### ARCHIVES OF MECHANICAL TECHNOLOGY AND MATERIALS www.amtm.put.poznan.pl



### Laser heat treatment of nickel-based alloys - a review

### Mateusz Kukliński<sup>a\*</sup>, Michał Szymański<sup>a</sup>, Damian Przestacki<sup>a</sup>

<sup>a</sup> Poznań University of Technology, Faculty of Mechanical Engineering and Management, Institute of Mechanical Technology, Piotrowo 3, 60-965 Poznań, Poland

\*Corresponding author, Tel.: +48-602-633-705, e-mail address: mateusz.kuklinski@doctorate.put.poznan.pl

#### ARTICLE INFO

Received 18 June 2019 Received in revised form 04 November 2019 Accepted 07 November 2019

#### KEY WORDS

nickel, laser, heat treatment, surface, coating

#### ABSTRACT

In this paper researches which focus on laser heat treatment of nickel-based alloys are reviewed. Studies published from 1970s until today are taken into consideration. Publications which focus on influence of laser thermal processing on surface layer condition both on solid materials and pre-deposited coatings are described. Laser technologies in which additional materials are delivered during the process are not considered. In order to focus on studies investigating microstructural changes resulting mainly from material remelting, laser shock processing is also disregarded.

#### 1. INTRODUCTION

The invention of laser opened new possibilities in materials engineering. Scientists obtained a source of concentrated power which can be easily adjusted for specific applications. One of these applications in processing of metals is laser heat treatment which leads to structural changes and surface texturing [1]. These modifications impact on properties which vary depending on chemical composition of the processed material and on its type as well as parameters of laser remelting process. This paper is a review of publications which focus on laser heat treatment of nickel-based alloys in solid form and in form of coatings predeposited with other technologies.

First researches on laser heat treatment of nickel-based alloys which were published in 1970s focused on analyzing effects of surface laser melting without specific purposes of the treatment [2,3]. In that period researchers mainly investigated new microstructures obtained after laser processing along with their compositions due to the fact that they were hard to achieve using other methods. This trend continued but over time it became important to study properties of produced nickel-based structures and some publications from times between 1990 and 2000 contain results from microhardness measurements [4], thermal stability tests [5], crack formation analysis [6] or intergranular stress corrosion cracking behavior [7,8]. In recent years laser heat treatment of nickel-based alloys has been investigated in terms of specific analysis on influence of processing conditions on microstructure and thus on final properties [9]. Moreover, due to the growing interest in processing of single-crystal alloys for high temperature applications, also laser heat treatment of these materials has been the objective of latest research [10,11].

Simultaneously with aforementioned publications which focus mainly on influence of laser heat treatment on mechanical properties of nickel-based alloys, changes in nickel-based biocompatible NiTi alloy were investigated. Since 1990s researchers involved in these studies have focused mainly on its corrosion resistance after the process [12]. In later researches different laser types and treatment conditions were carried out to determine optimum technology for obtaining non-corrosive and stable surface layer [13,14]. Studies on behavior of nickel-titanium alloy for

DOI: 10.2478/amtm-2019-0009

© 2019 Author(s). This is an open access article distributed under the Creative Commons Attribution-Non Commercial-No Derivs license (http://creativecommons.org/licenses/by-nc-nd/3.0/) medical applications after laser heat treatment, in more detail, are continued until today [15].

Nickel-based alloys are being laser heat treated not only in form of solid volumes but also as two-dimensional structures like coatings and layers. In this case, final properties of remelted areas, besides from laser processing parameters, depend on the condition of pre-deposited coating and of the substrate material. Experiments of this kind started to be performed in 1980s and were aimed to investigate the influence of laser heat treatment on condition of thermally sprayed coatings [16,17]. Obtained results encouraged researchers to study changes in corrosion resistance. Also later this prospective technology was carried out to improve properties of thermally sprayed nickel-based coatings. In the 21th century thermal sprayed coatings were laser heat treated to better understand formation of new phases and for improving their wear resistance and microhardness [18,19]. Moreover, in recent years studies on increasing solar absorption by laser heat treatment in nickelbased materials for green technologies were also published [20].

Concurrently with researches on laser heat treatment of thermally sprayed coatings, influence of the process on electroplated nickel-based coatings was investigated. Studies of this type began to appear in 1990s [21] and later focused mainly on Ni-P electroless coatings. The influence of laser surface processing on wear and corrosion properties as well as on friction coefficient was also studied [22]. Other researchers investigated final properties obtained with different process parameters [23,24], substrate materials [25] and additional elements in coating composition [26,27].

