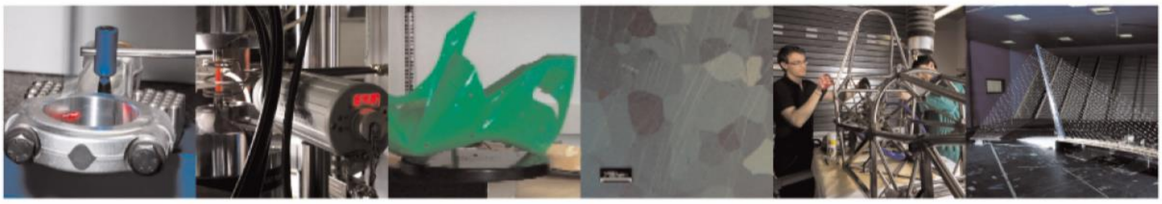

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Laves phases in selective laser melted TiCr1.78 alloys for hydrogen storage

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Abstract

Hydrogen is one of the most promising clean energy carriers within alternative fuels. The need for its absorption/release at reasonable p/T conditions within materials, like metallic Ti-Cr alloys, is primary for its use in renewable and sustainable energy applications.
In this work $TiCr_{1.78}$ compound was produced via selective laser melting (SLM) first time. Due to lack of commercially available powders of Ti-Cr compositions, two powders prototype precursors, premixed or prealloyed, were prepared and investigated. Correlation among powder type and microstructure of SLM built was studied. Prealloyed powders allowed Laves phases to be obtained in SLM parts while premixed did not fully react. Relative density of SLM products was strictly correlated to energy density.

Keywords: SLM, Laves phases, Additive manufacturing, microstructure.

Introduction

Ti–Cr alloys have been object of great research interest due to their promising high temperature strength, excellent wear, oxidation resistance and long-term stability at temperature above 1000°C for developing medical and aerospace applications [1-3]. $TiCr_2$ crystallizes in three Laves phases, namely C14, C36 and C15, exhibiting large interstitial sites to accommodate guest molecules, like H_2. $TiCr_2$ based alloys can be applied to sustainable energy applications for reversible H_2 storage [4-6], each Laves phases being able to absorb similar amount of H_2 [7]. H_2 absorption mechanism is a multistep process, involving adsorption on metal surface by molecular H_2, its split into single atomic species, followed by diffusion of atomic hydrogen into the alloy forming a hydrade [8]. As the mechanism involves surface interactions, materials with controlled microstructure and porosity are desired. Ti-Cr alloys have shown good physical/chemical properties, but brittleness remains their greatest limitation [9]. Consequently, powder metallurgy assisted by additive laser processing can be a valid alternative technique with respect to conventional deposition or melting methods for producing parts. Porosity obtained in conventional powder metallurgy processes relies on powder type, shape and processing conditions and controlled indirectly. SLM provides the possibility to design interconnected and engineered geometries, able to tailor both mechanical and chemical properties of H_2 storage device.
Only two works regarding fundamental aspects of laser deposition of TiCr alloys are described in literature. Zhang reported about in-situ laser micro-cladding of elemental powder mixtures. Composition gradient structure from Ti to $Ti_{60}Cr_{40}$ (at.%) was prepared. Rapid solidification resulted in generating metastable β-Ti(Cr) and $TiCr_2$ [10]. Banerjee observed metastable matrix of β-Ti(Cr) with different precipitates: α-Ti in its pure form and alloyed to Cr(α-Ti(Cr)), and C14 Laves phase [11]. Evidently the use of powder-bed fusion technique, like SLM, would allow for higher geometrical flexibility and details.
Accordingly, this work explores the use of SLM for producing $TiCr_{1.78}$ parts. Two viable precursors at a material prototyping level namely, elementally mixed spherical and prealloyed powders, were tested with a flexible and open SLM platform. Density and microstructure of built parts were assessed as function of precursor type. Small samples were produced varying energy density for both powder types. Microstructure was studied through X-Ray Diffraction (XRD) and Scanning

Electron Microscopy (SEM) while the density was measured through Archimedes's method. The results show limits of feasibility as well as insights for process optimization of the new alloy.

