metallausbeute höher als 85 % ist, Magnesium während des Schmelzens bevorzugt in der Gasphase verteilt wird und Scandium sowohl in der Metall- als auch in der Schlackenphase verteilt ist.

Schlüsselwörter:

Scalmalloy – Recycling – AM-Pulver – Salzschmelzen

Preuve de principe du recyclage de Scallmalloy® hors normes dans un sel fondu

Prueba de principio del reciclaje de Scallmalloy® fuera de especificación en sal fundida

1 Introduction

Within the metal manufacturing industry, one of the most important technological advances has been additive manufacturing (AM). AM is the umbrella term for a wide range of processes which have as their underlying principle the manufacture of products made layer by layer through the addition of melted material (except cold spray which does not melt the feedstock). These products generally have a complex design, and conventional methods such as subtractive or forming manufacturing fail to reach such a level of precision and complexity. That is why the central focus of the AM industry is on aerospace, automotive and medical sectors. Indeed, the principal advantages, which have established the AM industry, are higher precision and efficiency, as well as cost and time reduction.

The base material for AM technology is preferably powder (metal, composites or polymers). In the case of metallic parts, the powder is essentially produced by gas atomization. Several metallic alloy powders are available on the market, among the most employed are aluminium, cobalt, nickel, titanium, steel, and precious metal alloys. AM technology demands narrow and tailored particle properties such as composition and morphology, as well as properties related to the bulk material such as flowability.

In this manner, out-of-specification or unusable powders are generated in two ways: (1) by the production of the metal powder or (2) after completing a defined number of reuse cycles in the building process. During the atomization, the 5 to 15 % of the produced powder could be discarded because it is under the lower size limit; however, this value is highly dependent on the type of atomization and the parameters of the process. The literature has not given detailed information about particle size distribution in powder production of aluminium alloys. On the other hand, in AM processes the amount that is left in the chamber can range from 40 to 60 %. Some authors have mentioned the reuse of the powder [1, 2] in the building process. Powder left in the chamber process of powder bed fusion (PBF), which is the most common AM technology, can be reused in a certain number of cycles in the process. Depending on the alloy type, different properties can vary with the build cycles. The number of cycles has no significant effect on the properties of the Ti6AlV4 powders, for example [1]. However, the limit number of cycles eventually change from alloy to alloy and therefore, reused powder lacks reliability in its properties, in comparison with virgin powder.

For this reason, the aim of this research is to achieve a method that returns Al-based out-of-specification powders towards the process chain in the production and closes the loop, especially when it comes to scarce and costly materials. Scandium is a high-priced metal, ten-fold as expensive as silver. Scalmalloy is an aluminium, magnesium and scandium-containing alloy, with structured nano-precipitates of Al_3Sc and an aluminium matrix solid solution containing magnesium. Due to its production is done by rapid solidification processes, it forms a non-equilibrium structure. Typical chemical composition ranges of Scalmalloy® are shown in Table 1.

Table 1: Chemical composition of Scalmalloy®

Element	Min – max [wt.-%]
Mg	4.0 – 4.9
Sc	0.6 – 0.8
Zr	0.2 – 0.8
Mn	0.3 – 0.8
Si	0 – 0.4
Fe	0 – 0.4
Zn	0 – 0.25
Cu	0 – 0.1
Ti	0 – 0.15
V	0 – 0.05
O	0 – 0.05

2 Out-of-specification powders

The chemical and physical properties that powders must fulfil to be employed in AM building processes are often sited in a very narrow range. Chemical composition, morphology (shape and microstructure), moisture content, particle size, particle size distribution, flowability and density are the properties frequently examined. The limits of the ranges are determined by the types of AM building processes. For example, the particle size range of powders in some AM building processes is listed in Table 2.

