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# Titanium alloyed with rhenium by selective laser melting

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ABSTRACT

The paper presents results of processing Ti–Re alloys by consolidating mixtures of powders of both metals with the use of selective laser melting (SLM). Ti-based alloys containing 0.5, 1.0 and 1.5 at% Re were obtained in this way. Optimum process parameters were determined by accepting the criterion of minimum porosity of manufactured parts and maximum effectiveness of dissolving Re particles in molten Ti. Density of the SLM-processed parts reached over 99.9% and 90–85% of Re powder (by volume) was dissolved. The effects of Re content on the microstructure and mechanical properties of SLM-processed parts in as-built condition were investigated. Light microscopy and X-ray diffraction examinations revealed that rhenium changed the microstructure of CP-Ti lath-type α′ martensite to acicular-shaped by lowering the temperature of martensitic transformation. A very intensive effect of strengthening titanium by the addition of small amounts of Re was found, due to α′-lattice distortion and grain refinement. Alloying with 1.5 at% Re made it possible to obtain mechanical properties similar to those of the SLM-processed Ti6Al4V alloy in as-built condition.



## 1. Introduction

Selective laser melting (SLM) is an advanced manufacturing technology providing an alternative method of producing complex components directly from 3D computer models [1,2]. During the process, successive thin (below 100 μm) layers of metal powder are fully molten and consolidated on top of each other by a laser beam. The laser beam scans the powder bed surface to form layer-wise profiles according to CAD data of a part to be built. Consequently, almost fully dense parts are produced that usually require suitable heat treatment and finish machining. Since the highly localized heat input leads to fast melting and solidification, high residual stresses develop during fabrication [3,4]. Therefore, all SLM parts should be at least stress-relief annealed before the support structure is removed.

An advantage of the SLM technology is its ability to process powders of pure metals, metal alloys and metal–matrix composites into complex structures [2], also including hard materials, difficult-to-machine materials or those with high melting points, e.g., rhenium [5], molybdenum [6] and $TiB_2$ [7]. The only restriction is market availability of the required materials in the form of powders with necessary geometrical parameters, i.e., spheroidal shape and suitable size of the particles [1,2].

One of the challenges of the SLM technology is to manufacture hybrid and monolithic materials, as well as those designed for coatings, with complex functional properties, from mixtures of powders of materials significantly differing in their properties from the process viewpoint (melting point, thermal conductivity, absorptivity and passivation ability) and, at the same time, promising with respect to meeting the design properties (high-temperature creep resistance, abrasion resistance, rigidity and corrosion resistance).

Titanium is an hcp transition metal characterized by low density, high corrosion resistance and possibility of strengthening by alloying and deformation processing [8,9]. At 882 °C titanium undergoes an allotropic transformation from hcp structure to bcc high-temperature structure that permits the forming of a microstructure of its alloys by heat treatment. In spite of high melting point (1660 °C), the maximum useful temperature for structural applications of Ti and its alloys generally ranges from 427 °C to 595 °C [9]. With respect to low strain hardening exponent of approximately 0.15 [10] and low resistance to plastic shearing [11], wear resistance of titanium and its alloys is also relatively low [12]. This restricts the application of titanium alloys for critical parts working at high thermal load or under corrosion–erosion, fatigue and tribological conditions, as well as implants for orthopedics and dentistry. So, there exists a strong demand from aircraft, automotive and chemical industries for enhancing the temperature and wear performance of Ti alloys, as well as for improving their processing methods [13].

Rhenium is a rare, noble metal with a melting point of 3186 °C. It differs from the other refractory metals by its hexagonal close-packed (hcp) lattice and unique set of physical and chemical properties [14]. So far, applications of rhenium as a modifier of

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special properties of Ti and Ti alloys designed for use at both high and cryogenic temperatures, as well as in specific corrosion environment, are not numerous in comparison to applications of the other refractory metals, like Nb, Mo and Ta. However, alloys of titanium and rhenium deserve particular attention. Addition of rhenium considerably raises the hardness and strength of Ti, as well as its recrystallization temperature [15,16]. Kovtun and Ul'yanov [15] established that rhenium is very effective in preventing the growth of grains in the heated metal and slows down the diffusion of oxygen and nitrogen into the metal. Prasad [17] found that corrosion resistance of traditional dental Ti alloys under conditions of use could be improved by an addition of 0.5 to 1.0 wt% Re. Amin et al. [18] reported that addition of rhenium enhanced pitting corrosion resistance of Ti–Ni shape-memory alloys in aggressive environments. Kovtun and Ul'yanov [15] stated that alloying titanium with rhenium, particularly Ti alloys of complex composition, may turn out to be very effective in raising high-temperature strength of the alloys.

According to the Ti–Re phase diagram [19], rhenium as a β-stabilizer reduces the α/β transus temperature and entails complete stabilization of β phase at concentrations above 10 at%. Estimated solubility of Re in α-Ti is approximately 0.1 at% at 750 °C, while in β-Ti it reaches 40 at%. The alloys with concentrations of Re between 0.1 at% and 10 at% have two phase structures α+β. At high cooling rates, they undergo martensitic transformation starting at the temperature dependent on the concentration of Re dissolved in β phase.