Experimental

Two types of powder were tested: (i) prealloyed powder, having size range of 170-190 μm, was ground from small ingot buttons of nominal composition $TiCr_{1.78}$ (at.%), corresponding to Ti:Cr ratio equal to 9:16. Ingot buttons were prepared using vacuum arc furnace (Leybold LK 6/45) under high purity inert atmosphere; (ii) premixed powder was obtained from mixing elemental Ti (size range of 90-110 μm) and Cr (size range of 10-100 μm) powders, both 99.9% purity from Alfa-Aesar, in due proportion. A laboratory scale SLM system [11], equipped with 1 kW CW fiber laser (mod. YLS-1000 from IPG Photonics) and galvanometer (mod. Scanfiber from Elen), was used for producing small samples (6x6x6 mm^3 in size), built on grade 5 titanium platform. The system was equipped with an in-house built powder-bed capable of handling small quantities of powder in different shapes and sizes. This provides flexible control of the powder dosage by means of a vibrating plate and a silicon wiper, both being independently controllable via a LabVIEW interface. The system was effectively used with gas and water atomized powders in previous works [12-13]. Process parameters are listed in Table 1. The fluence, *F*, or energy density, was calculated as follows:

$$F = \frac{P}{v \cdot h \cdot z} \quad (1)$$

where P, v, h and z indicate laser power, scanning velocity, hatch distance and layer thickness, respectively.
Density of samples was measured via Archimedes's principle using an electronic balance. XRD patterns were collected with a Panalytical X'Pert PRO diffractometer with CuKα radiation. Compositional and microstructural analyses were carried out using a SEM (mod. Leo 1430), equipped with Energy Dispersive X-ray Spectroscopy (EDS).

Results and Discussion

Morphology of ground $TiCr_{1.78}$ prealloyed and mixed powders is shown in Fig.1a-b. Prealloyed powders showed flaky shapes deriving from mechanical grinding of bulk material, while mixed powders are spherical and with lower chemical homogeneity. In Fig.1c-d upper view of built samples realized using prealloyed powder with the lowest (P=200W and v=100 mm/s) and the highest energy density (P=250 W and v=90 mm/s) are depicted, respectively.
The quality of top surfaces, using prealloyed powder, is strongly related to *F*; similar results were obtained using mixed powder. For low *F* (Fig.1c) the sample is characterized by high irregular surface, balling and porosity, while high *F* promotes smoother and more regular surfaces (Fig.1d).
The porosity observed at the low energetic conditions is mainly associated to lack of fusion. In these conditions the powder is partially melted, leaving open gaps between adjacent tracks and layers. The balling can be generated during the formation of short molten track, which consequently splits along the track and solidifies in form of intermittent lines or droplets [14]. It can be favoured by oxidation, crucial problem for reactive materials, like Ti based alloys. Excessive *F* can cause instable melt pool, porosity and balling. Correct adjustment of *F* is usually the solution to reduce the balling and to improve part density [15]. The surface of samples carried out with low *F* indicated pores connected to the surface, highlighting the effects of lack of fusion and balling. Droplets around the melted area deteriorate surface roughness as well. High porosity carried out with low *F* is confirmed by density analysis (Fig.2). Relative density of built samples improves with *F* from 91% up to 94% for prealloyed and from 93% up to 96% for mixed powder, respectively.

Another issue related to the low density is the powder form. Spherical gas atomized powders are better suited to SLM for improving flowability and powder-bed density. These properties stabilize the process and reduce part porosity, as confirmed by higher relative density obtained using spherical mixed powders.

In Fig.3a-b SEM images of sample microstructure are presented. SLM process seems to induce different microstructures, passing from prealloyed to mixed powder. Prealloyed powders allow homogeneous composition to be obtained, probably due to a more homogeneous status of the powder. Different values of size and density of Cr and Ti powders can provoke their separation during the powder bed deposition, reducing the degree of homogeneity of mixed powder. Few TiCr oxides (see circles in Fig.3a) were detected. On the contrary, using mixed powders permits the formation of Ti and Cr rich phases, spread in the $TiCr_{1.78}$ matrix (see Fig.3b). The separation of Cr and Ti powders can happen due to different size and density of the two elements. EDS analysis confirms no modification of the composition changing the powder type and *F* (see Fig.3c-d). Fig.3e-f reports representative XRD patterns. In addition to the signal of the Ti support on which the specimen was mounted, the SLM built from prealloyed powders are mainly composed of C14 and C36 Laves phases, known to form hydrates with more H atoms per $TiCr_2$ units.

