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Recent Progress in Beam-Based Metal Additive Manufacturing from a Materials Perspective: A Review of Patents / Aversa, A., Saboori, A., Marchese, G., Iuliano, L., Lombardi, M., Fino, P.. - In: JOURNAL OF MATERIALS ENGINEERING AND PERFORMANCE. - ISSN 1059-9495. - ELETTRONICO. - 30:12(2021), pp. 8689-8699. [10.1007/s11665-021-06273-3]

*Availability:*

This version is available at: 11583/2964108 since: 2022-05-18T17:42:39Z

*Publisher:*

Springer

*Published*

DOI:10.1007/s11665-021-06273-3

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# Recent Progress in Beam-Based Metal Additive Manufacturing from a Materials Perspective: A Review of Patents

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Submitted: 10 November 2020 / Revised: 21 June 2021 / Accepted: 21 August 2021 / Published online: 15 October 2021

Over the last decade, the enormous potential of metal additive manufacturing (AM) processes has led these technologies to establish their position in many industries. Much effort is being made toward their widespread application; however, much remains to be done to achieve full industrialization of these processes. Therefore, many companies, research centers and universities are investing in comprehensive research and development activities in order to further promote the industrialization of metal AM. This review traces the progress of metal AM technologies through an investigation of patents. In the present study, beam-based metal AM patents were searched through the Orbit Intelligence database. First, the number of patents per year was studied, indicating that, as expected, there is strong growth in AM patenting activities. The patents were afterward examined in order to highlight the key players in the field, and it was found that the main players investing in this market are: multidisciplinary companies, AM machine producers, end users working, especially in the aerospace sector, universities and research centers. The patents were then analyzed to understand the technology domains covered by each key player and their trend of investments. Finally, the patents in the field of Materials and Metallurgy were studied individually to identify the main topics faced by the most used alloy classes: Al-, Ni- and Ti-based alloys and steels. The extensive study of these patents clearly indicated that the main gaps to fill in metal AM are strongly material dependent and that it is possible to find correlations between the alloy classes, their main industrial applications and their specific AM processability issues. The current study provides insights into global trends that can help industrial markets to identify the right investment direction and research to identify topics for future investigation.

**Keywords** additive manufacturing, directed energy deposition, electron beam melting, laser powder bed fusion, metals, patent

## 1. Introduction

Additive manufacturing (AM) was defined by ASTM as the “process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies, such as traditional machining”

This invited article is part of a special topical focus in the *Journal of Materials Engineering and Performance* on Additive Manufacturing. The issue was organized by Dr. William Frazier, Pilgrim Consulting, LLC; Mr. Rick Russell, NASA; Dr. Yan Lu, NIST; Dr. Brandon D. Ribic, America Makes; and Caroline Vail, NSWC Carderock.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s11665-021-06273-3>.

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(Ref 1). In the past years, this class of production technologies has also been referred to by different names such as 3D printing, rapid prototyping, additive fabrication, additive processes, additive layer manufacturing and freeform fabrication (Ref 2, 3). It is well known that AM processes were initially used only for prototyping activities, whereas nowadays, they are radically changing the approach to industrial production, leading to innovative designs and more flexible and efficient production processes.

AM has been rapidly growing since the development of the first stereolithography system in the mid-1980s. Since then, many AM processes that differ in the type of raw material and in the method used to consolidate the parts have been developed and have appeared on the market. Many data show that the impact of these technologies on the industry is continuously growing in terms of commercial machines, parts produced with complex geometries, research projects, patents and scientific publications (Ref 4, 5). It is also well documented that the rapid growth of AM technologies might have a disruptive impact on the global economy (Ref 5, 6). It is important to underline that the progress of these technologies in recent years has been feasible partly thanks to the remarkable growth of computing tools and digital processes, which have strongly increased the applicability and reliability of the AM processes (Ref 6).

AM indicates a large class of production technologies able to process many materials such as polymers, metals, ceramics, composites, and biomaterials. Metal AM represents a part of this large group, including all processing technologies that

allow layer-by-layer production of complex structural metal components (Ref 7).

Nowadays, a large number of different metal AM processes—which can be distinguished mainly based on the material feedstock and on the method used to consolidate the layers—are being used to produce a wide range of metal components. Among these methods, the most common ones use a focused energy source to consolidate the material.

The primary beam-based AM processes are reported here and briefly described.