This paper is a review of studies on laser surface processing of nickel-based alloys in which no additional material is delivered into the molten pool. Thus, researches on laser alloying, laser cladding and additive manufacturing technologies are not considered. Moreover, in order to describe treatment in which a major factor influencing structure of material is heat, laser shock processing is also neglected.

# 2. LASER HEAT TREATMENT OF SOLID NICKEL-BASED ALLOYS

The first attempt to modify microstructure of nickelbased alloys with focused laser beam was described in 1976 by Breinan et al. [2]. It was also one of first surveys in which material was melted using a continuous laser beam instead of pulsed laser. Therefore, before the process, authors could base their assumptions mainly on experiments in which rapid cooling of melted material was obtained with techniques other than laser processing. However, conscientious planning of the experiment with taking into consideration influences of:

- power density on materials temperature,
- laser interaction time on depth of melting,

• melt depth and laser density on average cooling rates resulted in obtaining authoritative results. A continuous beam was generated using  $CO_2$  laser of maximal power equal to 3 kW and focused to 0,5 mm diameter on the workpiece by reflective optics. This system provided a maximum incident power density of approximately  $1.5 \times 10^6$  W/cm<sup>2</sup>. For achieving determined interaction times, dependent on laser beam scanning velocity, specimens were put on rotating disc mounted on a variable speed motor. Three classes of nickelbase alloys were selected for the process: eutectic, particle strengthened and lamellar eutectic. Authors found that after laser heat treatment dendritic microstructures composed of nickel solid solution and hard particles (borides or carbides) which were not found in as-cast structure formed. Specific compositions and contents of these particles depend on cooling rates and composition of an alloy. Moreover, it was observed that these phases occurred uniformly throughout obtained structures.

Three years later, Narasimhan et al. made a step further in their research on solidification of Udimet 700 alloy after CO<sub>2</sub>laser melting, describing particular areas in remelted zone [3]. Authors observed four zones of different microstructures and claim that these differences result from varying solidification rates and thermal gradients. These zones are shown in figure 1. It was observed that the featureless zone was closest to the substrate which consolidated with the highest cooling rate (area 1). Above, there is a structure composed of dendrites parallel to the maximal thermal gradient (area 2) and two areas including branches growing along the direction of laser motion (areas 3 and 4).



Fig. 1. Area laser remelted on Udimet 700 [3]

Aforementioned researches revealed that laser heat treatment of nickel-based alloys leads to achieving new microstructures with unknown properties which can be useful. Since then, it has become important to investigate obtained microstructures and the influence of process parameters on their properties.

Thus, in 1990, Gadalov et al. investigated the structure and properties of heat-resistant nickel alloys after laser treatment, additionally including the influence of cooling rate on these factors [4]. In this study three alloys containing chromium, molybdenum, tungsten, titanium, aluminum, niobium and carbon in different contents were produced by two methods: casting in wax patterns and plasma spraying on cylindrical rollers. Then specimens were irradiated using continuous CO<sub>2</sub> laser beam. As in papers from 1970s, dendritic structure of two directions of growth was observed. Also new phases (metal carbides and  $\gamma + \gamma'$  eutectic) appeared which were not present in as-cast specimens. In plasmasprayed specimens fine crystalline structure occurred after laser heat treatment. The analysis of the influence of cooling rate on the microstructure of high-chromium nickel alloys revealed that increasing cooling rate leads to refinement of the dendritic structure and a decrease in the size of  $\alpha$ -Cr phase precipitates. Moreover, if cooling rate is more than or equal to approximately 2°C/s eutectic $\gamma$ -( $\alpha$ -Cr) and  $\alpha$ -Cr phase do not form.

Besides from microstructural analysis, authors investigated properties of laser heat treated zones. Due to the fact that phase composition differs from as-cast specimens, modifications in properties were expected. Indeed, microhardness and wear tests performed on specimens before and after the laser treatment revealed that the microhardness increases from 1.4 to 2.7 times after the process. Level of this increase is dependent on laser treatment parameters which influence the amount of precipitates and subsequently the chemical composition of other phases. When it comes to the wear resistance, the rate of wear decreased almost 3 times after the laser heat treatment and it indicates the high effectiveness of the process.

