Direct SLS of powder compositions used for self-propagating high-temperature synthesis.

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Abstract

The conditions of a direct selective laser sintering (SLS) were researched experimental in a volume and by layers for the eutectic and near-eutectic powder compositions, which usually used for the self-propagating high-temperature synthesis (SHS) technology. It was shown a possibility to realise during SLS process a control exothermic reaction of combustion exactly in the focus of cw-laser beam on Nd-YAG. The necessary parameters of a laser influence (a power, scan velocity and diameter of the laser beam), a dispersion and composition of the powder mixtures were determined for the such regime. The 3D parts from intermetallic compounds were created without any post-process procedures, that expands the functional opportunities of the sintering models.

Key words: direct SLS, eutectic powder compositions, self-propagating high-temperature synthesis (SHS), control exothermic reaction of combustion.

Introduction

The selective laser sintering (SLS) of powder compositions is a world-wide spread method of creation of 3D parts in the SFF technology. Initially developed for wax and plastic materials, today researchers are announcing about possibility directly to produce the volume parts from a polymer coating metal, bimetals and ceramic powder materials (see a pioneer work [1], Proceedings of SFF Symposiums and, at last, our works [2,3]).

Better results are obtained when applying a liquid phase sintering process, based on a mix of two or more powder materials, with a high and low melting point, respectively. During the part build, the phase with a low melt point fuses and binds a phase(s) with a high melt point. But conversation of a such 'green part' to a real metallic one is demand the post-processing techniques. There are procedures of powder preparation, a sintering in the special conditions (control of a bed temperature and around atmosphere), a post processing annealing in an oven and/or infiltration gives in the result a relatively long and complex process. It decreases the advantages of SLS method together with another its problems (a high porosity, a large shrinkage/distortion and etc.). No reject the all achievements the method of SLS at present time, we propose an alternative strategy of the research for the expansion of the uses opportunities of 3D parts and partial decision of above mention problems in the SLS process. It is a search of new powder compositions and a combination in a single technological process a some related processes. For example, the SLS can combine with a laser soldering [3], that allows to receive intermetallic compounds as in a paper [4] and for account of a high adhesion of the melt of a solder powder to non-melting phase to improve the properties of the volume models.

In this paper, the approach by the combination of the SLS process and a self-propagated high temperature synthesis (SHS) is examined. The investigated powder materials were a famous in SHS technology the mixtures on the basis Ni-Al and Ni-Ti in eutectic and near-eutectic compositions. A possibility of control exothermic reaction of combustion was realised exactly in the focus of a laser beam during a selective laser scanning by the surface of those powder compositions.

Materials and equipment

The SLS process was conducted with use the scan laser beam from a computer controlled Nd-YAG. Laser worked in regimes with turn on (~ 3 kHz) and turn off (i.e., cw) an internal resonator modulation. On the laser the replaceable lenses are used with focus distances f = 149 and 336 mm (a diameter of laser spots was d = 50 and 100 mkm, accordingly). A laser power changed in a range 1-16 W and was supervised on the surface of powder with help of a measurement device. The control of laser beam with a computer had been used in a range of field 50x50 and 100x100 mm (i.e., 1024x1024 pixels) and had allowed to conduct a scan by any predefind counter, reproducing thus by layer a 3D part. The duration of a laser scanning determined the times of laser beam transition from point to point, a calm deflector in each point and could be changed by software over a wide range of values.

During SLS process the powders of the following marks are used (tabl.1). The size of powder fraction was determined with a help of the sieve analysis and an optical microscopy on NIOPHOT-30.

Table 1. Properties of used powder materials [2,5,6].

N / N	Type of powder materials	Particle size distribution, (mkm)	Density, ρ (g /cm^3)	Solid density, ρ_s (g /cm^3)	Void fraction, $\varepsilon=1-\rho/\rho_s$	Melt temperature, (T^{0}C)	Latent heat of melt, (kJ/ mole)	Atom mass, (kg)	Stehiometric coefficient in SHS
1	Nickel powder (ПГСР4)	50-160	4,7	~8,8	0,47	~1200	17,5	58,6	3
2	Aluminium powder (АСД3,4)	10-50	1,25	2,7	0,54	660	10,8	27	↑1/3↓
3	Titanium powder	30-60	1,23	4,5	0,73	1668	15,5	47,9	1

There is important to take a size of particles no more than a laser spot, for account of we achieved an overlapping by the laser beam a few particles at once laser passage. A size of particles < 50 mkm was used. The following compositions were prepared for the realization of the next exothermic chemical reactions:

$$3Ni + Al \rightarrow Ni_3Al + Q_1, \qquad (1)$$

$$Ni + 3Ti \rightarrow Ti_3 Ni + Q_2. \qquad (2)$$

It would occur to create the intermetallic compounds Ni_3Al and Ti_3Ni. That systems are selected as the model systems, which usually are using in the SHS technology. For those test systems the basis characteristics are known: an ignition temperature - T_i, energy activation of chemical reaction - E, a heat effect of reaction $Q_{1,2}$ on the one mole of Ni (see table 2 and fig.1).

