IN-SITU SYNTHESIS NI-TI ALLOY BY LASER CLADDING

[1]Sergei IGOSHIN, [2]Dmitriy MASAYLO, [3]Artem KIM, [4]Anatoliy POPOVICH

[1]Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation,
sergei.igosshin@gmail.com
[2]Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation,
dmasaylo@gmail.com
[3]Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation,
artem_7.kim@mail.ru
[4]Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation,
popovicha@mail.ru

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Abstract

The NiTi alloy shape memory effect can have a much larger field of application in industry and everyday life than it is now. The high cost of obtaining this material and the laboriousness of the process limit its scope of application. The use of modern 3D technology may help solve this problem This paper explores the possibility of growing samples of simple geometric shapes in the form of tubes from Ni and Ti elemental powders. Samples from 3 types of powder mixtures have been produced. The first mixture with an excess of Ni relative to the equatorial ratio, the second with a deficit of Ni, the third with 5 % addition of Cu. The microstructure of samples before and after thermal treatment in argon at 900 ˚C was studied. The heat treatment contributed the process of homogenization of the solid solution, but had no significant effect on the sample hardness or reduction of secondary phases. Heat treatment changed hardness by an average of 10%. Phase analysis before and after the heat treatment showed a significant proportion of NiTi phase as well as secondary phases of $NiTi_2$, Ni_3Ti, TiO_2.

Keywords: Additive technology, laser cladding, powder metallurgy, automated production, nitinol

1. INTRODUCTION

Functional material nitinol (NiTi) has unique properties of the shape memory effect (SME), which can potentially be widely used in most household devices and mechanisms. Today this material is used only in industries with high profitability and where the SME is not replaced by another analogue. Typical examples are orthodontic arcs in dentistry, prosthetics, expanding bushings in aircraft construction and mechanical thermal alarm. The high labor content of this material which directly affects the final cost of a particular product make it difficult to implement it everywhere.

The main commercial method of producing an alloy consists of the following technological processes [1]:

1) vacuum arc remelting to obtain a well mixed alloy
2) vacuum induction melting to reduce impurities
3) casting followed by hot or cold rolling to obtain a uniform structure
4) intermediate annealing and cutting
5) final deformation of the product and heat treatment with the product locked in place to "memorize" the shape

The nitinol material was obtained quite a long time ago. In 1962, William Buhler and Frederick Wang discovered the SME of a nickel and titanium-based alloy [2]. A study of the synthesis methods of this material and an attempt to create more optimal methods for its preparation are still being developed.

There is modern research on experimental methods of producing nitinol alloy with the aim of cheapening the synthesis process or shortening the process chain to expand its areas of application. Some examples of methods for the production of nitinol, other than vacuum-arc remelting are implemented by the following methods:

- Hot isostatic pressing (HIP) [3]
- Injection molding [4]
- Self-propagating high-temperature synthesis (SHS) [5]

In this paper the method of laser cladding from elemental powders of nickel and titanium for the synthesis of NiTi alloy was proposed. This approach allows to combine the process of material melting and forming [6–8]. In well known papers of nitinol synthesis on additive technologies equipment sealed chambers with an inert medium are used [9,10]. In this article the synthesis is performed under the conditions of inert gas (argon) flow directly in the melting region.

The manifestation of the SME is influenced by martensite transformations of two types – forward and reverse. Each of them is manifested in its own temperature range. Temperatures of martensite transformations are determined by the chemical composition and purity. Therefore, even small changes in chemical composition lead to a shift in these temperatures [11]. To solve the problem of obtaining the SME in a certain temperature range it is necessary to carefully select the ratio of initial elemental powders, as well as to control the phase composition and size of structural components.

The main task of the work is to determine the degree of diffusion of components in a sample width of one track, study the chemical, phase composition, structure, as well as the effect of thermal treatment on samples obtained by laser cladding.

Features of NiTi alloy synthesis by laser cladding method are as follows: the laser provides melting of the elements caught in the melting zone, and its relatively slow cooling rate, which should ensure homogeneity of the synthesized alloy. The scheme of the growing process is shown in **Figure 1**. Powder mixture of Ni and Ti elemental powders is fed into powder feeding nozzles by a powder feeder.