In the same year, Nikitin et al. decided to analyze microstructures of nickel-based alloys after laser heat treatment in terms of thermal stability and possible impact on strength and plastic properties [5]. Moreover, the influence of energy density and scanning velocity on the microstructure was investigated. The process was performed with continuous beam produced with CO2 laser. The experiment was conducted on two nickel-based alloys of slightly different chemical composition, thus before the process specimens were heat aged for obtaining almost equal contents of  $\gamma'$  phase in both materials. As in aforementioned researches, after laser heat treatment carbides and eutectic phase  $\gamma + \gamma'$  occur, however, authors additionally noted that morphology of  $\gamma'$  phase changes during the process. Particles become spherical and their size distribution is more uniform. After microstructural analysis, researchers aged specimens which were laser heat treated as well as these in original condition at 850 °C (imitating the service conditions) in order to compare differences in thermal stability. After microstructural investigation it was concluded that the thermal stability of laser heat treated specimens is higher than only after stepped aging. Particles of  $\gamma'$  phase were of lower sizes and their distribution was more uniform in material which was laser processed.

New features of microstructures obtained with laser heat treatment of nickel-based alloys were discovered by Solov'ev et al. in 1995 [6]. Authors processed materials with pulsed and continuous laser beam and after the process they observed same uniformly dispersed phases in dendritic structure as their predecessors have been recognizing since 1970s. Additionally, they described the dependence between energy and length of the laser pulse and the size of remelted area. Novelty of the paper lies in analysis of crack formation in areas processed with pulse laser which has proven to be dependent on microhardness and depth of treated areas. It was discovered that if microhardness and depth of remelted layer are higher, more microcracks form within its volume. Moreover, the number of pulses applied on the surface increases the number of microcracks and can even result in their enlargement into macrocracks. Thus, the application of a continuous laser beam was recognized as more efficient due to the fact that the thermal cycle can be regulated in a wider range both at the heating and cooling stages.

Research on cracking behavior of laser modified nickelbased alloy was carried out by J.H. Suh et al. in 1998 [7]. The experiment described how the laser surface melting with continuous  $CO_2$  laser beam improves resistance to intergranular stress corrosion cracking in oxidizing environments of nickel Alloy 600. Due to the fact that this alloy is applied in pressurized water reactors in power plants and it is crucial to increase their operating efficiency, this study was significant for the industry. Authors performed slow strain rate tests in solution of Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> for investigating the cracking behavior. It was discovered that laser heat treatment changes fracture model from a brittle intergranular to ductile. Authors claim that this effect is achieved by elimination of microstructure inhomogeneities at the grain boundaries and redistribution of solute atoms, especially chromium.

After discovering that chromium precipitations have significant role in increasing resistance to intergranular stress corrosion cracking, in year 2000 Yun Soo Lim et al. investigated the mechanism of forming Cr-rich particles which were observed in previous studies in Ni-base Alloy 600 [8]. Authors decided to perform aging of the Alloy 600 at 600 °C for 24 h after laser heat treatment using  $CO_2$  laser. It was found that chromium-rich precipitations form mainly at high angle grain boundaries and crystal defects. Due to the fact that more defects like dislocations and excess vacancies occur in the structure after laser heat treatment, it was stated that laser remelting process is more effective in increasing intergranular stress corrosion cracking resistance than conventional heat treatment.

In 2012, S. Petronić et al. carried out an investigation of microstructure, microhardness and roughness after laser surface treatment process on the Nimonic 263 alloy [9]. The material was exposed to a Nd:YAG pulsed laser with a pulse duration of 170 ps. The experiment was performed using two laser beam energies: 40 mJ and 10 mJ in air and 40 mJ in atmosphere enriched with helium. Another varying parameter was number of pulses and it was equal to 10, 100, 400 and 1000. As the result of laser processing, researchers obtained modified spots of the shape of concentric circles which can be divided in four zones, starting from the center: zone of thermal processing which is characterized by the melted material, zone of thermo-mechanical processing in which melting and plastic deformation occur, zone of mechanical processing which was plastic deformed and the deposition zone which is a layer formed by precipitation of evaporated material. Processed surface was described as degassed and porous with some cracks formed due to rapid cooling. It was observed that surface roughness increases with an increase of the number of laser pulses due to more expressed ablation and after 1000 pulses crater formation occurs. On the other hand, analysis of chemical composition confirmed that in the irradiated area the increased content of Ti and Cr which together with the increased microhardness suggests the formation of carbides in the processed zone. Moreover, it was stated that microhardness increases with the number of pulses and the highest microhardness was measured on the sample processed in helium-enriched atmosphere.

