PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No. PCT/EP 2018 / 0 0 0 0 5 3

International Filing Date 09. FEB. 2018 (09. 02. 18)

TELECOPY

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)*

Box No. I TITLE OF INVENTION

Insitu metal matrix nanocomposite synthesis by additive manufacturing route

Box No. II APPLICANT ☐ This person is also inventor

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

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Schweiz

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Facsimile No.

Applicant's registration No. with the Office

E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so.

☒ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent).

E-mail address: birgit.seemann@oerlikon.com

State *(that is, country)* of nationality: Schweiz

State *(that is, country)* of residence: Schweiz

This person is applicant for the purposes of: ☒ all designated States ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☐ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

Telephone No.

Facsimile No.

Agent's registration No. with the Office

E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so.

☐ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent).

E-mail address:

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. V DESIGNATIONS

The filing of this request **constitutes under Rule 4.9(a) the designation** of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

☐ DE Germany **is not designated** for any kind of national protection

☐ JP Japan **is not designated** for any kind of national protection

☐ KR Republic of Korea **is not designated** for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing or subsequently under Rule 26bis.1, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application.)

Box No. VI PRIORITY CLAIM AND DOCUMENT

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application *(day/month/year)*	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 13/02/2017	EP 17000219.0		European Patent Organisation	
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

Furnishing the priority document(s):

☒ **The receiving Office** is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application(s) was filed with the receiving Office which, for the purposes of this international application, is the receiving Office)* identified above as:

☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

☐ The **International Bureau** is requested to obtain from a digital library a certified copy of the earlier application(s) identified above, using, where applicable, the access code(s) indicated below *(if the earlier application(s) is available to it from a digital library)*:

☐ item (1) access code _____ ☐ item (2) access code _____ ☐ item (3) access code _____ ☐ other, see Supplemental Box

Restore the right of priority: the receiving Office is requested to restore the right of priority for the earlier application(s) identified above or in the Supplemental Box as item(s) (_____). *(See also the Notes to Box No. VI; further information must be provided to support a request to restore the right of priority.)*

Incorporation by reference: where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if more than one International Searching Authority is competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used)*:

ISA/ EP

Sheet No. .....

Box No. VIII (i) DECLARATION: IDENTITY OF THE INVENTOR

The declaration must conform to the standardized wording provided for in Section 214; see Notes to Boxes Nos. VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (i). If this Box is not used, this sheet should not be included in the request.

Declaration as to the identity of the inventor (Rules 4.17(i) and 51*bis*.1(a)(i)):

In relation to this international application,
Siva Phani Kumar YALAMANCHILI of Zürcherstrasse 9, 7320 Sargans is the inventor of the subject matter for which protection is sought by way of this international application

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (i)".

Sheet No. .....

Box No. VIII (ii) DECLARATION: ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4.17(ii) and 51*bis*.1(a)(ii)), in a case where the declaration under Rule 4.17(iv) is not appropriate:

In relation to this application Oerlikon Surface Solutions AG, Pfäffikon is entitled as employer of the inventor Siva Phani Kumar YALAMANCHILI

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (ii)".

Sheet No. .....

Box No. IX CHECK LIST for PAPER filings – this sheet is only to be used when filing an international application on **PAPER**

This international application **contains the following:**	Number of sheets
(a) request form PCT/RO/101 (including any declarations and supplemental sheets)	5
(b) description (excluding any sequence listing part of the description, see (f), below)	3
(c) claims	1
(d) abstract	1
(e) drawings (if any)	3
(f) sequence listing part of the description (if any)	
Total number of sheets	13