- **Laser Powder Bed Fusion (LPBF):** an AM process in which a focused laser beam selectively fuses regions of a powder bed. In the past years, this technology has also been named Selective Laser Melting (SLM), LaserCUSING, Direct Metal Laser Melting (DMLM), Direct Metal Printing (DMP), Direct Metal Laser Sintering (DMLS), Laser Additive Manufacturing (LAM), etc. (Ref 8, 9).
- **Electron Beam Melting (EBM):** an AM process in which a focused electron beam selectively fuses regions of a powder bed. This technology is also known as electron beam powder bed fusion (EB-PBF), Powder Bed Electron Beam Additive Manufacturing (PB-EBAM), Selective Electron Beam Melting (SEBM), etc. (Ref 10-12).
- **Laser Directed Energy Deposition (L-DED):** an AM process in which a focused laser beam is used to fuse materials by melting as they are being deposited. Several authors and industries refer to this process as Laser Energy Net Shaping (LENS), Laser Metal Deposition (LMD), Laser Cladding (LC), Direct Metal Deposition (DMD), Laser Aided Manufacturing Process (LAMP), Direct Laser Fabrication (DLF), etc. (Ref 13, 14).
- **Electron Beam Directed Energy Deposition (EB-DED):** an AM process in which a focused electron beam is used to fuse materials by melting as they are being deposited. Other names of this process are Electron Beam Additive Manufacturing (EBAM), Electron Beam Freeform Fabrication (EBF3), etc. (Ref 15, 16).

Metal AM can be seen as an innovative approach to industrial production and therefore has a substantial impact on several industrial sectors in areas such as aerospace, automotive, energy and medicine (Ref 7). Many companies working in these fields have thus been investing in a large amount of research to understand and exploit the advantages and returns that metal AM processes can bring to their production lines (Ref 4). These studies show that, for certain production volumes, using an AM technology instead of a conventional one implies energy and cost savings, simplification of the process chain and time-to-market reductions (Ref 17, 18). As reported by Bourell et al., however, there are still some challenges that limit the complete exploitation of metal AM processes in some industries (Ref 4). The main issues are related to size limitations of current AM systems and to lack of available materials, standardization and consistency among machine producers (Ref 4-6, 19, 20). Recently, also DebRoy et al. reported these challenges in detail and showed that there is a gap between scientific, technological and economic challenges (Ref 6). Based on their study, it is reasonable to suggest that one of the main technological issues is related to the time-consuming and expensive process of parts qualification, which is now generally performed using a trial-and-error

approach. Other relevant critical technical aspects are related to the size or geometrical limitations of some AM systems and to the difficult scale-up of building processes moving from small samples to large complex components. Moreover, an important technological issue is the lack of clear specifications about feedstock quality, processing, post-processing and safety issues related to powder handling (Ref 21). Finally, from an economic point of view, the aspect of intellectual properties, together with the low market share, was also considered by DebRoy et al. as a critical challenge in AM developments. According to these authors, the scientific challenges, by contrast, are mainly related to microstructural and mechanical aspects of AM parts and to the understanding of the phenomena that arise during the beam-metal interaction (Ref 6).

For these reasons, in recent years, many efforts have been carried out by companies, research centers and universities in order to overcome the current technological barriers to the complete applicability of metal AM systems in more fields. These efforts have led to a large number of patents that cover most of these critical aspects. Nevertheless, there is yet no comprehensive review of the patents that have been published on the latest advancements in the whole metal AM process chain: from powder production to post-processing phases. Hence, this review summarizes the patenting activities in the beam-based metal AM field from 2000 to 2019. This study describes the beam-based metal AM patent landscape, outlining the patenting trend and the most important key players together with the topics most covered in the field. In addition, this review provides relevant insights into global trends that can help industrial markets to identify an appropriate economic growth strategy.

## 2. Patents Search and Classification

The patent search was performed through the Orbit Intelligence database using the International Patent Classification (IPC) codes. The IPCs used in this search are reported in Table 1, together with their descriptions and the Orbit Technology Domain (TD) to which they belong. These codes were selected in order to include metal AM methods and exclude the polymer AM ones.

The advanced search was performed by using the following method:

**IPC:** B33Y+(B22F or B23K).

The patents were at first analyzed through the Orbit Charts section in order to inspect the number of patents per year, the key players and the main technological domains covered.