In recent years a trend has been observed in investigating processing of single-crystal high temperature nickel alloys. One of the outcomes of this trend in laser surface treatment is a research published by Yao-Jian Liang and Hua-Ming Wang in 2016 [10]. Authors did not strictly analyze the results of laser treatment but the influence of conducting solution treatmentat 1300 °C for 4h before the laser heat processing on the stray-grain formation in molten pool. Formation of

stray grains breaks single crystal structure because of different crystal directions than in the substrate and it is crucial to minimize this effect. The experiment was performed on SRR99 alloy using laser power equal to 1000 W and laser beam scanning velocity 5 mm/s. It was discovered that applying the solution treatment before performing some laser heat treatment processes on single crystal alloys can effectively avoid the stray grain formation. This is due to homogenizing the substrate and thus decreasing the number of potential positions for forming stray grains which appear from structural impurities.

In the same year, the authors of aforementioned publication went a step further in analyzing the laser heat treatment of single-crystal alloys and decided to formulate the mathematical model for predicting microsegregation in remelted areas [11]. In this study the analysis of the influence of laser processing parameters on microsegregation behavior revealed that the microsegregation behavior is governed by the solidification velocity and the temperature gradient. Thus, microsegregation can be reduced by using a set of parameters which can obtain high solidification velocity and temperature gradients. The model described in this study is useful for selection of parameters for preparation of single crystal nickel alloys components with laser heat processing.

The effect of homogenization of microstructure in nickelbased alloys after laser heat treatment became useful also for medical applications. This trend started in 1990s and one of the first researchers who laser processed shape memory NiTi alloy that is biocompatible were Villermaux et al. who published their results in 1997 [12]. The aim of the study was increasing corrosion resistance of the alloy because nickel could be selectively dissolved in physiological environment and nickel is toxic or even carcinogenic if present in high amount in an organism. The experiment was performed using excimer pulsed laser. Study showed that the corrosion behavior of NiTi sample is improved by laser heat treatment. Reasons of this effect were recognized as thickening of the oxide layer, a nitrogen incorporation and a surface homogenization which increased the range of surface passivation.

In 2001, Man et al. remelted NiTi alloy for investigating an influence of the process on corrosion resistance using continuous Nd:YAG laser beam [13]. The authors carried out the experiment with various process parameters and in two shielding gases: air and argon. Surface obtained after the laser modification was described as clean and free from porosity and cracks. Corrosion resistance was improved in all samples. Depending on the type of shielding gas, microstructures and phase compositions differ from each other. It was found that the improvement in corrosion behavior for samples treated in air resulted from the increase of the amount of passive TiO<sub>2</sub> layer whereas for samples treated in argon this enhancement was due to the increase of Ti/Ni ratio on the surface layer.

Z.D. Cui et al. published another paper describing corrosion and nickel release behavior of NiTi alloy after laser surface melting using Nd:YAG laser [14]. Besides from the influence of laser heat treatment on corrosion resistance, authors decided to investigate changes in stability of this material. The research revealed that laser heat treatment can significantly improve the corrosion resistance of NiTi alloy. Moreover, lower nickel ion release rate was observed after the process which means that the stability was improved. Authors stated that these changes may be attributed to obtaining the clean and compact microstructure with high concentration of titanium which is crucial to form  $TiO_2$  passive layer on the surface.

Studies on laser heat treatment of NiTi alloy are still performed and an example is a paper published in 2019 by Chakraborty et al. [15]. Surface was processed for investigating the influence of laser radiation on its corrosion performance properties. Furthermore, authors focused on finding optimum process parameters for obtaining surface of greatly enhanced corrosion resistance. Remelting was carried out using ytterbium fiber laser with constant scanning velocity and various laser beam powers. The material was remelted after chemical etching. As in aforementioned studies, authors observed a decrease in the concentration of nickel elements in surface layer which improves the corrosion resistance. Moreover, it was discovered that the optimum mixing of the molten pool has a significant role for formation of specific intermetallic or other titanium and nickel-rich phases. Thus, for obtaining a uniform titaniumrich top surface which guarantees high corrosion resistance, particular laser fluence need to be used and it was found to be between 6 and 8 J/mm<sup>2</sup>. If the lower laser fluence is used, martensite phase forms and it is more prone to corrosion. On the other hand, if the laser fluence is higher, more intermetallic phase occurs as dendritic structure which also deteriorates the corrosion resistance of remelted surface. Another advantages of processing NiTi alloy with laser beam of fluence between 6 and 8 J/ mm<sup>2</sup> discovered in this research, are significant increases of elasticity modulus and hardness which were not observed if different process parameters were used.