The parts built using mixed powders show some residual Cr, and probably part of Ti signal comes from not-reacted powder. This is deleterious for hydrogen absorption as metal segregation reduces the amount of Laves phases. $TiCr_2$ lines are much broader than for prealloyed powder, suggesting chemical inhomogeneity and so preventing C14/C36 quantification. Part of material crystallizes as β-Ti(Cr), confirming Zhang's results [10]. Lattice parameter a~3.03 Å indicates Ti:Cr~1:2 according to Chen et al. [16]. No significant texture effect was observed in Laves phases.

The amount of Laves phases in built from prealloyed powders was estimated from relative intensities of low angle diffraction peaks. The C14 amount increases with *F* from 35% to 45%, while C15 vanishes from 10% to 0% and C36 remains constant around 50-55%. Using mixed powders Cr consumption (and $TiCr_2$ formation) increases with *F*. Same effect could be reached by thermal treatment only at very high temperature, as Ti and Cr are generally led to melting to react followed by heat treatments at ~1400° for Ti-Cr homogenization [16-17]. Prolonged annealing steps at lower temperature are supposed to stabilize different Laves phases.

According to the phase diagram, only C15 would be expected at RT, whereas C14 and C36 are observed. Probably C14 and C36, known to be stable at high temperature, will form upon cooling and retained at RT as their transformation to C15 is known to be sluggish [18]. This is in good agreement with literature: few works report the formation of C14 Laves phase during laser cladding of Ti-Cr alloys [10, 11].

Conclusion

Feasibility of producing $TiCr_{1.78}$ components via SLM using two types of not-commercially-available powders was investigated. The main conclusions can be summarized as follows:

- SLM processability of $TiCr_{1.78}$ alloy is quite difficult, due to the intermetallic nature of the alloy. Feasibility was demonstrated but process optimization is required for improving the part properties.
- Increasing energy densities reduces balling and promotes smoother surfaces.
- Relative density increases with energy density for both powder types. Mixed powders with spherical shape lead to higher relative density.
- Despite a lower relative density, prealloyed powders allow full formation of chemically homogeneous Laves phases while mixed powders do not.
- Energy density can tailor Laves phases due to different heating/cooling rates.
- Further studies on elemental mixing can be useful for determining ideal composition for improved processability. Final precursor should be in spherical form to ensure adequate flowability and density.

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Figures:

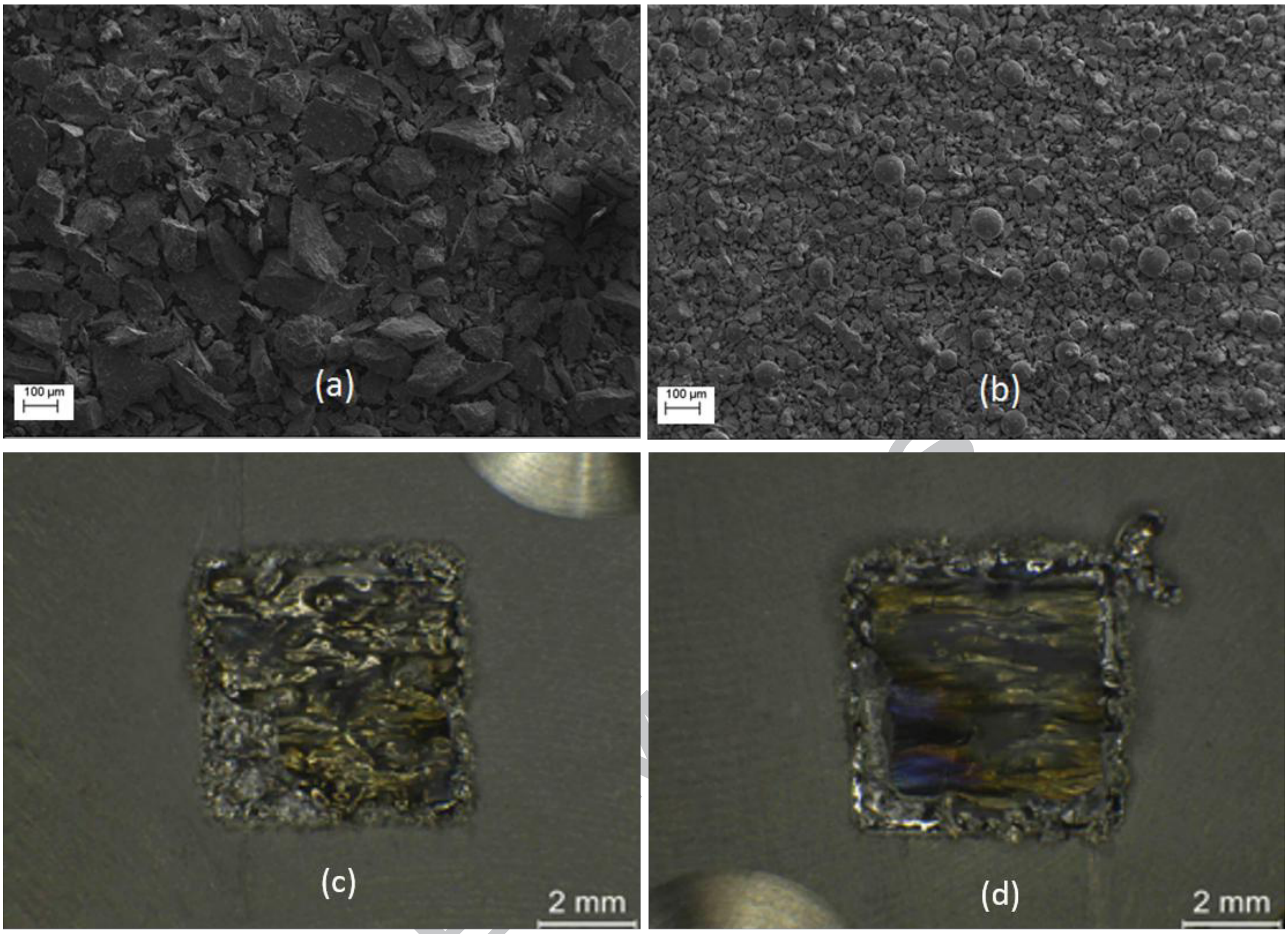


Figure 1: SEM images of the prealloyed (a) and premixed (b) powder; upper view of the samples produced via SLM with the lowest (a) and highest energy density (b) using prealloyed powder.