This international application is **accompanied** by the following item(s) *(mark the applicable check-boxes below and indicate in right column the number of each item):*	Number of items
1. ☐ fee calculation sheet	
2. ☐ original separate power of attorney	
3. ☐ original general power of attorney	
4. ☐ copy of general power of attorney; reference number:	
5. ☐ priority document(s) identified in Box No. VI as item(s)	
6. ☐ Translation of international application into *(language)*:	
7. ☐ separate indications concerning deposited microorganism or other biological material	
8. ☐ *(only where item (f) is marked in the left column)* copy in electronic form (Annex C/ST.25 text file) on physical data carrier(s) of the sequence listing not forming part of the international application, which is **furnished only for the purposes of international search** under Rule 13*ter* *(type and number of physical data carriers)*	
9. ☐ *(only where item (f) (in the left column) and item 8 (above) are marked)* a statement confirming that "the information recorded in electronic form submitted under Rule 13*ter* is identical to the sequence listing as contained in the international application" as filed on paper	
10. ☐ copy of results of earlier search(es) (Rule 12*bis*.1(a))	
11. ☐ other *(specify)*:	

Figure of the drawings which should accompany the abstract:	2b	**Language of filing** of the international application:	

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Heine-Kempkens

Dr. Claus Heine-Kempkens
European Patent Attorney
(Head of Patent Department Oerlikon Surface Solutions AG, Pfäffikon)

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1. Date of actual receipt of the purported international application:	09. FEB. 2018 (09. 02. 18)	2. Drawings: ☐ received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		☐ not received:
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid	

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Date of receipt of the record copy by the International Bureau:

Form PCT/RO/101 (last sheet – paper) (July 2017) *See Notes to the request form*

Insitu metal matrix nanocomposite synthesis by additive manufacturing route

The present invention relates to a method to form insitu metal matrix nanocomposites by additive manufacturing. Examples are carbides, nitrides, oxides, borides or a combination of them in a metal matrix of feed stock material.

Prior Art:

Selective laser melting (SLM) is the work horse for additive manufacturing of metallic components. The process is thoroughly investigated and published in research articles like C. Y. Yap et al., Review of selective laser melting: Materials and applications, Appl. Phys. Rev. 2, 041101(2015) 041101. The state of the art process is schematically shown in figure 1. In brief, the process consists of spreading the powder (preferably atomized powder) followed by laser rastering to cause selective melting (Fig. 1a). Powder spreading and laser rastering is re iterated until the desired shape is achieved (Fig 1b). Though the state of the art was claimed to mass produce metallurgically sound intricate geometrical designs in industrial scale, it suffers from limited compositional and micro-structural freedom, i.e., the phase constituents of the printed components are essentially defined by the feed stock material. The final micro-structure is often an equilibrium and metastable phase mixture of the constituents from the feed stock.

In contrast to the state of the art, in the proposed method according to the present invention an insitu nanoscale precipitate structure is formed in the metallic matrix of the feed stock in a uniquely designed process configuration as for example shown in figure 2. The proposed process comprises the steps of laser rastering on the powder bed in a reactive plasma environment, coupled with applying an electro static potential (bias) to the build plat form. By appropriately interfacing the laser rastering, reactive plasma and the bias voltage, a nanocomposite is formed insitu, in the metal matrix as schematically shown in figure 2. The proposed method has a very high compositional freedom, i.e. nano particles of nitrides, oxides, carbides, and silicides of various stoichiometry can be incorporated in almost any metal matrix. More interestingly, such a nanocomposite is thermally stable as the particle growth by the Ostwald ripening process is experimentally negligible due to relatively a low mutual solid solubility between the particles and matrix.

It is known from the current literature that a homogeneous distribution of nanoparticles of nitrides, carbides, borides or oxides in a metal matrix will significantly enhance the high temperature structural properties by hindering the plastic flow, even with a volume fraction as low as 5 %, see for example:

(a) GJ. Zhang et al., Microstructure and strengthening mechanism of Oxide lathanum dispersion strengthened molybdenum alloy, Adv. Eng. Mater. 2004, 6, No.12,

(b) http://www.ifam.fraunhofer.de/content/dam/ifam/en/documents/dd/Infobl%C3%A4tter/dispersion-strengthened_materials_fraunhofer_ifam_dresden.pdf)

In summary, 3D printed components in the proposed configuration are characterized with a thermally stable non-equilibrium mixture of nanoscale ceramic particles homogeneously distributed in the feedstock matrix. Such nanoscale particle reinforced 3D printed components display significantly superior structural properties at room and elevated temperature of 0.7 Tm (Tm is the melting temperature of the matrix alloy)

The goal is to provide for an additive manufacturing synthesis route to form metal matrix nanocomposite insitu almost with any metallic feed stock. The schematic of the proposed synthesis route is enclosed in figure 3.