The patents belonging to the *Materials and Metallurgy* technological domains were then investigated more in detail to understand the patenting trend of the main alloying systems. In particular, new searches were performed based on the following approach:

**IPC:** B33Y+(B22F or B23K)

**Technological Domains:** “*Materials and Metallurgy*”

**Keywords** (in Title and Abstract): X

**Table 1 IPC codes and description**

IPCTech. Domain	Description
B33Y Other Special Machines	Additive manufacturing, i.e., manufacturing of three-dimensional (3D) objects by additive deposition, additive agglomeration additive layering, e.g., by 3D printing, stereolithography or selective laser sintering [2015.01]
B22F Machine Tools	Working metallic powder: manufacture of articles from metallic powder; making metallic powder (making alloys by powder metallurgy C22C); apparatus or devices specially adapted for metallic powder
B23K Materials and Metallurgy	Soldering or unsoldering; welding; cladding or plating by soldering or welding; cutting by applying heat locally, e.g., flame cutting; working by laser beam (making metal-coated products by extruding metal B21C 23/22; building up linings or coverings by casting B22D 19/08; casting by dipping B22D 23/04; manufacture of composite layers by sintering metal powder B22F 7/00; arrangements on machine tools for copying or controlling B23Q; covering metals or covering materials with metals, not otherwise provided for C23C; burners F23D)

**Table 2 Examples of subjects categorized in topics (Relevant: Powder Production, Materials Development, AM Technical Aspects, AM Production and Post AM)**

Topics	Examples
Powder Production	Improvement of particles' sphericity Powder recycling Particles coating with polymer or graphite Reduction of internal porosity within particles
Materials Development	New or modified compositions Tailored chemical compositions Grain refiners and dendrite structure modifications Metal matrix composites (MMCs) Functionally graded materials (FGMs)
AM Technical Aspects	Specific phases formation Wavelength modifications New DED nozzles Multi-laser AM systems Process atmosphere (high-pressure chambers, DED glove box, etc.)
AM Production	Components Thin walls Lattice structures A specific range of process parameters
Post AM	Heat treatments (stress relieving, aging, etc.) Hot isostatic pressing Machining Parts coatings
Out of topic	Non-beam-based metal AM (binder jetting, wire arc additive manufacturing, etc.) X indicates the material of a component of the AM system not specifically needed for X AM processing Not belonging to the alloy family (X is an alloying element and does not indicate the parental alloy)
All patents are reported in Supplementary materials	

where X can be aluminum (or aluminum), nickel, titanium and steel (or iron). These patents were downloaded and individually analyzed and classified based on their topics. The topics were defined as represented in Table 2. The goal of this search is to distinguish the patenting trends of

each alloy family and, most importantly, to categorize the main covered aspects. The topics trends found in the patents belonging to different alloys, calculated based on the total number of topics, were compared and discussed.