Figure 2 is a visual presentation of increases in corrosion potential of NiTi alloy surface in different environments due to laser heat treatment with various process parameters, based on [12-15]. Sample A was treated using pulsed excimer laser with intensity of 1,2 J/cm<sup>2</sup> and air as a shielding gas. Its corrosion resistance was investigated in Hank's solution. Samples B and C were processed using Nd:YAG continuous beam with 6300 J/cm<sup>2</sup> and argon as a shielding gas. Corrosion was investigated in 3,5% NaCl solution and Hank's solution respectively. Sample D was treated using ytterbium fiber continuous beam with intensity of 800 J/cm<sup>2</sup> in argon and its corrosion resistance was investigated in a simulated body fluid.



Fig. 2. Percentage increase of NiTi surface layer corrosion potential due to laser heat treatment, based on [12-15]

## 3. LASER POST-TREATMENT OF NICKEL-BASED COATINGS

First paper focusing on effects of laser remelting nickelbased coating after deposit was published in 1983 by Bhat et al. [16] Authors decided to melt plasma sprayed 80Ni-20Cr coatings using  $CO_2$  laser to investigate its influence on the surface layer properties. It was found that laser heat treatment leads to almost total disappearance of porosity and forming a dense, continuous coating. Moreover, change in corrosion resistance was investigated and it was observed that sealing of pores due to laser modification results in increasing corrosion resistance of the coating.

Another study on 80Ni-20Cr coatings was performed in 1990 by Enami et al. [17] In this case authors mainly focused on improvement of corrosion resistance after laser heat treatment. Coatings were thermal sprayed and remelted with infrared laser. Besides from concluding an improvement in corrosion resistance after the process, it was found that if coatings are fully remelted and strongly bonded to the substrate, they become diluted by iron atoms from the substrate and it allows to use materials produced this way only in relatively mild environments. However, the excellent anti-corrosion performance was observed on the specimen of only thin layer remelted on Ni-Cr coating, preventing iron from diffusing into laser processed areas.

Researchers in 1990s who worked on laser heat treatment of pre-deposited lavers, also concentrated their studies on electrodeposited coatings. An example is a survey on effects of excimer laser treatment of nickel-coated cast iron published in 1998 by Panagopoulos et al. [21]. Laser treatment was performed using different power density and number of pulses per step. Authors observed that the process leads to mixing of substrate and coating atoms. The effect of this is an increase in microhardness which is strongly dependent on power density and the higher power density is, the higher microhardness is obtained. Moreover, corrosion resistance was investigated and the experiment revealed that the laser heat treatment process enhances corrosion behavior and level of this improvement is a function of the number of laser pulses. Also, the roughness after the process was found to be dependent on the number of pulses.

One of the most often applied nickel-based electroless deposited material is nickel-phosphorous coating which improves corrosion, mechanical and tribological properties. One of first researches on laser heat treatment of Ni-P coating was this published by Matsukawa et al. in 1994 [22]. The effect of pulsed laser annealing on wear and corrosion properties of this type of coating deposited on stainless steel was investigated. Laser treatment was performed using YAG laser. It was found that the friction coefficient of the coating decreases of about ten percent in comparison with platings untreated with the laser beam. Moreover, corrosion to salt-spray greatly enhanced after remelting the surface.

Two more articles on laser melting of Ni-P coatings were published by Garcia-Alonso et al. in 1996 and 1997 [23,24]. In both experiments, authors investigated influence of CO<sub>2</sub> laser radiation on coatings of some various initial layer thicknesses deposited on mild steel. Papers differ from each other in aims and methods of research. In 1996 authors investigated corrosion behavior of laser melted Ni-P coatings and it was found that corrosion resistance depends mainly on laser scanning rate and initial coating thickness. Moreover, iron dilutions from the steel substrate which mix with the coatings during the laser heat treatment reduce the corrosion resistance, additionally due to crystallization of its phase within the dendritic structure. In this paper authors also suggest to achieve cooling rates so high that the diffusion of atoms to form the equilibrium phases is not allowed because the amorphous structure provides higher corrosion resistance. Coating as-plated and laser heat treated which was investigated in this study is presented in figure 3. In 1997, by analyzing microstructures of samples produced with different scanning rates and initial layer thicknesses, authors found optimum conditions for producing coatings with no iron dilutions but still more resistant to corrosion by obtaining dendritic structure after applying the suitable laser heat treatment.