Table 2.

Phase	T_i, (°K)	E, (kJ/mole)	Q, (J/kg)
Ni_2Al_3	—	—	$1{,}9x10^6$
NiAl	910±25	135±27	$9{,}7x10^6$
Ni_3Al	925±16	115±25	$2{,}4x10^6$
Melt (Ni+Al)	—	48,24	$1{,}3x10^6$

Discussion

From the beginning, the powders are treated in a free pour volume, significantly more than a depth of a sintering mono-layer. We had been researched the conditions of combined SLS and control SHS processes for an one laser passage depend of a laser power, beam diameter, scan time and powder composition. Under control regime of the SHS we understood a realisation of the exothermic reaction of a combustion without a heat explosion and only in the zone of laser influence (i.e., in the so-called diffusion or kinetic regime of the SHS). It allows to determine the interval of sintering depths for the one laser passage under a minimal deformation on the layer.

Figures 2,3 show the experimental results of the laser influence on the Ni-Al powder equilibrium composition. Under a small laser power $P < 7$ W and a great velocity of laser beam $v > 25$ cm/s the sintering depths were a such little, that a sintered material looses from a touch. With an increasing of the power (fig.2) and decreasing of the beam velocity the depth of sintering stripe is growing. In the interval of laser powers among ~ 8,4-8,8 W (fig.2) and scan velocities ~ 2,9-8,6 cm/s visually we had been seen a control exothermic reaction combustion exactly in the zone of laser passage. At last, under values $P > 8{,}8$ W , $v = 25$ cm/s (fig.2) and $P = 8{,}8$ W, $v < 2{,}9$ cm/s (fig.3) an exothermic chemical reaction had been gone over to the regime of explosion and a front of combustion began to spread in the all directions independently without a laser influence. It can consider those regimes a critical. In according of SHS theory, a diffusion regime of combustion, which characterises of a stationary distribution of a synthesis wave, transforms to the regime of a heat explosion. It needs to remark (fig.1), that on the heating stage at the $T < T_e = 640$ °C only a Ni_2Al_3 (γ - phase) was arisen and diffusion grew on the contact surfaces of the Ni and Al particles. Then at the range 1132 °C > T > T_e, a NiAl (ε - phase) has been begun to create. When temperature is reached T = 1638 °C and would occur eutectic melt, then on the cooling stage from this melt an intermetallic NiAl and Ni_3Al (ε -phase) will crystallise. The laser influence parameters must be warm up so, that it would be sufficient a laser energy and a heat effect of exothermic reaction for the creation of those compounds.

An increasing of size particles in the Ni-Al mixtures was shown, the SLS process took place without SHS. As a result, for the laser spot d = 100 mkm an optimal interval (P,v) was changed for the combined SLS and SHS processes.

Also, we are investigated a near-eutectic Ni-Al powder compositions (mixtures - 1:1, 1:2, 1:4, 1:5). Deviation from an equilibrium composition sharply narrows the optimal interval of process's combination and practically a laser sintering was seen. Sintering mono-layers were a very brittle.

For the Ni-Ti powder composition (chemical reaction (2)) the combination SLS and SHS was realised also on the regimes with v = 2,6 cm/s and P = 7,2 - 8,8 W. However, the sintering monolayers were brittle although they had depths compare with before researched powder composition NI-Al. Addition in Ni-Ti composition a material with a low melt temperature (braze powder) decreased a brittleness.

From our experimental results we can estimate a time — t_{LI} during which powder composition was under the laser influence and accomplished a transformation from the ignition regime to non-stationary a heat explosion regime. In the first case (fig.1, P > 8,8 W) t_{LI} = d/v is equal 0,2 ms and in the second case (fig.2, P = 8,8 W) t_{LI} = 1,7 ms. A modern theory of ignition and explosion [8] allows to calculate the some parameters of SHS process, which a very closely describes a real situation. In the theory of ignition an important parameter is an adiabatic period of induction

$$t_{ind} = \frac{c}{Qk_0} * \frac{RT_i^2}{E} * \exp(\frac{E}{RT_i}), \qquad (3)$$

which by the sense corresponds our t_{LI}. In equation (3), k_0 - in front of exponent multiplier (it proportionate the number of molecule collisions during a chemical reaction (1)), c - a heat capacity, R - a gas constant (= 8, 3144 J/mole*K). A width of zone of exothermic chemical reaction in the moment of the ignition is equal

$$L_i = \left[\frac{\lambda}{Q\rho k_0} * \frac{RT_i^2}{E} * \exp(\frac{E}{RT_i})\right]^{1/2}, \qquad (4)$$

where λ - a heat conductivity.