Table 2: Particle size range for additive manufacturing techniques

AM process	Particle size range [µm]
SLM/LPBF	20 – 60
SMS	15 – 45
DED	50 – 150
EBM	50 – 150
LBM	10 – 60
Spray deposition	5 – 50

3 Treatment in molten salts

The recycling of aluminium based alloys is an established technology for scraps and by-products. The re-melting processing takes place in molten salts. In order to remove the oxide layer of the particles or pieces, the material is loaded in a equimolar composition of KCl–NaCl at 750 to 800 °C, in addition of a small part of fluoride compound which provides the fluoride anion attack on the surface of the particles. The main functions of the flux salts are, therefore, to protect the molten metallic phase from further oxidation and to advance and improve the coalescence of molten metal. The coalescence efficiency has a strong dependency on physical properties of the flux salts and on the composition of aluminium material input [5].

The viscosity and the density of equimolar NaCl–KCl are minimally affected by the addition of cryolite (Na_3AlF_6), one of the most utilized fluoride additive [3]. Viscosity of the suspension (salt slag) is dependent on the solid fraction, and the suspension can be assumed to act as a Newtonian fluid for concentrations below 25 vol.-% of solid particles. In addition, interfacial tension plays an important role during the stripping of oxide film with salt fluxes, the lower the surface tension, the greater the ability of the salt to release oxides from the surface of the aluminium droplets. Interfacial tension is reduced by the presence of magnesium in the metal as well as with the fluoride addition.

In terms of composition, the oxide content and magnesium content – a common alloying element – affect the recyclability of aluminium. Normally, the generation of spinel ($MgO \cdot Al_2O_3$) caused by the reaction of magnesium oxide and alumina (Al_2O_3) occurs. In addition, the major detrimental impact is caused by the oxygen content in the system, which is partially caused by the high surface area of the feeding material [5]. Furthermore, the native oxide layer can increase its thickness in the range of nanometers by increasing the temperature.

While salt flux prevents oxidation of metal bath and collects oxides and impurities, the density and viscosity increases during the melting which can lead to metal entrapment in the salt slag. Therefore, the focus of the first trials is to have a view of the coalescence efficiency with given conditions based on the literature.

3.1 Reactions

Multiple heterogeneous reactions may occur in the system of aluminium alloy and chloride and fluoride salts, such as ion exchange reactions, dissolution of oxides with molten salt, metal with gases interaction and formation of oxide species (salt slag). Chlorination is likely not taking place for the main alloying elements of Scalmalloy. The equilibrium constant of ion exchange with chlorides indicate that the reactions are not feasible. Since the reaction of Mg with calcium fluoride (CaF_2) to produce MgF_2, has a negative Log K, CaF_2 is chosen to be employed in the experiments. The fluoride addition creates cracks in the oxide layer of the aluminium which are formed by chemical and surface phenomena, followed by the detachment of these oxides generated by a gradient of interfacial tensions, and their entrapment in the salt. Furthermore, fluorides promote the absorption of Na and K in the metal [4].

4 Experiments

The starting material is as-received powder with a particle size <25 µm. The material was subjected to TG and DTA analysis to verify the melting point and potential humidity as shown in Figure 1. The onset temperature shows a melting point of 623.4 °C and the TG curve displays a moisture content of 0.07 % approximately.

The melting experiments were conducted in an electrical resistance furnace with a SiC crucible. The arrangement to perform the experiments is shown in Figure 2. The superfine powder Al–Mg–Sc is loosely charged in equimolar NaCl-KCl-salt by means of a lance equipped with argon as shielding and carrier gas. In this step, it is crucial to set a suitable argon flow to provide a laminar flow and to avoid a turbulent flow, which will interfere the proper feeding, returning the powder to the entrance of the lance. The powder is mixed with CaF_2 beforehand. In addition, an argon flow circulates from the bottom to the top of the chamber where the crucible is placed, to ensure a safe procedure. The stirrer has the function to supply an entry to the powder in the salt melt and therefore, to allow its sinking, in addition to promote the contact between powders and flux salts, which enhances the kinetics.