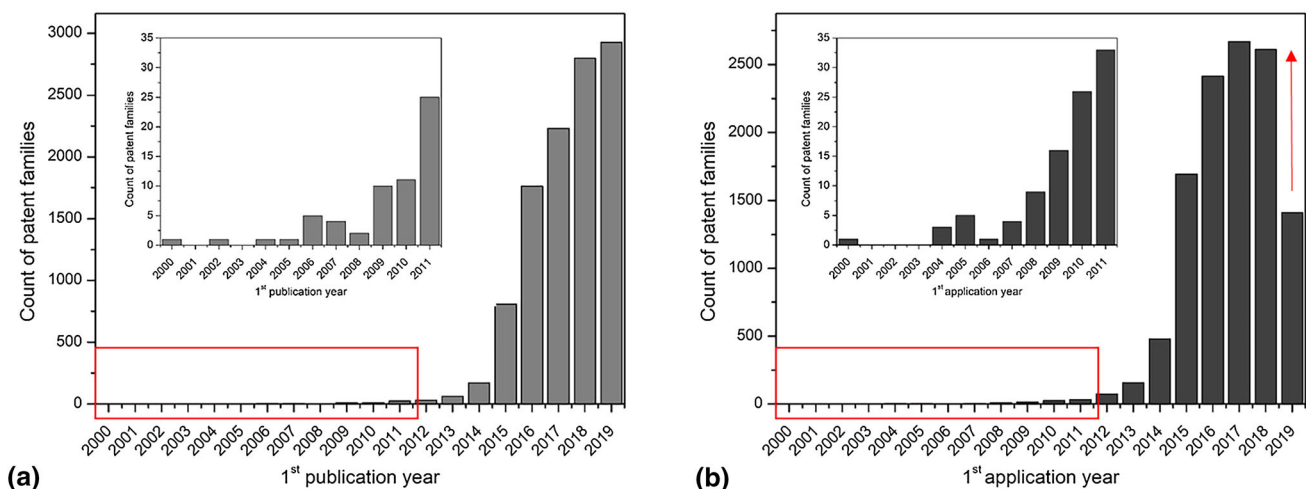


Fig. 1 Trend of AM patent families from 2000 to 2019

### 3. Results and Discussion

#### 3.1 Trend of AM Patents from 2000 to 2019

Patents are generally defined as “legal titles that give inventors the right, for a limited period (usually 20 years), to prevent others from making, using or selling their invention without their permission in the countries for which the patent has been granted.” These documents are, therefore, full of technical and commercial information. Because of this reason, the patent analysis, together with the state of the art of scientific literature, is one of the most suitable and reliable methods to investigate and forecast the growth of a technology (Ref 22). Furthermore, in some cases, patents are used to achieve marketing advantages and not necessarily technological improvements, indicating, therefore, the industrial interest in using a specific technology.

Figure 1 presents the number of published patents in the metal AM field based on the first publication year (Fig. 1a) and the first application year (Fig. 1b) from 2000 to 2019. It must be underlined that data of 2018 and 2019 of Fig. 1(b) are expected to grow as they refer to granted patents as a function of their first application year. Many patents filed in those years might be indeed still pending.

It is important to underline that the early patents on metal AM were not included in the present search. For instance, the first patent on metal AM was filed on March 2, 1988, by Frank Arcella and Gerald Lessman from the Westinghouse Electric (EP0289116, Method and device for casting powdered materials) and describes a powder bed metal AM system (Ref 23, 24). This patent is not considered in the present search as it does not have the B33Y IPC code, probably because it was not defined yet when the patent was filed. The absence of the first patents on metal AM is, however, not critical as the goal of this study is to understand the metal AM technology growth in recent years together with the current key players and most covered aspects.

From the graphs of Fig. 1, it is evident that the beam-based metal AM patents rapidly increased over the last years, demonstrating the substantial industrial attractiveness of these technologies. It can be noticed in particular that the rapid growth started about in 2012 and that only a few patents per year were submitted in the early 2000s (insets of Fig. 1).

This patenting trend can be correlated with the growth of AM technologies, which has been often compared with the hype cycle suggested by Gartner (Ref 25). This cycle explains the correlation between the visibility of an emerging technology and its maturity. The expectation trend is due to a first hype of the technology, followed by a period of disillusionment and, finally, its stabilization finding the correct role on the market (Ref 22). The position of AM technologies in this curve has been extensively discussed in recent years (Ref 26).

The technological development, highlighted by this patent trend, is in line with the commercial growth of AM systems identified by Wohler reports (Ref 27). Based on their data, the metal AM growth started about 10 years later with respect to that of the polymer AM. In fact, at the end of the 1990s, only a few companies were present on the market, such as AeroMet, Optomec and Röders. It was only at the beginning of 2000 that most AM companies such as EOS GmbH, Concept Laser GmbH, MTT and Trumpf commercialized their first metal AM systems mainly able to process steels. But it was definitely after 2010 that the strongest improvement in metal AM systems was observed; new materials for AM were put on the market, and different systems were developed. Furthermore, in 2010 Materialise released the Magics Metal SG support generation software making the AM production more simple and efficient (Ref 27).

#### 3.2 Main Key Players and Technology Domains

As already stated, the overall AM market continues to trend upward with many players, more than ten billions of dollars and innovative products designed for AM (Ref 28).

Since the 1990s, the main companies investing in the AM field certainly changed, including not only machines manufacturers and AM experts but also powder producers and end users. Figure 2 presents the 30 top key players having the most significant number of AM patents in their portfolios.