Fig. 3. Cross sections of Ni-P coating 180 μm thick before (a) and after (b) laser heat treatment [23]

Studies on laser heat treatment of Ni-P electroless coatings were continued and are still performed in recent years with various substrate materials, experimental procedures and additional alloying elements in coatings compositions. For example, in 2008, Gholam et al. investigated the influence of laser processing of electroless Ni-P coating deposited on Al-356 substrate [25]. Coatings of four different thicknesses grouped in three types were remelted: low (10  $\mu$ m), medium (14  $\mu$ m and 18  $\mu$ m) and high (24  $\mu$ m). 1 kW Nd:YAG pulsed laser of different laser energy densities was carried out for the process. It was found that due to the formation of fine intermetallic Ni-Al phases,

microhardness and corrosion resistance significantly increase. Moreover, authors mentioned that laser heat treatment decreases the number of porosities and cracks on the surface which are found to be the predominant sites for pit nucleation.

In 2010, Liu et al. laser-annealed electroless Ni-W-P coatings with 2.3wt% tungsten in their composition plated on mild steel [26]. Samples were processed after electroplating using continuous wave diode laser with power equal to 150 W and scanning velocities ranged from 6 mm/s to 11 mm/s. After the investigation authors stated that coatings which are amorphous after electroless plating transformed into nanocrystalline phases along with remained amorphous phase. It was found that the crystallinity increases with decline of scanning velocity. Laser treatment reduced the porosity within coatings due to the relief of hydrogen from them, however, a new type of pores was spotted. These changes in porosity result in significant improvement of corrosion performance in 10 wt.% HCl solution. On the other hand, corrosion resistance against 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is strongly dependent on scanning velocity and enhances if it is equal to 7 mm/s and 8 mm/s. For higher speeds, corrosion resistance lowers with increasing laser beam scanning velocity.

Another study on electroplated nickel-based coatings was described by Hashemi and Shoja-Razavi in 2016 [27]. Authors investigated the effects of laser heat treatment of electroless Ni-P-SiC coating with 28 mass % of SiC deposited on Al356 alloy. Thickness of coatings ranged from 55 to 60  $\mu$ m. Specimens were processed using Nd-YAG pulsed laser with laser power ranged between 25 and 120 W and scanning rate from 5 mm/s to 10 mm/s. Influence on microstructure, phase changes and microhardness were investigated. It was found that laser treated zone contains mainly Ni-P crystal phases and SiC particles are distributed homogeneously. Microhardness is dependent on processing parameters and the higher laser power is, microhardness increases more. The best hardness profile was spotted in specimen treated with 5 mm/s and 75 W laser power.

It is presented in figure 4 how the initial thickness of Ni-P coatings deposited on Al356, as well as parameters of their laser heat treatment influence microhardness of the surface layer. Results labeled as "Ni-P" indicate these described in [25] and were obtained by electroplating and electroplating with further laser heat treatment of coatings with various thicknesses using laser energy 250 mJ and laser beam scanning velocity 30mm/s. Results labeled as "Ni-P-SiC" were described in [27] and they present microhardness of coatings 55-60  $\mu$ m thick and processed with scanning rate 5 mm/s and different laser powers. It can be seen that both initial layer thickness of the surface layer.

Besides from laser heat processing of electroplated coatings, researchers in the 21th century performed studies on thermal-sprayed coatings. An example of these researches was published in 2007 by Liu et al. [18]. In this study copper samples with Ni-Cu alloy (containing 20% Cu, 2% Si, 1.1% B and 0.5% Fe and 0.03% C) deposited by plasma spraying were laser treated using Nd:YAG pulsed laser Process parameters were constant and laser power was equal to 70 W and scanning speed was 1 mm/s. It was observed that laser treatment led to obtain coatings of smooth and uniform profiles with dense and homogeneous structure without

cracks and pores on the surface layer. Moreover, hard particles like Ni<sub>3</sub>B and FeNi<sub>3</sub> were formed within solid solution (Cu,Ni). Decline of cracks number and forming hard particles resulted in increasing resistance to wear nearly 4 times in comparison with as-sprayed coatings.



Fig. 4. Microhardness of Ni-P and Ni-P-SiC coatings before and after laser heat treatment, based on [25,27]

Studies on laser heat treatment of sprayed coatings are continued until now. In 2018 Chun et al. investigated the influence of laser heat treatment of Metco-16C® coatings thermal-sprayed with HVOF method on copper substrate [19]. The deposited material, besides nickel, consists of 0.6% C, 17% Cr, 3.7% B, 4% Si, 3% Fe and 2.5% Mo. Diode laser of maximal power density equal to 2.5 kW/cm<sup>2</sup> was carried out and scanning speed was equal to 1 mm/s. During the process, temperature was measured with pyrometer and laser power was automatically controlled to regulate the temperature between 1073 and 1473 K for proper microstructural homogenization. An increase in the treatment temperature resulted in disappearing of microstructural nonhomogeneities. At the temperature of 1423 K which was found to be optimum for the process, microstructure of thermal-sprayed layer consists of the matrix phase with fine carbides and borides. Moreover, at this temperature the hardness of coatings increased from 750 HV in as-sprayed state to 1280 HV.