The set parameters are presented in Table 3. The experiment was done twice in order to have a view of the outcome‘s repeatability. The ratio salt/powder is taken as high as possible in order to maximize the action of salts and calculate the metal yield. The composition of the salts is fixed in order to have a point close to the eutectic point and to reach the maximum dissolution of 2 % of fluorspar into $KCl–NaCl_{equi.}$ at 750 °C. The holding time is an approximation of the time that a particle or a droplet takes to descend in a viscous fluid, which is estimated with the equation of motion through the calculation of terminal velocity. For example, at 750 ºC a particle of 20 µm and a droplet of 1 mm, take 15.7 h and 21 seconds to descend, respectively.

In addition, the stirrer is placed 3.5 cm above the inner crucible bottom to avoid the contact with the metal pool. The steps considered during the experiment are shown in Figure 3.

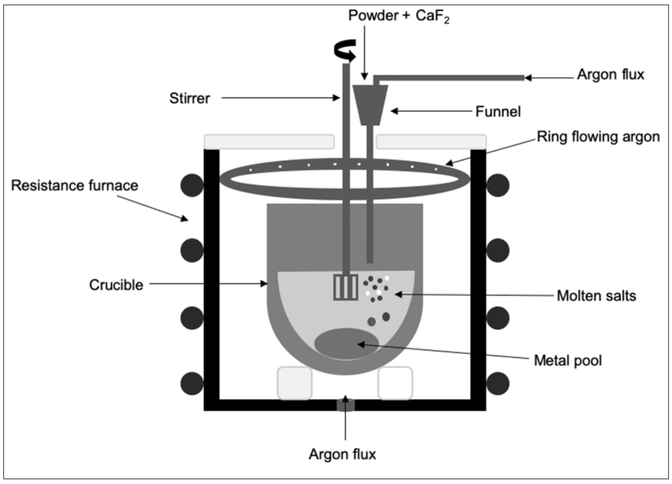

Fig. 2: Scheme of equipment utilized in first trials

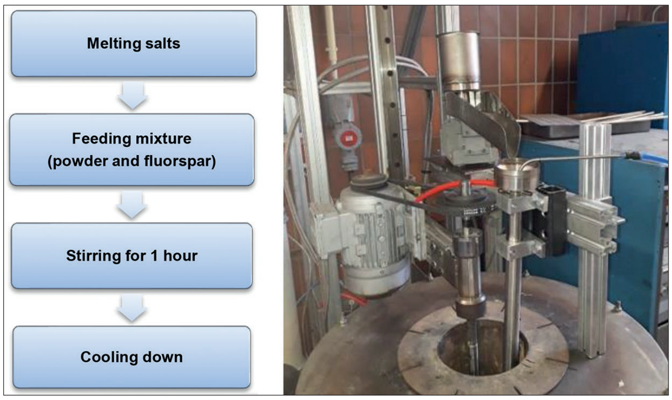

Fig. 3: Steps in the process (left) and arrangement of the experiment in the furnace (right)

Table 3: Set parameters in the experiments

Parameter	
Ratio salt/powder	4:1
Composition of salt	equimolar KCl+NaCl + 2 wt.-% CaF_2
Temperature	750 °C
Holding time of stirring	1 h
Solidification rate	Solidification to room temperature
RPM stirrer	150 rpm