Among the key players, General Electric (GE), working on multidisciplinary activities, made significant investments in the AM field and has, therefore, the highest number of patents. This company, which is strongly investing in AM, recently has founded the GE Additive division and acquired a large part of Concept Laser GmbH and Arcam AB. The first company is a supplier of LPBF machines, while the second one is specialized





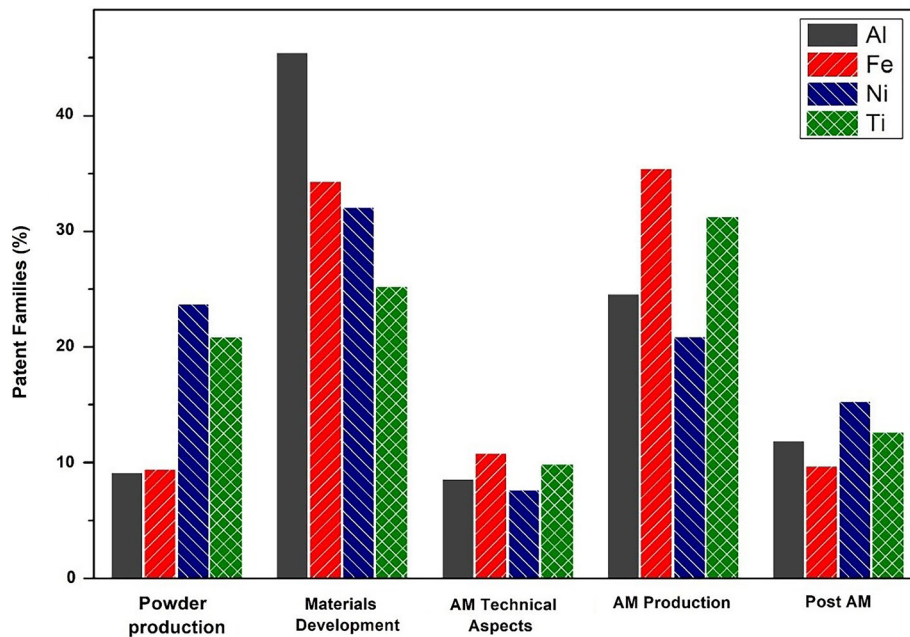


Fig. 4 Topic trends of Al-, Fe-, Ni- and Ti-based alloys (out of topic patents are not provided in these graphs)

patents, and this might be due, on the one hand, to the fact that it was the first alloy class being processed by AM and, on the other hand, to the frequent use of steel parts in AM systems. Titanium and aluminum alloys follow steel as number of patents and also present a large number of “Out of Topic” patents. This high number is due to the fact that Ti and Al are often used as alloying elements in other alloy systems. A large number of Ti patents is also due to the biocompatibility features of this class of alloys as well as their good processability through different metal AM technologies. It is well documented that in the biomedical sector, there is a marked necessity for the production of complex shape biocompatible parts such as implants and dental crowns (Ref 30). Therefore, several patents have been published on the application of additively manufactured titanium and titanium alloys in this field. The significant amount of Al patents is mainly due to the strong interest of aerospace companies to produce complex lightweight components taking advantage of the AM design freedom. Finally, nickel alloys have the lowest amount of patents among these four alloy classes. This can be correlated with the applicability of these alloys only to very specific cases where the components work in a harsh environment (e.g., corrosive or high-temperature environments), such as aerospace and chemical industries.

The results of the relevant Al, Fe, Ni and Ti patent classifications, performed on the basis of criteria of Table 2, are reported in Fig. 4. From this analysis, it is interesting to observe a different patenting trend for each class. This patent classification is discussed below per each alloy family.

Aluminum has by far the highest number of *Materials Development* patents, which mainly focus on new Al alloy compositions and composites. These new compositions have been mainly patented by universities, research centers and companies such as Arconic, Constellation, Thales, UTC Aerospace Systems and others. Most of the new or modified compositions contain transition metals, rare earth elements or grain refiners. These elements are generally introduced as they