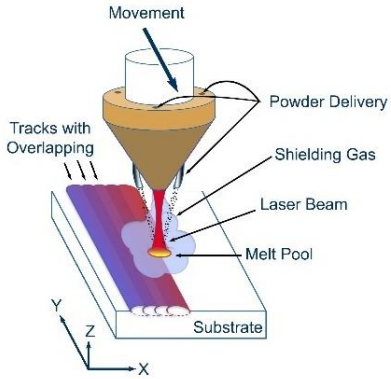

Figure 1 Scheme of the process of sample growth by laser cladding method

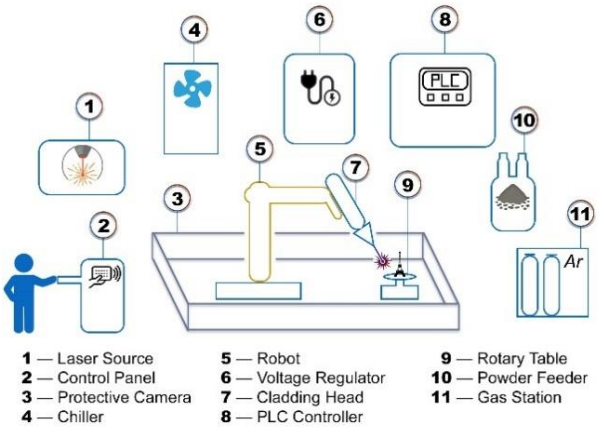

Figure 2 Scheme of plant components for in-situ NiTi synthesis by laser cladding

2. METHODOLOGY AND EXPERIMENT

Synthesis and production of NiTi samples using laser cladding technology was carried out at the plant developed in SPBPU, the scheme of which is shown in **Figure 2**. The main components of the unit continuous ytterbium fiber laser iPG LS-3, powder feeder PF 2/2, optical system (cladding head) KUKA MWO-1 and Fanuc M20i robot. Initial components for the production of the mixture: spherical titanium powder of the brand VT1-0

with a particle size distribution 45-100 microns and not spherical nickel powder with a particle size distribution 5-30 microns is used. Mixing of powders was carried out by a mechanical method. Based on the results of the theoretical study, three types of mixtures with different proportions of components were selected and manufactured (**Table 1**).

Table 1 Composition of mixtures for NiTi synthesis

Mixture type	Mixture component percentage (wt%)
Mixture 1	57 Ni, 43 Ti
Mixture 2	51 Ni, 49 Ti
Mixture 3	44 Ni, 51 Ti, 5 Cu

Model of samples for growing as a tube can be seen in **Figure 3**. Growing was performed in a closed, leaky chamber filled with argon. A part of the produced samples was subjected to heat treatment (HT) - homogenization annealing in a vacuum furnace in argon medium at heating 900 ˚C, holding time – 1 hour.

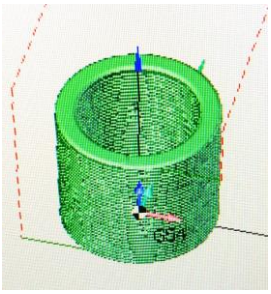

Figure 3 CAD sample model

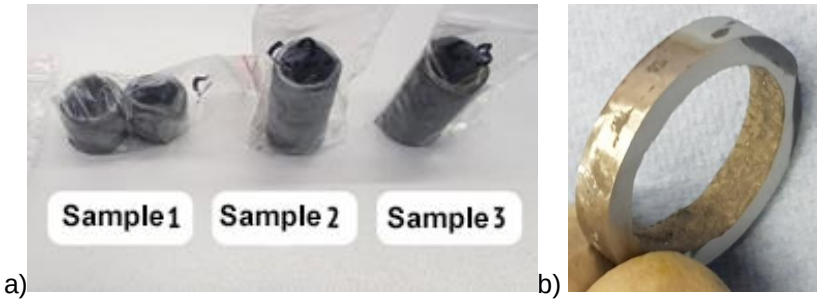

Figure 4 Manufactured NiTi samples from elemental powders by laser cladding, where a - general view, b - sample in section