It would be interesting to compare the times t_{LI} with a prediction of the theory. A calculation by equation (3) gives for the NiAl system t_{ind} = 41 ms and for the Ni_3Al system — t_{ind} = 0,74 ms. Here we used the values from the Tables 1,2 and c_{Ni} = 462 J/kg*K, c_{Al} = 879 J/kg*K [7]; λ(NiAl) = 9±1 W/m*K, λ (Ni_3Al) = 20±2 W/m*K, Q*k_0(NiAl) = (14±2)x10^{16} W/kg, Q*k_0(Ni_3Al) = (57±8)x10^{16} W/kg [5]. It is seen, that the calculated periods of induction by the order are agreed with the t_{LI}. Moreover, a t_{ind} for intermetallic compound Ni_3Al is located in an experimental interval 0,2-1,7 ms. So we proposed, there is a great probability to receive Ni_3Al phase. A calculation of the zone width (4) gives a next: L_i (NiAl) = 430 mkm, L_i (Ni_3Al) = 82,3 mkm. It is also a very important result, because a laser sintering process is demand a great selectivity. The pointed out values shown, that for the Ni_3Al phase a width of exothermic chemical reaction's zone is compared with a diameter of a laser spot d = 50 mkm and no more that two time greater than a size of powder particles. So we can consider, what a combination of SLS and SHS processes will exist successfully exactly by the counter of created 3D part. A time for period of induction for NiAl phase is not sufficient, then for the laser influence times a NiAl will not grow and a large L_i (NiAl) (which is order of 8-9 the laser beam diameters) could not be taken to attention. An X-rays analysis of treated powder compositions would be give a more exact result and we will plan to realise it.

The 3D parts a simple form (a cub, spheroid and etc.) were created from the (Ni-Al) powder composition of equilibrium mixture without any post-processes procedures. Investigations of properties of those 3D parts will plan in future also, but now can say, that their durability is more high then a sintered parts.

Conclusions

1. The combination of SLS and SHS processes in a single technological process was successfully realized for the eutectic and near-eutectic powder compositions on the basis of Ni-Al and Ni-Ti systems on the cw - Nd-YAG laser.

2. Optimal regimes of the laser influence were determined for the support of the control exothermic reaction of combustion exactly in the focus of the laser beam.
3. A compares of laser influence times — t_{LI} with a theoretical period on induction is present for experimental determined laser parameters (P,v,d). It is shown, that those t_{LI} are enough for synthesis of the intermetallic compound (Ni_3Al phase) exactly in the laser effected zone.
4. A good selectivity could be achieved during combination of SLS and SHS processes. A width of control exothermic reaction's zone — L_i (Ni_3Al) = 82,3 mkm is compared with a laser beam diameter.
5. The 3D parts of simple form had been obtained, which contended an intermetallic compound system without any post-processes procedures.

In a future research an attention must be given to investigate of intermetallic phases in the created 3D parts and those properties during the combination of SLS and SHS processes depend of laser influence parameters.

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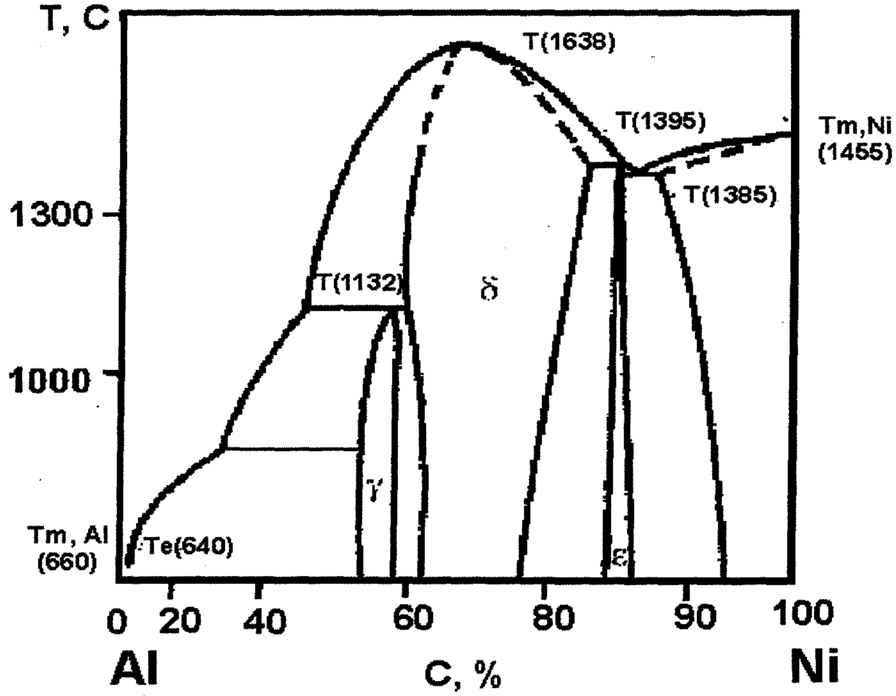