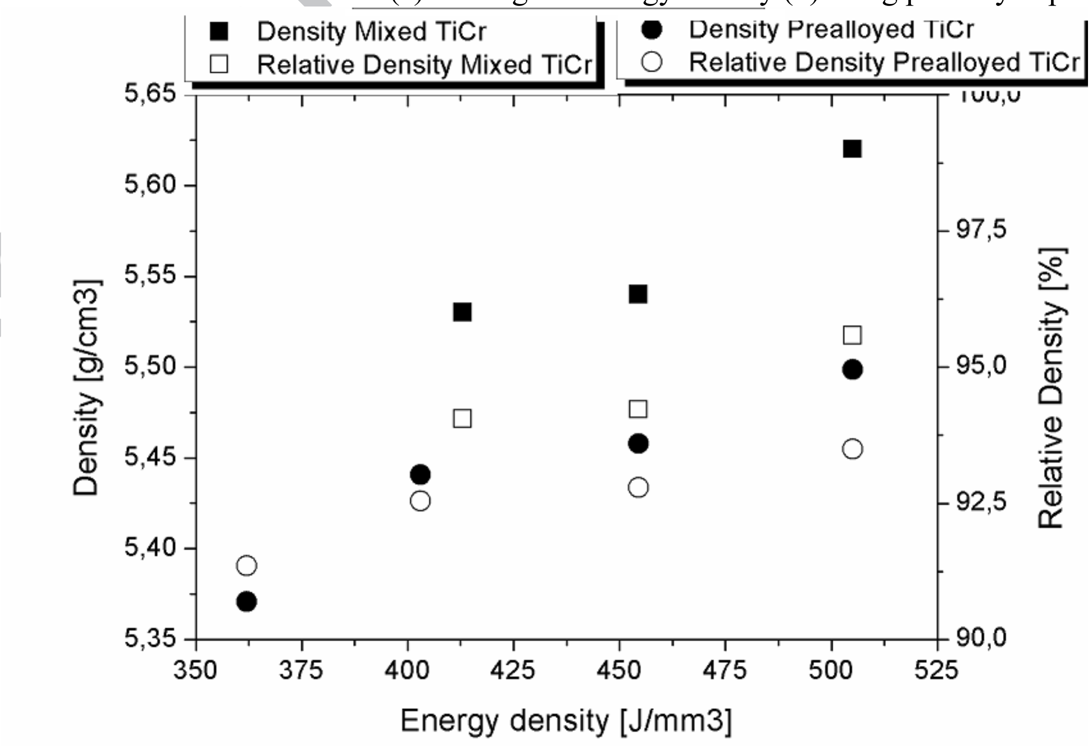


Figure 2: Density and relative density as a function of energy density

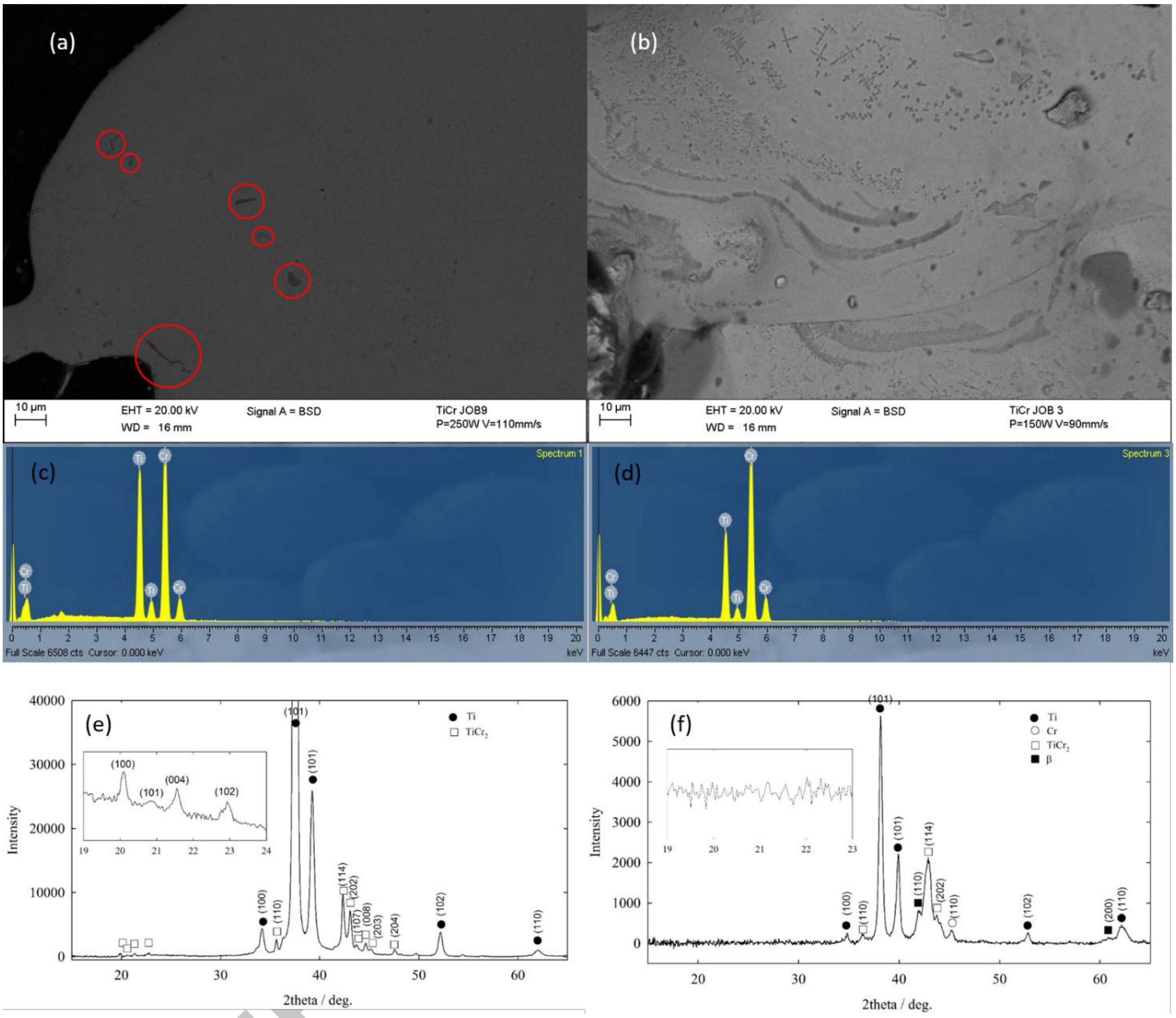


Figure 3: SEM images, EDS spectra and XRD patterns of samples built using prealloyed (on the left) and mixed powder (on the right), respectively.