The study of the structure was carried out on prepared grinders after mechanical grinding and polishing. Chemical etching was carried out in a solution of 10 ml HF, 20 ml HNO_3, 30 ml H_2O. Chemical analysis was carried out on SEM Tescan Mira 3 electron microscope with EDS attachment. X-ray phase analysis was carried out on Bruker D8 Advance diffractometer in the range of 200 to 1000 angles with 0.02 step and 2 s exposure time at each step. Quantitative phase analysis was performed using TOPAS5 software. Hardness measurement was performed using the Vickers method.

3. RESULT AND DISCUSSION

The appearance of the obtained samples is shown in **Figure 4.** Visually all samples turned out to be homogeneous without any visible defects in the form of non-smelts and cracks. The microstructure of samples before and after heat treatment is shown in **Figure 5**.

The obtained images of the microstructure show a cast dendritic structure consisting mainly of two phases. Homogeneity of the structure is revealed, which varies from the track centre (the zone with maximum energy density) to the peripheral zone. In general, 3/4 of the track thickness is a homogeneous solid solution and 1/4 heterogeneous areas associated with incomplete re-melting. The reason for this is Gaussian energy density of the laser spot and increased crystallization rate of the external wall material. It is important to note that the pronounced defect of heterogeneity observed at the edges can be corrected by mechanical removal of a layer of material.

The heat treatment resulted in diffusion processes that increased homogeneity within the sample. This can be clearly seen from the change in structure in **Figure 5 d**. There was no change in the structure of sample 3 after

heat treatment. The results of the measurement of the chemical composition of the original samples in the middle of the cut of the sample and at the edge are presented in **Table 2**.