allow the precipitation of strengthening phases coherent with the Al lattice and the consequent solidification of fine equiaxed grains that reduce the solidification cracking phenomena. The patent from Arconic is a clear example of these types of innovative compositions. It focuses in fact on the production of crack-free components by AM thanks to nanoscale grain refiners having specific particle size distribution and volume content. The grain refiners can be small quantities of fine ceramic particles, such as TiB, TiB<sub>2</sub>, TiC, SiC, Al<sub>2</sub>O<sub>3</sub>, BC, BN, Si<sub>3</sub>N<sub>4</sub>, Al<sub>4</sub>C<sub>3</sub> or AlN, or intermetallics containing specific elements. With respect to the same alloy having larger second phases, materials with the reduced size of grain refiners present improved strength, fracture toughness, corrosion resistance, fatigue resistance and fatigue crack growth resistance (Ref 31). Another relevant example of a patent on new aluminum alloys reports an Al-Fe-Si-V-Cu matrix containing TiB<sub>2</sub>, TiC or SiC (Ref 32). The alloying elements of the matrix are selected in order to form AlFeVSi and Al<sub>2</sub>Cu strengthening phases. The alloy is processed by AM methods which, thanks to the rapid cooling, entail that some of the alloying elements remain in a supersaturated solid solution. Moreover, most of the Al matrix composites patents focus on the development of materials with high mechanical strengths thanks to the introduction of TiB<sub>2</sub>, SiC and Al<sub>2</sub>O<sub>3</sub> particles (Ref 32, 33). For example, Zhang et al. patented the production of Al alloy matrix composites having SiC as the second phase. The parts production method starts with the obtaining of a composite powder batch by mechanically mixing AlSi10Mg particles with 8-12 wt.% of the SiC ones. The production of the components is then performed by LPBF using specific parameters (Ref 33). In other cases, a second phase characterized by a high laser absorption such as graphene, graphite or carbon nanotubes is added to the Al-based powder to improve its laser AM processability (Ref 34). The poor laser absorption of the Al powder is a key topic which several companies are trying to solve in *AM Technical Aspects* patents. One of the most investigated methods is the usage of a low wavelength laser beam that can facilitate its processability.

Wang et al., for example, developed a metal AM device for high-reflection materials having a blue-green laser (Ref 35). Other patents belonging to this topic describe methods to improve the AM quality by modifying the chamber pressure, by using a method to preheat the powder or by specifically designed DED nozzles. Many patents also cover the *AM Production*, and a very wide range of components such as heat exchangers, lattice structures and complex-shaped parts having cooling channels are reported (Ref 36-38). The analysis of the AI patents clearly shows that the lack of high-strength alloys is a key issue for metal AM companies and end users, which is widely studied by companies, universities and research centers.

Steel patents (labeled as Fe) cover a wide range of topics. One of the most investigated aspects is *AM Production*. Most of the patents describe the AM production of steel pistons, pipes, components for power plants or molds containing conformal cooling channels. Lei et al., for example, patented the LPBF production and post-processing of a H13 steel mold having conformal cooling channels (Ref 39). The Shanghai Nuclear Engineering Research & Design Institute developed the AM production of a nuclear power plant regulator spin core. The part is made by LPBF using one of the following stainless steel powders: 304L, 304LN, 316L or 316LN (Ref 40). Many of these patents report, together with the description of the components, the range of AM building parameters to use. For examples, the Xi'an Aero-Engine Corporation described the DED production of a force-bearing gimbal ring made using S-04 high-strength stainless steel, reporting the DED parameters and the post-processing conditions (Ref 41). A relatively large amount of patents also covers the *Materials Development* aspects with some new compositions designed to have specific mechanical or magnetic properties or high corrosion and wear resistance (Ref 42). Many *Materials Development* patents also focus on composite materials obtained by AM using mainly carbides, borides or oxides as strengthening phases. In this regard, EOS GmbH recently patented the LPBF processing of a powder mixture made of steel particles having a specific composition and non-metallic nanoparticles having certain sizes and morphologies (Ref 43). Furthermore, a large number of steel patents about *Materials Development* describe the production of FGM by DED process. The possibility to tailor the AM part properties by varying the composition is in fact very promising for steel applications such as mold or drilling rods. FGM parts are generally obtained by preparing mixed powder batches having different ratios of two alloys (Ref 44). The remaining steel patents are approximately well distributed among *Powder Production*, *AM Technical Aspects* and *Post AM*. The patents belonging to these topics describe the methods for the production of powders characterized by high purity and specific particle size distribution (Ref 45), technical aspects of AM steel processing, heat treatments to obtain the desired microstructure or surface treatment to achieve specific textures (Ref 46).

Concerning the Ni-based alloys, the three most advanced topics are *Materials Development*, *Powder Production* and *AM Production*. The first topic, as number of patents, is *Materials Development*; these patents mainly focus on the production of Ni-based alloys with a high quantity of  $\gamma'$  phase attempting to reduce their elevated crack susceptibility during AM processes. More in detail, Ni-based alloys with a high content of Al and Ti (approximately superior to 6 wt. %) tend to form cracks during welding. However, there is an enormous interest for this kind of alloys since they can work at high operative temperatures,