It is worth pointing out that microstructural changes resulting from laser heat treatment of nickel-based thermalsprayed coatings are recently also effective in improving technologies for generating renewable energy. In 2015, Gao et al. published a paper which focused on enhancing solar absorbing property of Ni-Mo based coatings by laser surface treatment [20]. Two types of coatings (70%Ni-30%Mo and 66%Ni-28.5%Mo-5%Co) were sprayed onto the AISI 307L substrate with HVOF method and laser processed using Nd:YAG pulsed laser. The laser scanned coatings in a velocity of 180 mm/min and power of 100 W. After the process solar absorptance of Ni-Mo sample increased from 0.84 to 0.88 and of Ni-Mo-Co sample from 0.75 to 0.83. Two primary mechanisms were proposed to be responsible for the enhance. The first is change of phase composition. Laser radiation led to decrease nickel oxide volumetric content from 69.67% to 51.38 % and to increase metal phase (Ni+Mo) volume from 28.61% to 47.34%. The second mechanism is found to be an optimization on surface morphologies after the laser treatment. The significant reduction of micro defects in HVOF coatings was spotted

after the process which combined with the greater surface roughness enhanced the absorbing effect.

#### 4. DISCUSSION

Over 40 years of research on laser heat treatment of nickel-based alloys many effects on material properties were described. However, all of these changes result from forming new microstructures. Laser surface processing provides possibility of obtaining homogeneous dendritic structure with phases hard to obtain with other methods. The existence of new phases which furthermore are distributed uniformly increases microhardness, wear resistance and thermal stability of nickel-based alloys. Moreover, in NiTi alloy for medical applications changes in microstructure and surface morphology are also desirable for increasing corrosion resistance due to the fact that nickel dissolved from material can be toxic or carcinogenic for human organisms. Redistribution of solute atoms has also an influence on cracking model which transforms from brittle to ductile, especially in Cr-rich alloys. On the other hand, it is important to remark that pulsed laser treatment can form cracks and porosity on treated surface, thus it is crucial to select proper laser heat treatment method for specific application.

Laser heat treatment of nickel-based coatings lead to similar microstructural and morphological changes. However, due to the fact that nickel coatings are mainly deposited to protect substrate material from corrosion and mechanical damages, the process is performed and studied for enhancing this protection. Researchers found that laser heat treatment of nickel-based coatings leads to reduction of pores and cracks on surface layer as well as increasing a density and bonding to the substrate and these effects increase microhardness, wear and corrosion resistance. Moreover, in NiMo coatings structure homogenization, in contrast, leads to increase in solar absorption and thus laser heat treatment can be effective in improving green technologies. Because final properties of processed coatings depend on initial coating condition and substrate material as well it is extremely important to specify and apply proper process parameters to prevent undesirable diffusion of substrate atoms to the surface layer.

#### REFERENCES

- [1] **Steen W., MazumderJ.**,Laser Material Processing. 4th ed, eBook: Springer, 2010.
- [2] Breinan E.M., Kear B.H., Banas C.M., Greenwald L.E., Surface treatment of superalloys by laser skin melting: Superalloys, Metall and Manuf, Proc of IntSymp, 3<sup>rd</sup>, Seven Springs (1976) 435-450
- [3] Narasimhan S.L., Copley S.M., van Stryland E.W., Bass M., Solidification of a laser melted nickel-base superalloy, Metallurgical Transactions A 10 (1979) 654-555
- [4] Gadalov V.N., Ryzhkov F.N., Pozvonkov A.F., Structure and properties of heat-resistant nickel alloys and plasma coatings after laser heat treatment, Metal Science and Heat Treatment 32 (1990) 514-517
- [5] Nikitin A.A., Potipalova E.V., Travina N.T., Shtanskii D.V., Structure formed by laser heat treatment in heat-resistant nickel alloys and its stability in subsequent aging, Metal Science and Heat Treatment 32 (1990) 517-520
- [6] Solov'evYu.V., Isakov V.V., Prokopinskaya S.G., Maslenkova E.A., Structure changes and special features of crack formation

in high-temperature nickel alloys after laser irradiation, Metal Science and Heat Treatment 37 (1995) 28-32