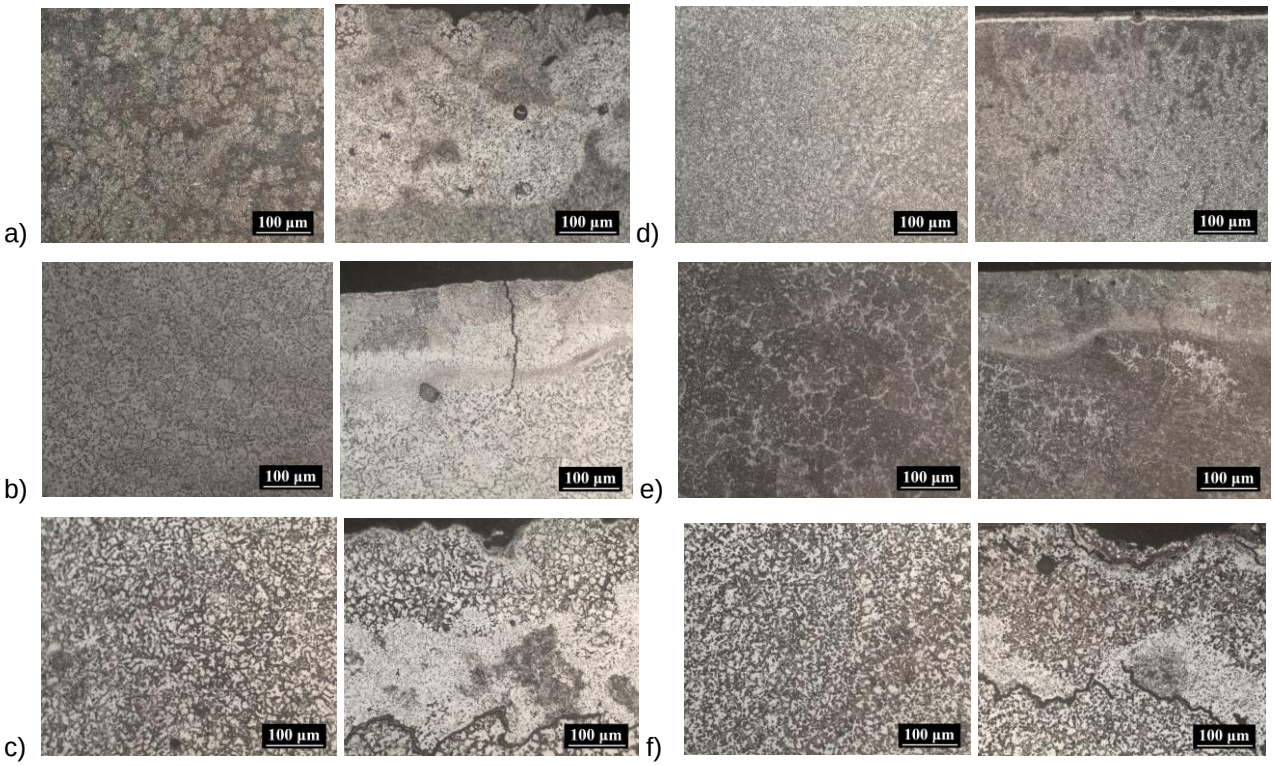

Figure 5 Microstructure (zoom 200) after cladding in the centre of the sample (left) and on the border (right), where the samples before heat treatment: a - sample 1, b - sample 2, c - sample 3 and samples after heat treatment: d - sample 1, e - sample 2, f - sample 3

Table 2 Results of measuring the chemical composition of NiTi source samples (in wt%)

Simple 1				**Simple 2**			**Simple 3**			
elements	O	Ti	Ni	O	Ti	Ni	Cu	O	Ti	Ni
center	12.6	31.2	5.2	2.0	46.3	51.7	5.3	7.8	42.1	45.6
edge	8.6	39.8	51.6	2.4	44.6	53.0	6.4	6.1	35.3	51.6

Chemical analysis in the centre of samples showed that the deviation in the chemical composition of Ni is 1 – 2 % relative to the content in the elemental mixture. Titanium seems to be significantly oxidized in an un-tight chamber. This results in the addition of oxygen. Sample 2 is closest to the initial composition that can be obtained when the condition of absence of oxygen in the synthesis zone is fulfilled. The chemical composition at the edge of the sample has no obvious dependencies.

Table 3 X-ray crystallography quantification results

	Sample 1			**Sample 2**			**Sample 3**	
Phase	**Original**	**HT**	**Phase**	**Original**	**HT**	**Phase**	**Original**	**HT**
NiTi	42.5 %	44 %	B2	10.1 %	46.3 %	NiTi0.8Cu0.2	19.9 %	20.2 %
Ni_3Ti	35.2 %	45 %	B19'	71.1 %	37.5 %	NiTi2	67.9 %	66.4 %
Ni	6 %	2.7 %	NiTi2	18.8 %	16.2 %	CuTi2	6.7 %	7.2 %
$NiTi_2$	16.3 %	8.2 %				Ni	5.5 %	6.2 %

The phase composition of the initial samples 1-3 and after heat treatment is shown in **Figure 6**. The results of XRC show that the structure of sample 1 is characterized by two main phases of NiTi and Ni_3Ti. The small amount of Ni is due to incomplete mixing of components in the melting process. Subsequent heat treatment promotes dissolution of the impurity phases. The results of the quantitative analysis are presented in **Table 3**.