higher than 850 °C, allowing the fabrication of components such as turbine blades for the aerospace sector. For instance, Etter et al. from General Electric presented a patent related to a Ni-based alloy powder enriched in Al and Ti in order to promote the formation of 60-70 volume % of  $\gamma'$  phases as a consequence of the post-processing heat treatments (Ref 47). The chemical composition of the alloy is designed to reduce its hot crack susceptibility thanks to strict control of minor chemical elements such as Si, Zr and Hf. The elevated hot cracks susceptibility of Ni-based alloys with high content of  $\gamma'$  forming elements can result in a high fraction of cracks during the AM processes, reducing the performance and lifetime of the material. Therefore, reducing the hot cracking susceptibility can increase its processability by means of LPBF and EBM processes. Likewise, another example is the patent of Engeli et al. from Ansaldo Energia IP (Ref 48). In this case, the inventors developed a Ni-based alloy powder with a chemical composition deriving from a modification of the traditional Inconel 738LC alloy and therefore another alloy characterized by high contents of Al and Ti. Also in this case, the chemical composition presents a strict control of minor chemical elements (such as Si) to decrease the crack formation. In this way, they stated that almost crack-free components can be produced by both the LPBF and the EBM processes. Moreover, the production of Ni-based composites with the addition of ceramics particles (e.g., TiC, TiB<sub>2</sub>) and dispersed oxides in order to improve the mechanical performance of the based alloy has also been patented. Cao et al. patented a composite made using a Ni-based alloy powder (from 10 to 45  $\mu\text{m}$ ) with the addition of ceramic particles of TiC, TiB<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with dimensions ranging from 40 to 100 nm (Ref 49). The addition of nanoreinforcements can help to improve the mechanical performance of the material, such as strength, toughness, high-temperature properties, creep resistance and corrosion resistance. In this case, the powder is designed to be processed by laser beam technologies. The second most developed topic for Ni-based alloys is *Powder Production*. These patents cover several aspects related to the characteristics of the AM powder. In particular, the studies are mainly focusing on improving the morphology of the particles as well as to reduce the presence of internal impurities. For instance, Liu et al. reported an invention to produce Ni-based alloy particles suitable for laser beam technologies (Ref 50). The patented process produces highly spherical particles with a limited presence of satellites and reduced internal porosity. Moreover, this process involves a low oxygen content and a limited presence of impurities within the particles. The third category is *AM Production* concerning the interest in the development of components for the industries such as turbine blades subjected to a harsh environment, components with internal channels and hollow structures. A part of the patents classified on this topic also provides a range of process parameters to build Ni-based components. For example, Safran patented the possibility to repair or build parts of turbomachines by AM technologies (Ref 51) and Siemens Energy patented an invention related to the possibility to produce gas turbine engine blades using traditional casting technologies coupled to AM processes (Ref 52). It should be noted that the *Post AM* category reports a discrete number of patents too. In fact, post-processing heat treatments can be employed to modify the microstructure and the mechanical properties of the Ni-based alloys. Das from United Technologies reported a heat treatment employed on a Ni-based alloy to promote the formation of phases inside the grains as well as

along the grain boundaries to develop specific mechanical properties (Ref 53). Moreover, there are also patents mentioning the hot isostatic pressing as a post-processing method to consolidate cracks and pores generated during the AM building process.