Because of low solubility in α-Ti and high solubility in β-Ti, rhenium can significantly affect properties of α+β alloys with a high volume fraction of β phase, as well as single phase β alloys. A strong action by solid solution hardening of β phase and α′ martensite is expected, and thus there is improvement of the tribological properties. Rhenium should stabilize the mechanical properties of α+β and β alloys at elevated temperatures. Occurrence of the 'rhenium effects'[20] is possible in β phase alloys. It seems to be very promising, considering excellent properties obtained by Vrancken et al. [6] for the SLM β-alloy by an addition of Mo.

The attempt of using Re to modify the properties of Ti alloys by SLM was undertaken considering that rhenium, like Mo and other refractory metals or compounds, like $TiB_2$, readily dissolves in molten titanium [7,21,22]. Liquid titanium is chemically very reactive, especially in superheated state. It dissolves rhenium through the liquid metal corrosion mechanisms [23,24]. The temperature of liquid titanium decides the solubility limit of Re in Ti and the diffusion rate of Re away from the liquid/solid interface. In the SLM process, the factors increasing the solution rate are temperature and concentration gradients, as well as stirring motion of liquid in the molten pool. In addition, the presence of standard impurities (O, N) in molten Ti can significantly speed up the liquid–metal corrosion [22,24].

Laser melting offers high cooling rates of the order of $10^3$–$10^8$ $Ks^{-1}$ [12]. Thus, in the alloys fabricated by SLM containing < 3.6 at% Re a microstructure of α′ martensite with or without the residual β phase should be formed [25].

In the light of the above data, there are rational grounds to suppose that an addition of rhenium can be used for modifying the microstructure and properties of titanium and complex Ti alloys in order to improve their behavior under specific service conditions and that SLM has the capability to process powder mixtures of titanium (Ti alloys) and rhenium.

The objective of this work was to use the SLM technology for alloying CP-Ti with the addition of small amounts of Re by consolidating mixtures of powders of both metals. The obtained Ti–Re alloys were subjected to examinations of microstructure and mechanical properties. On these grounds, the effectiveness of the SLM technology in processing powder mixtures of metals with significantly differing melting points was described, and the modifying influence of rhenium on the properties of the generated Ti–Re alloys was determined. The obtained results are expected to make a ground for developing new Re-modified Ti alloys with improved low and high temperature properties, as well as biocompatibility, wear and corrosion resistance, and resistance to form 'α-case' in oxidizing environments.

## 2. Materials and methods

Test specimens were fabricated from mixtures of titanium and rhenium powders in proportions of 20, 40, 60 g Re per 1 kg of Ti powder. Three Ti-based alloys containing 0.5, 1.0 and 1.5 at% Re (1.95, 3.85 and 5.66 wt% Re) were obtained in this way. Experiments aimed at obtaining alloys with higher Re (> 3.6 at%) concentration are planned as the next stage of the research. Commercially pure Ti powder grade 1 (0.13 wt% O and 0.03 wt% N) consisted of spherical particles dia. 20–60 μm. Commercially pure Re powder (99.9 wt% Re; 0.25 at% O and 0.01 at% N) composed of irregularly shaped particles was subjected to plasma-atomization process to obtain spheroidal particles and to improve its flowability. The alloys were manufactured using a fraction of Re particles ≤ 40 μm, separated by the sieve method. The powder mixture (Fig. 1) had a good flowability.

All the SLM specimens were prepared using a SLM Realizer II (MCP-HEK) machine equipped with a continuous wavelength (CW) Ytterbium fiber laser with a beam spot size of 180 μm and maximum power of 100 W. High-purity argon was used as the shielding gas.

As a starting point, the criterion of obtaining fully dense material was accepted for selecting the process parameters. To this end, series of cuboidal specimens 12.5 × 10.0 × 6.5 $mm^3$ were built at constant parameters: laser power 100 W, 75 μm layer thickness, 100 μm distance between scan vectors (hatch spacing) and variable scanning speed. The cuboidal specimens of the reference CP-Ti material were fabricated at a scanning speed of 115 mm/s (scanning time of one point = 520 μs and distance between scanning points = 60 μm). In order to evaluate the influence of scanning speed on the effectiveness of dissolving rhenium particles in molten titanium, the cuboidal specimens of Ti–Re alloys were prepared at scanning speeds of 115 mm/s and 24 mm/s (scanning time of one point = 520 and 2500 μs, respectively, and distance between scanning points = 60 μm). Concentrations of O, N and H in the manufactured specimens were determined by hot gas extrusion and concentration of carbon was determined by the gravimetric method.

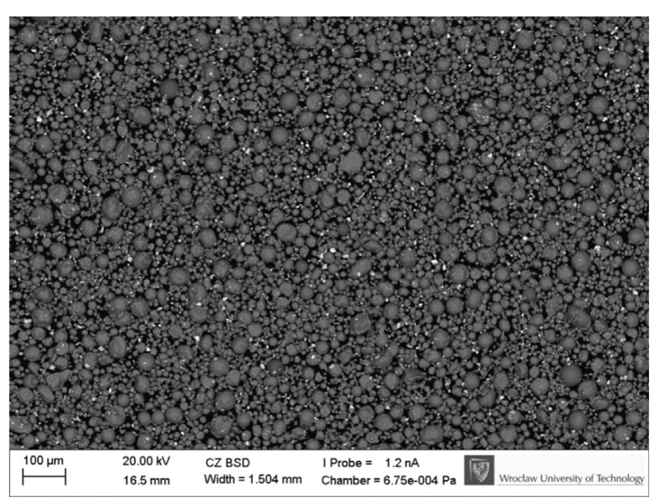


**Fig. 1.** CP-Ti+Re powder mixture. The bright particles are Re.