The method according to the present invention comprises 6 steps:

Step1: Reactive plasma is ignited in the chamber preferentially on the powder bed, preferably a ME powder bed where the Me powder is a metal comprising powder and simultaneously an electrostatic potential of several 100 eV is applied in the melt zone via the build plat form.

Step2: Laser rastering on the powder bed causes molten pool formation very locally.

Step 3: Reactive gas ions (N+) are electrostatically driven in to the molten pool with an energy of several 100 eV.

Step 4: The chemical interaction between the molten feed stock and reactive gas ions causes ceramic compounds such as carbides, nitrides, oxides, silicides formation insitu for example by the following reaction path way: {Me (l) +X+ (g) --> MeN (s)}.

Step 5 (optional step, however preferably): By tuning the laser power, rastering speed, bias voltage; plasma reactivity, hydrodynamic forces and fluid recirculation pattern of the molten feedstock is influenced to cause nitride precipitates break down preferentially to nanoscale before the liquid pool solidifies.

Step 6: Formation of metal matrix composite with nanoscale dispersion after solidification.

Please note that in the steps as described above N+ can be replaced by any reactive gas such as for example (O+, Si+, B+, C+) or mixtures thereof. In step 4 l, g, and s are numbers reflecting the atomic percentage. Me could be, for example Ti and/or Al and/or a mixture thereof.

Though the process is illustrated for SLM process, experts in the field will agree that this can be applied in other melting based additive manufacturing route.

Figure 1: Schematic illustration of (a) layer spreading and laser melting, (b) forming desired shape by selective laser melting process

Figure 2: Structural differences of the additive manufactured component with the a) state of the art and b) the proposed synthesis route

Figure 3: Pictorial representation of Insitu metal matrix nanocomposite formation in the proposed synthesis route. Numbers in the picture represents sequential process steps explained in the text.

Claims

1. Additive manufacturing synthesis method to form a component comprising a metal matrix nanocomposite, the method comprising the steps of:

- Reactive plasma ignition in the chamber preferentially on a Me powder bed, where the Me powder is a metal comprising powder and simultaneously applying an electrostatic potential of several 100 eV in the melt zone via the build platform

- Laser rastering on the powder bed to cause molten pool formation very locally

- Electrostatically driving reactive gas ions X+ as for example (N+, O+, Si+, B+, and/or C+) into the molten pool with an energy of several 100 eV.

- Causing chemical interaction between the molten feed stock and reactive gas ions to form ceramic compounds such as carbides, nitrides, oxides, and/or silicides insitu for example by the following reaction path way: {Me (l) +X+ (g) —> MeX (s)},

- Solidifying and thereby forming the metal matrix composite with nanoscale dispersion.

2. Method according to claim 1, characterized in that the laser power and or rastering speed and/or bias voltage is tuned to influence plasma reactivity and/or hydrodynamic forces and/or fluid recirculation pattern of the molten feedstock to cause nitride precipitates break down preferentially to nanoscale before the liquid pool solidifies.

3. Method according to one of the claims 1 and 2, characterized in that reactive gas ions X+ are N+ ions.

4. Method according to one of the claims 1 to 3, characterized that Me is Ti and/or Al or a mixture thereof.

ABSTRACT

A unique and novel additive manufacturing route has been proposed to form a thermally stable in-situ metal matrix nano composite by interfacing reactive plasma in the selective laser melting process chamber. The proposed route gives very high compositional freedom, i.e. nitrides, carbides, oxides, silicides and other ceramics with different stoichiometries can be reinforced in nanoscale in any metallic matrix. Components with such a nanocomposite structure display superior high temperature structural properties.