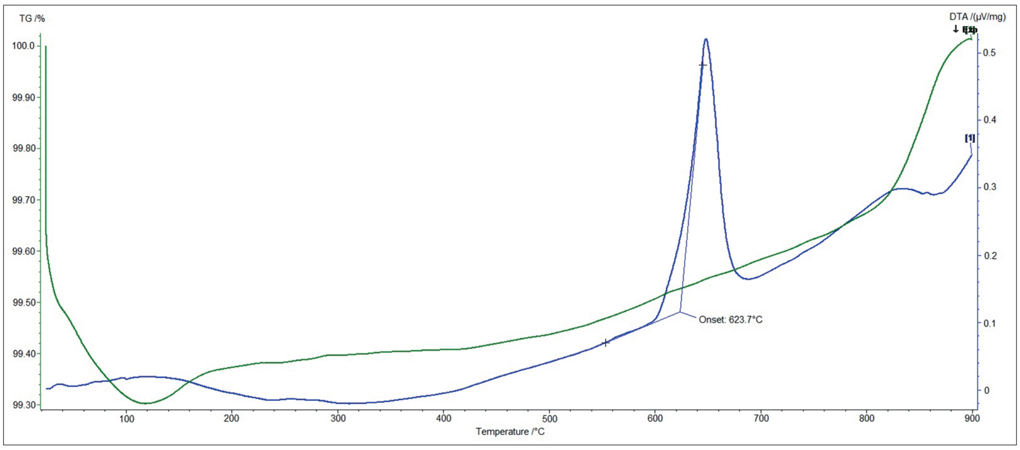

Fig. 1:
TG and DTA of Scalmalloy under argon atmosphere

5 Results

The first aspect evaluated in the experiment was the coalescence of the powders. The coalescence was virtually complete with the arrangement and set parameters as depicted in Figure 4. The picture displays that from the bottom to top; the metal, the salt slag and over these, the clearer salt are visible separated.

Metal yield was another important value calculated, which is defined as the ratio of the mass of metal block produced to the mass input. For both experiments, the metal yield was above 85 % including the losses due to handling issues as depicted in Figure 5.

In addition, the metal yield is supposed to be very close to the metal recovery (ratio of the mass metal produced to the mass metallic input) due to the input material purity of the powder, which can only be affected by oxygen uptake once it is being handled.

On the other hand, besides the experimental set-up used, other approaches for charging the material were conducted in order to facilitate the loading of the material and prevent losses due to handling as depicted in Figure 6. However, it exists the advantage of loading the powder into the molten bath to remove immediately its film, however, having simultaneously the difficulty to charge it into the salt bath.

Compacted powder can carry entrapped oxygen in the interstitial sites of the compacted piece. In the same manner, the powders melted at the same time together with the salts can increase its oxide layer during the heating of the mixture, not achieving the agglomeration visible in Figure 3.

Fig. 4:
Assessment of coagulation of powders (left), metal block (right)

Fig. 5: Adhered powder on the crucible wall

5.1 Chemical analysis

The distribution of the alloying elements was also investigated. A sample preparation procedure was done for both the metal phase and the salt slag. From the metal phase, 5 g of turnings from the block were taken for analysis. The chemical analysis was performed by ICP-OES. The results show the distribution of principal alloying elements in the metal phase as well in the residue after washing the salt slag. The chemical composition of the received material and chemical analysis of the bulk generated are shown in Table 5.

Since some elements such as Mg and Mn have reduced their amount in the metallic phase obtained, other elements such as Sc and Zr increased their proportion in the alloy. The minor elements in the metallic phase were also

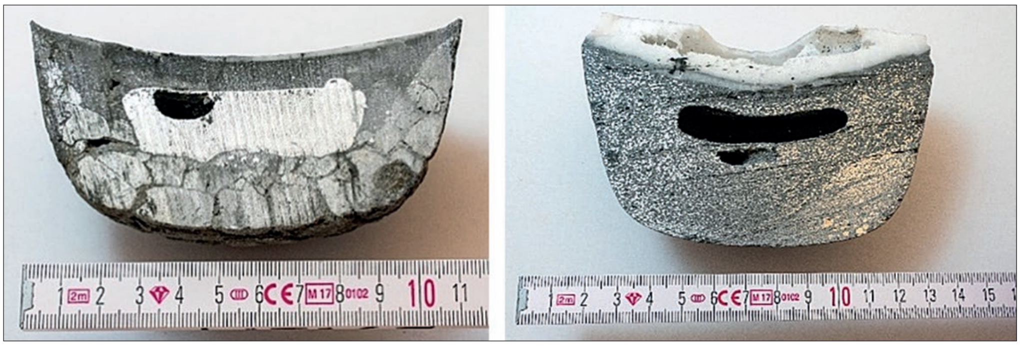

Fig. 6:
Compacted material with stirring (left) and powder loosely charged with salts (right)

Table 5: Distribution of main elements in the metal phase

Element	As-received [wt.-%]	Exp. 1 [wt.-%]	Exp. 2 [wt.-%]
Mg	4.6	0.25	0.95
Sc	0.66	1.33	1.77
Zr	0.42	0.87	0.9
Mn	0.49	0.17	0.16
Al	Bal.	Bal.	Bal.