- [7] Suh J.-H., Shin J.-K., Kang S-J.L., Lim Y.-S., Kuk I.-H., Kim J.-S., Investigation of IGSCC behavior of sensitized and lasersurface-melted Alloy 600, Materials Science and Engineering A 254 (1998) 67-75
- [8] Yun S.L., Kim J.S., Hyuk S.K., Effects of sensitization treatment on the evolution of Cr carbides in rapidly solidified Ni-base Alloy 600 by a CO<sub>2</sub> laser beam, Materials Science and Engineering A 279 (2000) 192-200
- [9] Petronić S., Milovanovic D., Milosavljević A., Momcilovic M., Petrusko D., Influence of picosecond laser irradiation on nickel-based superalloy surface microstructure, PhysicaScripta T149 (2012) 014079
- [10] Liang Y.-J., Wang H.-M., Origin of stray-grain formation and epitaxy loss at substrate during laser surface remelting of single-crystal nickel-based superalloys, Materials and Design 102 (2016) 297-302
- [11] Liang Y.-J., Cheng X., Wang H.-M., A new microsegregation model for rapid solidification multicomponent alloys and its application to single-crystal nickel-base superalloys of laser rapid directional solidification, ActaMaterialia 118 (2016) 17-27
- [12] Villermaux F., Tabrizian M., Yahia L'H., Meunier M., Piron D.L., Excimer laser treatment of NiTi shape memory alloy biomaterials, Applied Surface Science 109/110 (1997) 62-66
- [13] Man H.C., Cui Z.D., Yue T.M., Corrosion properties of laser surface melted NiTi shape memory alloy, ScriptaMaterialia 45 (2001) 1447-1453
- [14] Cui Z.D., Man H.C., Yang X.J., The corrosion and nickel release behavior of laser-surface melted NiTi shape memory alloy in Hanks, solution, Surface & Coatings Technology 192 (2005) 347-353
- [15] Chakraborty R., Datta S., Raza M.S., Saha P., A comparative study of surface characterization and corrosion performance properties of laser surface modified biomedical grade nitinol, Applied Surface Science 469 (2019) 753-763
- [16] Bhat H., Herman H., Coyle R.J., Laser processing of plasmasprayed NiCr coatings, Lasers in Materials Processing, Conference Proceedings – American Society for Metals: Los Angeles, CA, USA, 1983
- [17] Enami Y., Takemoto M., Laser treatment of sprayed Ni-Cr coating for enhancing corrosion resistance performance, Corrosion engineering 39 (1990) 465-478
- [18] Liu F., Liu C., Chen S., Tao X., Xu Z., Wang M., Pulsed Nd:YAG laser post-treatment Ni-based crack-free coating on copper substrate and its wear properties, Surface & Coatings Technology 201 (2007) 6332-6339
- [19] Chun E.-J., Park C., Nishikawa H., Kim M.-S., Microstructural characterization of Ni-based self-fluxing alloy after selective surface-engineering using diode laser, Applied Surface Science 442 (2018) 726-735
- [20] Gao Y., Xiong J., Gong D., Li J., Ding M., Improvement of solar absorbing property of Ni-Mo based thermal spray coatings by laser surface treatment, Vacuum 121 (2015) 64-69
- [21] Panagopoulos C.N., Markaki A.E., Agathocleous P.E., Excimer laser treatment of nickel-coated cast iron, Materials Science and Engineering A 241 (1998) 226-232
- [22] Matsukawa K., Kataoka M., Morinushi K., The effect of pulsed laser annealing on wear and corrosion properties of electroless Ni-P plating, Tribology Transactions 37 (1994) 573-579
- [23] García-Alonso M.C., Escudero M.L., López V., Macías A., The corrosion behavior of laser treated Ni-P alloy coatings on mild steel, Corrosion Science 38 (1996) 515-530
- [24] García-Alonso M.C., López V., Escudero M.L., Macías A., Laser melting treatment of Ni-P surface alloys on mild steel: Influence of initial coating thickness and laser scanning rate, Revista de Metalurgia (Madrid) 33 (1997) 250-257
- [25] **Gholam R.G., Shoja-Razavi R., Hashemi S.H., Isfahani A.R.N.,** Laser surface alloying of an electroless Ni-P coating with Al-

356 substrate, Optics and Lasers in Engineering 46 (2008) 550-557

- [26] Liu H., Viejo F., Guo R.X., Glenday S., Liu Z., Microstructure and corrosion performance of laser-annealed electroless Ni-W-P coatings, Surface & Coatings Technology 204 (2010) 1549-1555
- [27] Hashemi S.H., Shoja-Razavi R., Laser Surface heat treatment of electroless Ni-P-SiC coating on Al356 alloy, Optics & Laser Technology 85 (2016) 1-6