Table:

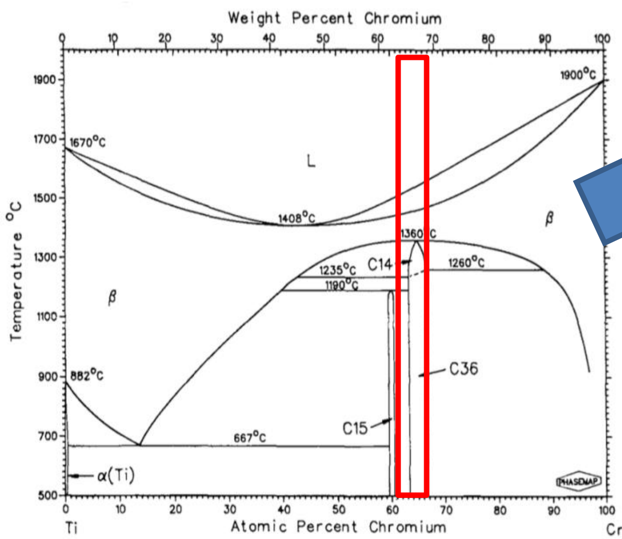
Laser power (P)	200-250 W
Scanning velocity (v)	90-100 mm/s
Layer thickness	50 μm
Atmosphere	Argon
Laser spot size	210 μm
Hatch distance	110 μm

Table 1: List of the varied and fixed process parameters

Highlights:

- Feasibility of selective laser melting (SLM) of prealloyed and mixed $TiCr_{1.78}$ powders was demonstrated.
- Energy density plays a relevant rule on microstructure, phases and relative density.
- Ground prealloyed powders induce the formation of Laves phases, while spherical mixed ones increase the relative density.

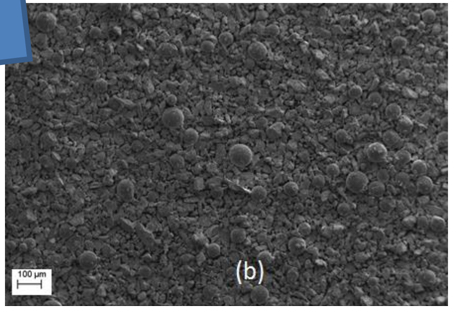
TiCr phase diagram:



TiCr1.78 alloy

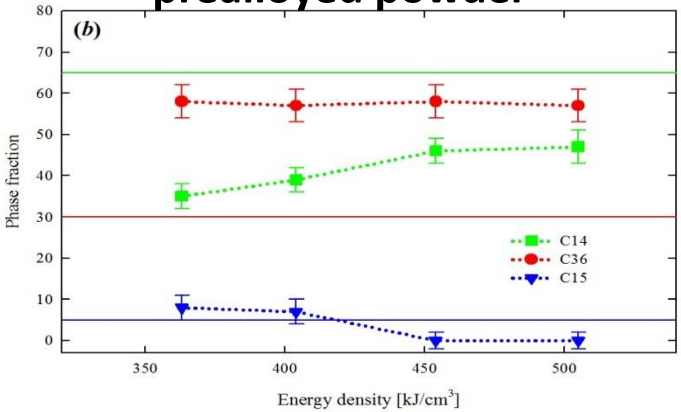
Ground prealloyedpowder

Small ingot

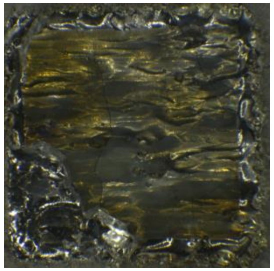


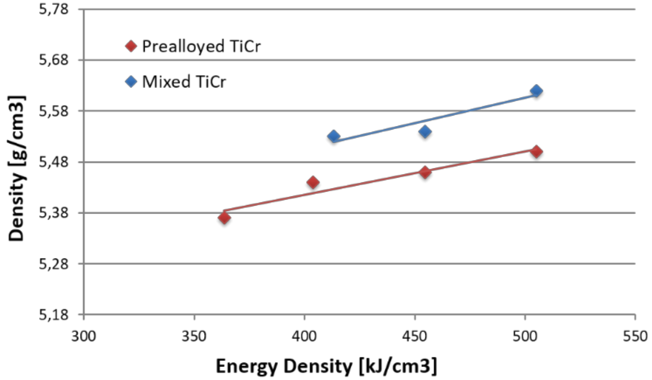
Mixed elementary powder

Formation of Laves phases using prealloyed powder



SLM built parts:





Increase of relative density using