Table 6: Distribution of minor elements in the metal phase [ppm]

Element	Exp. 1	Exp. 2
Na	620	840
K	520	110
Cl	0.051	0.421
Ca	117	106
F	<0.1	<0.1
Fe	930	920
C	220	360
Si	438	513
O	454	192

Table 7: Chemical composition of the slag residue after washing the salt slag

Element [wt.-%]	Exp. 1	Exp. 2
Al	12	9.76
Fe	0.1	0.045
Mn	0.0174	0.0034
Mg	4.28	6
Sc	0.12	0.095
Si	0.48	0.365
Cl	0.15	0.16
Zr	0.063	0.065

examined to verify the impurities which may be carried from the flux salts to the metal phase as well as the oxygen uptake from the surroundings as displayed in Table 6.

One of the most important values to consider is the oxygen content which must be under the limit of the 500 ppm (0.05 wt.-%) to fulfill the chemical acceptable values for powder production as listed in Table 1. Both experiments reached an admissible oxygen value. Principal impurities found in the block are Fe, Na, K, Si and C. The available information is only offered for Fe and Si, and in both cases, the composition requirements are met. Fe can be transferred by the lance and the tube of the stirrer, both made of stainless steel 316L, but visibly corroded by the molten salts after the trials. On the contrary, no information is provided about admissible values of Na, K and C. In the case of C, this can likely be transferred from the stirrer made of graphite.

It can be observed from Figure 7 that intermetallic phases or non-metallic inclusions are present in the metal phase. Further analysis such as SEM-EDS can provide the chemical composition of given grains in order to determine the compounds inside the metallic matrix. Besides, black dots on the optical micrograph can indicate the occurrence of pore formation.