Fig. 1

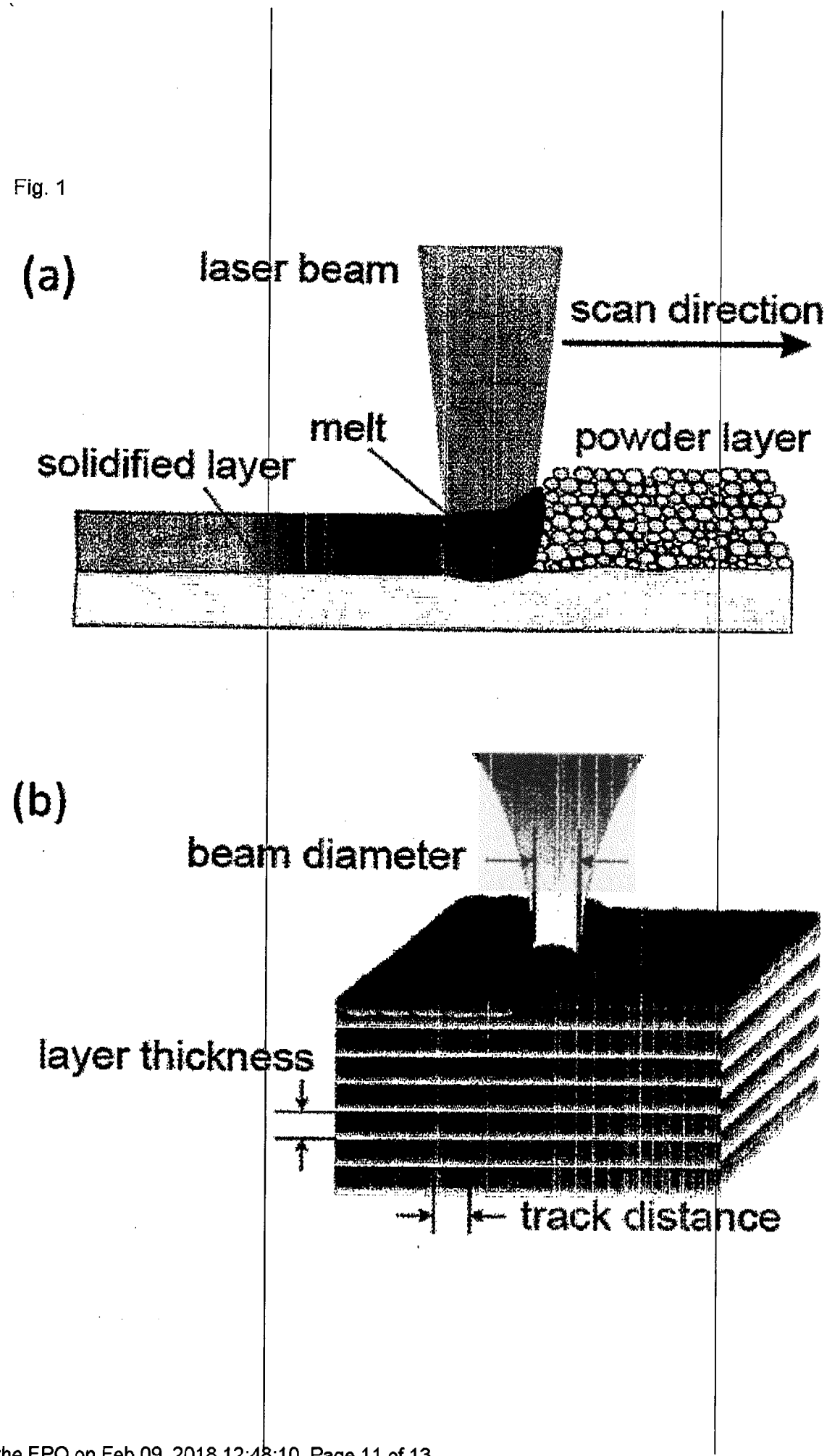

(a)
laser beam
scan direction
melt
powder layer
solidified layer
(b)
beam diameter
layer thickness
track distance