Figure 1. Equilibrium diagram of system Ni-Al.
(γ - phase Ni_2Al_3, δ - phase NiAl, ε - phase Ni_3Al)

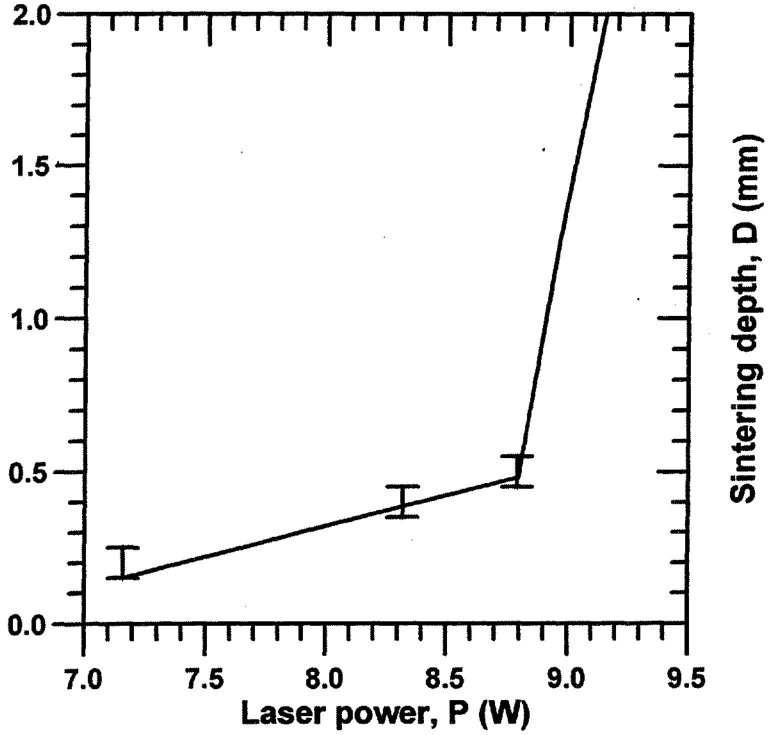

Figure 2. Effect of laser power on sintering depth. Powder mixture for chemical reaction (1). Laser scan velocity v = 25 cm/s, d = 50 mkm.

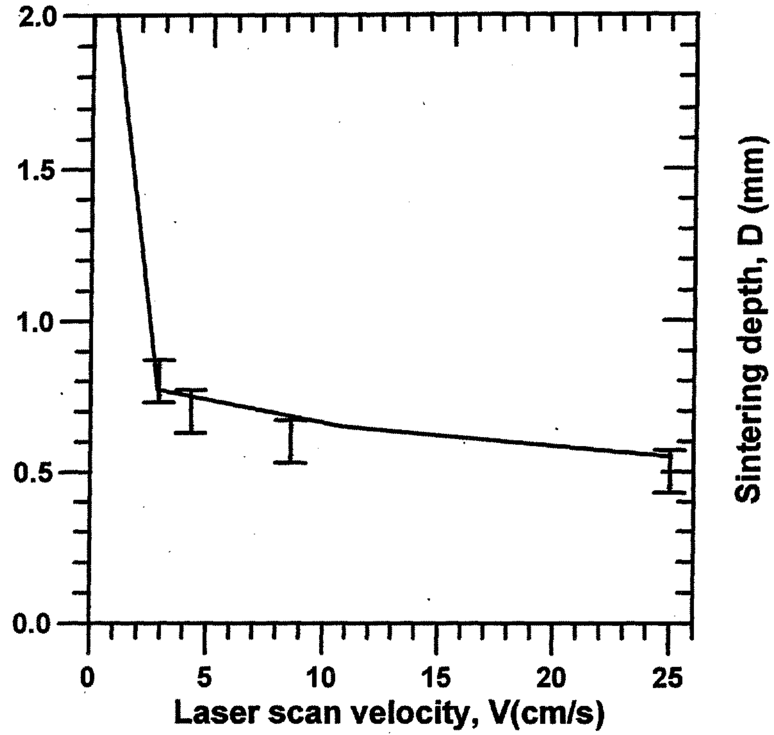

Figure 3. Effect of laser scan velocity on sintering depth. Powder mixture for chemical reaction (1). Laser power P = 8,8 W, d = 50 mkm.