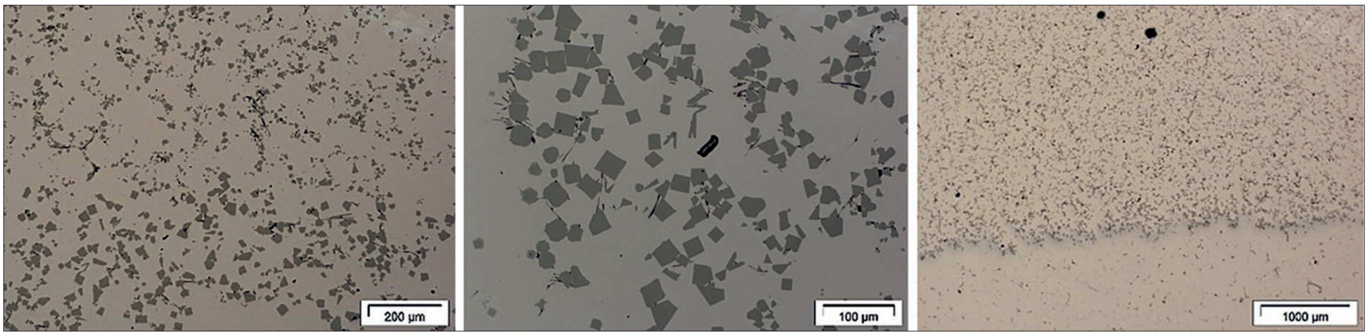

Fig. 7: Micrographs of transversal cut of metal block sample

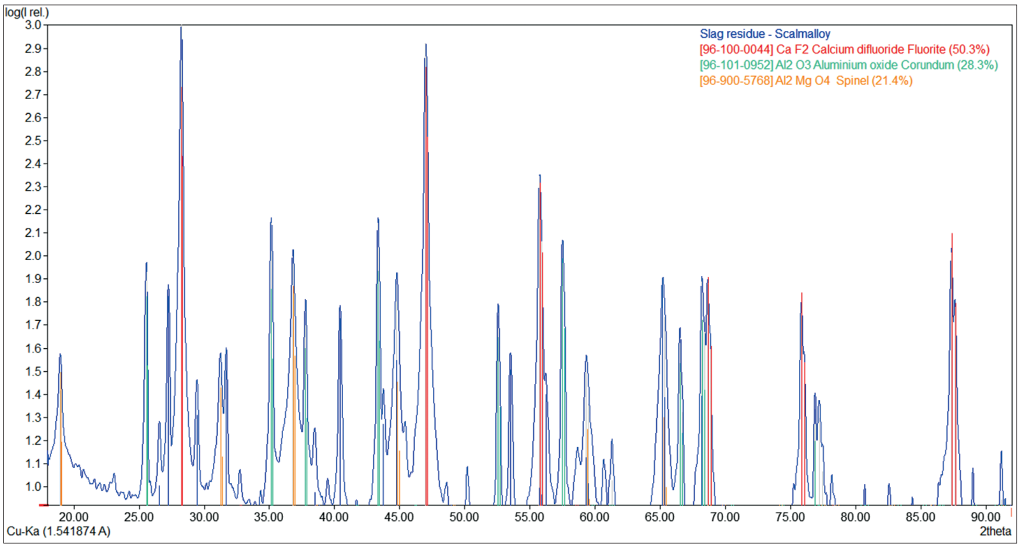

Fig. 8: Diffractogram of the slag residue after washing the salt slag

In order to trace alloying elements in the salt phase, a salt slag sample was washed in sufficient distilled water to guarantee complete dissolution of the chloride salts at room temperature. The chemical analysis of the residues obtained after washing are shown in Table 7.

It is known that some compounds are prone to form during recycling aluminium with magnesium content, mostly the magnesium aluminate spinel ($MgO{\cdot}Al_2O_3$). Moreover, it is likely that some particles do not coalesce and remained at 20 µm. The rest can be considered as the oxygen in the oxide compounds formed, as well as other elements not analyzed. Additionally, XRD analysis of the residue is depicted in Figure 8. It can be identified the presence of fluorspar, which has a low solubility product constant, alumina and magnesium aluminate spinel (MAS), with a high predominance of the former (>50 %).

6 Discussion and conclusion

Design of experimental set-up must be as accurate as possible to avoid any possibility of powder loss due to handling issues. In addition, it is relevant to know to which extent parameters influence the distribution of elements on metal/slag phases. Different parameters are involved in achievement of the metal coalescence and the recovery of the aluminium alloy, which in future experiments may be introduced as variables in order to optimize the process, such as composition of the salt mixture, type of fluoride, rotation speed and distance of the stirrer from the bottom, among others. Therefore, it is foreseen from the first trials that many parameters can be varied and additionally, a statistical approach can be applied to maximize the information with the minimum of experiments (Taguchi, factorial designs, etc.).

Trials with compressed material were conducted in the same set-up with no achievement of a unique solid metal part, but a mixture of the phases and partially agglomerated. In summary, the findings from the proof-of-principle tests with Scalmalloy powder are:

- Powders can be treated safely in argon atmosphere when they are loosely or compactly introduced, however, only loading the powders loosely, the highest coagulation was achieved.
- Powders can be coagulated in KCl-NaCl medium, and stirring enhances the solid-liquid contact, promoting the coalescence.
- The high surface area to the bulk volume does not show a significant impact in the coalescence and metal yield.
- Magnesium loss represents a problem that cannot be avoided. Since magnesium has low-pressure vaporization, it can leave the system when powder is fed by touching the hot surface. Therefore, a chemical adjustment in the atomization process must be done.

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