Fig. 2a

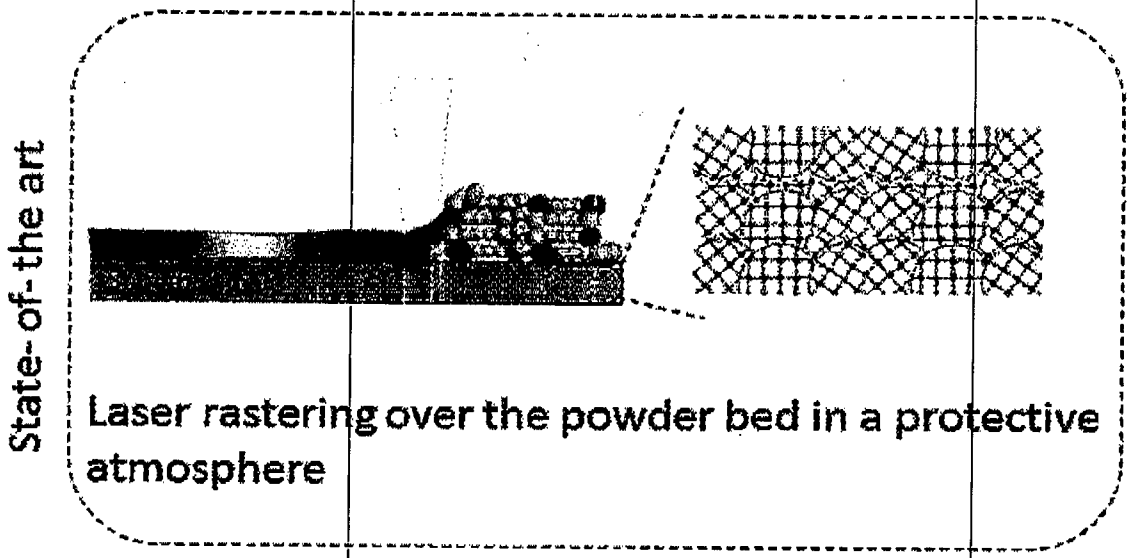

State-of-the art
Laser rastering over the powder bed in a protective atmosphere

Fig. 2b

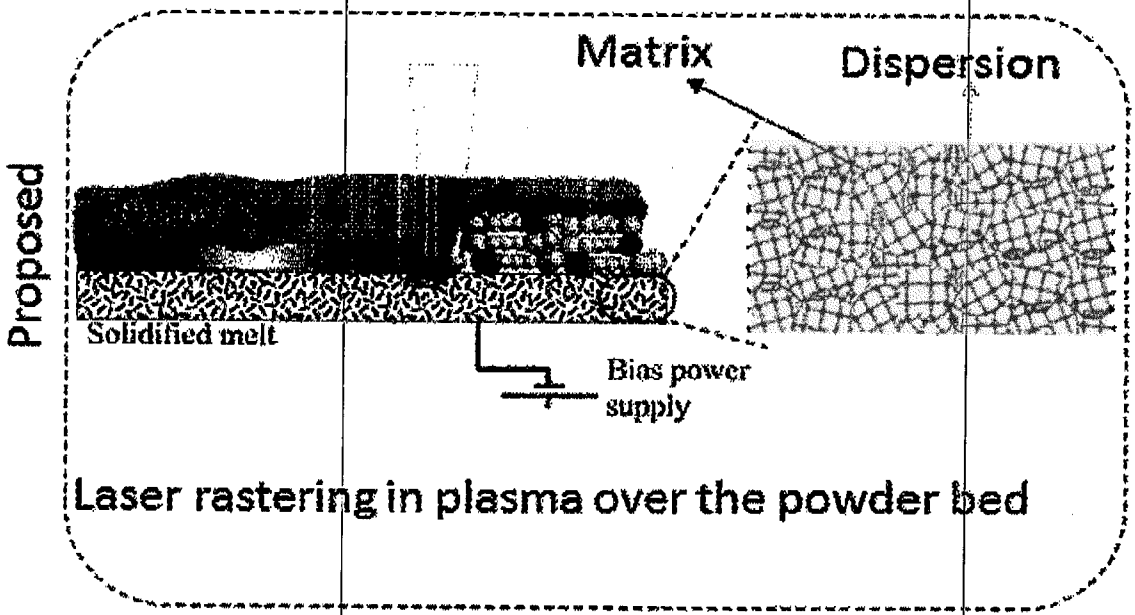
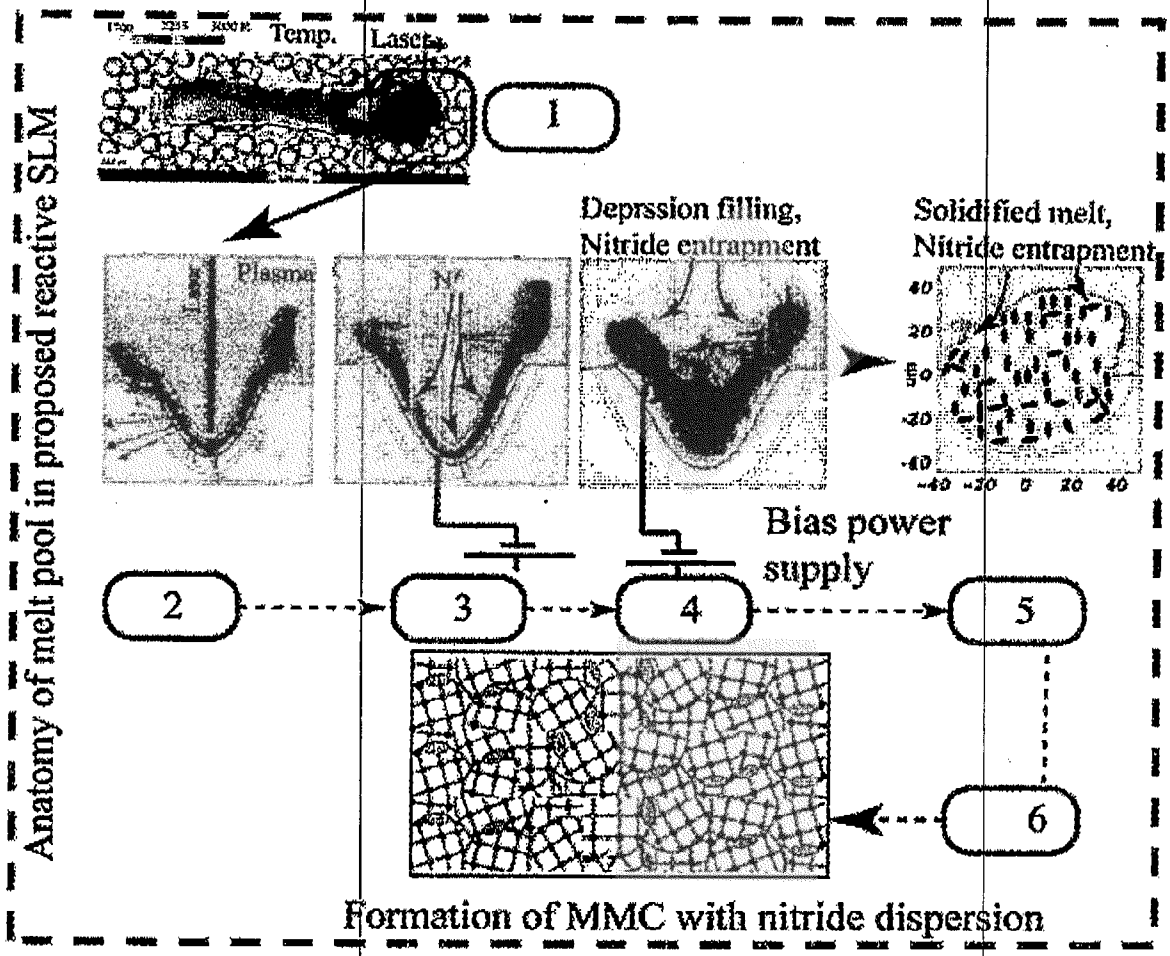

Matrix
Dispersion
Proposed
Solidified melt
Bias power supply
Laser rastering in plasma over the powder bed

Fig. 3


Anatomy of melt pool in proposed reactive SLM
Temp.
Laser
1
Plasma
N2
Deprssion filling,
Nitride entrapment
Solidified melt,
Nitride entrapment
Bias power
supply
2
3
4
5
6
Formation of MMC with nitride dispersion