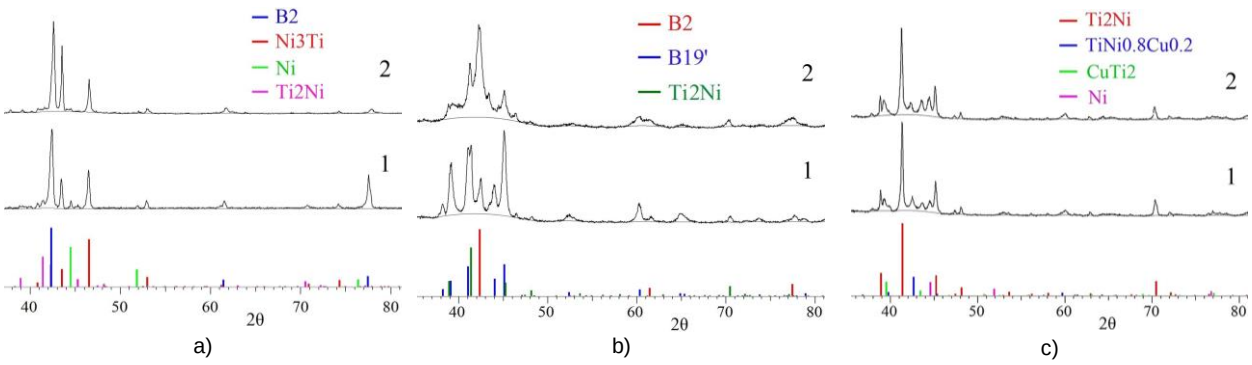

Figure 6 Phase analysis, where a - sample 1, b - sample 2, c - sample 3, curve 1 - initial, curve 2 – after HT.

In sample 2, the presence of the austenitic and martensitic phases of nitinol, as well as the $NiTi_2$ phase, is observed. Heat treatment significantly reduces the martensite content in the structure from 71.1 % to 37.5 %, and increases the proportion of the austenitic component to 46.3 %. In the sample 3 doped with Cu, the main one is the martensitic phase doped with Cu. Heat treatment did not significantly affect the phase composition of the sample. The results of measuring the hardness of the samples are presented in **Figure 7**.

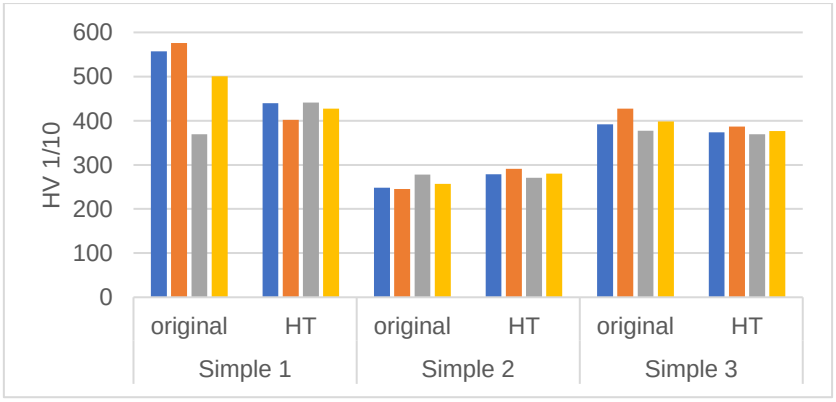

Figure 7 The hardness of the samples. Each 4th column shows an average value

The wide spread of hardness values in sample 1 confirms the heterogeneity of the structure. Heat treatment did not significantly reduce the hardness, but only increased the homogeneity of the sample structure.

4. CONCLUSION

As a result of the paper carried out the samples of tubular form were produced by laser cladding from Ni and Ti elemental powders.

Studies of microstructure showed a predominantly homogeneous structure in the middle of the sample and the presence of a pronounced zone of heterogeneous structure along the edges of the samples. The chemical

composition of samples at a distance of 0.5 mm from the edge is uncontrollable, so this part should be removed.

Manufacturing in an un-tight chamber in an argon environment led to significant oxidation of the material. The "purest" sample from mixture 2 contains approx. 2 % oxygen, which is a good result considering the affinity of Ti to oxygen. Hardness measurements have also shown that sample 2 has the lowest hardness compared to other compositions, which may indicate the plasticity of the material. On average, the Ni content of all mixtures has a spread of 1-2 % of the original mixture, while Ti has a much greater spread due to oxygen substitution. As it is known, to control the temperature of martensite transformation, the values are 0.1 %, so it is not possible to accurately select the content of the initial components in this plant.

The phase analysis showed that heat treatment allows to regulate the phase composition of samples synthesized by laser cladding and control the content of secondary phases Ni_3Ti and $NiTi_2$, as well as to increase the proportion of austenitic phase B2.

Thus, the results obtained show the prospects for the synthesis of NiTi alloy by laser cladding and in-situ manufacturing of products.

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