In the case of titanium alloys, the first three important topics are *AM Production*, *Materials Development* and *Powder Production*. Since one of the main applications of these alloys is related to the biomedical field, several patents can be found on the production of biomedical parts such as artificial bones, artificial implants and dental crowns (Ref 54). For instance, Zhou et al. from Yinbang Clad Material focused on the AM production of a dental crown prepared using a titanium alloy powder. They found that the AM part has good biocompatibility and suitable esthetic properties so that AM can be considered a good method to produce a dental crown (Ref 54). Furthermore, since titanium alloys can be processed via all beam-based AM technologies, there are several patents on the optimization of process parameters to produce dense parts. The patent from Beijing Satellite Manufacturing Factory is a clear example of the optimization of process parameters for the LPBF production of a titanium alloy thin-walled component (Ref 54). Shanghai Research Institute of Materials has also patented a method for producing Ti6Al4V parts based on the LPBF process using a specific combination of process parameters (Ref 54). *Materials Development* for Ti alloy class has been carried out for several reasons, such as the reduction of elastic modulus of Ti alloys for the biomedical applications, the production of antibacterial alloys for porous dental root implants, the production of high strength, low elastic modulus, non-toxic titanium alloys for dental implants and the improvement in the high-temperature properties of the titanium alloys for aerospace components. As an example, Fouchet et al. invented a process for manufacturing by AM a Ti-Nb-Zr (TNZ) beta alloy with a low elastic modulus for biomedical applications. The  $\beta$ -alloy is obtained thanks to the AM process of Ti powder mixed together with nanometric Zr and Nb particles (Ref 55). Howmet Aerospace has also patented a new titanium alloy including Al, V and Fe as alloying elements. This composition has improved combination of mechanical properties as compared to conventional Ti alloys (Ref 56). The patent from Boeing is another clear example of this trend (Ref 55). In fact, Boeing developed a new titanium alloy which consists of 0.001-1.0 wt.% in total of at least one lanthanide's series element. The introduction of these alloying elements allows the solidification of a fine microstructure with the obtainment of high strength, ductility and fatigue properties. Zhang et al. used boron as alloying element in Ti-6Al-4V alloy to develop a new material for LPBF characterized by reduced anisotropy issues (Ref 57). In another patent, Lin et al. from Arconic developed a new Ti-based body-centered cubic alloy containing Al, Nb and Mo to be processed via AM processes (Ref 56). In addition, new titanium matrix composites have also been developed to improve the wear resistance, mechanical performance, bioactivity and biocompatibility of titanium alloys for different applications. The third most important topic of this alloy class is *Powder Production*. In fact, there are several patents that have been published on titanium powder production. In this group of patents, several targets are fixed, such as the increase in particle sphericity, the increase and the control of powder purity, the reduction of powder manufacturing cost and the recycling of the processed powder (Ref 58, 59). For instance, Lin from Arconic developed a new electrolytic-based method

for recycling titanium particles. In this method, the used Ti powders are processed in order to remove the oxide layer thanks to a reduction in an electrolytic cell.

The analysis of the patents of the four alloy classes showed that there is a strong interest to study and develop new alloys and composites for AM processes, both in the industrial and in the academic fields. In the literature, these objectives have recently been approached using Integrated Computational Material Engineering (ICME). This innovative inter-disciplinary methodology describes processing–structure–property relationships through materials models such as CALPHAD (Ref 60, 61). With these atomistic models, it is possible to explore the whole periodic table to develop new materials and to foresee their microstructures and consequently their mechanical properties.

In particular, the ICME-based method can be used in the AM field to approach the following aspects:

- Alloy design based on predicted phase diagrams;
- Powder production via gas atomization;
- Optimization of AM building parameters;
- Microstructural and mechanical characterization of AM materials;
- Selection of post-processing heat treatments;
- Guidelines for AM monitoring systems.

In this regard, the ICME method has recently been used by Thapliyal et al. to develop a new Al-Cu-Sc-Zr alloy for LPBF (Ref 61). The composition was designed using simulation tools optimized to reduce the crack sensitivity of the alloy and to obtain a suitable precipitation strengthening. A similar approach was also used by Motaman et al. to design a single-phase face-centered cubic high-manganese steel (Ref 60). It is important to underline that ICME is not clearly cited in the analyzed patents. However, a promising approach could be to study the large number of complex correlations existing between the chemical composition, the design parameters and the final performances. The use of a computational approach can strongly reduce the time required for experimental activities. On the basis of these considerations, it is possible that a broader application of materials modeling in the AM industries could be beneficial for their production lines.

## 4. Conclusions

In this review, the beam-based metal AM patenting trend was investigated to study the continuous growth of these technologies and to highlight the main key players and the most investigated aspects. The results can be summarized as follows:

- The beam-based metal AM patent number has continued to grow since the development of the first metal AM systems. Growth increased rapidly from around the beginning of 2010 when most of the main current metal AM machine producers entered the market.
- The key player analyses showed that the main assignees are companies, universities and research centers. Among the companies, both AM machine producers and end users are present. The end users are mainly multidisciplinary and aerospace companies such as GE, Siemens, Bosh and Rolls-Royce plc.

- Examination of the patents belonging to four alloy classes revealed that there is a different patenting trend in each category. This highlights the most critical aspects on which it is necessary to focus in order to solve the current limitations for complete industrial applicability of AM systems. The analyses revealed that Al alloy patents mainly focus on aspects related to Materials Development and, in particular, on the production of new alloys and composites. Steel patents, on the contrary, seem to be more connected to AM industrial production and focus therefore on the methods used to produce and post-process components, which have complex shapes and conformal cooling channels such as pipes and molds. Ni-based alloys patents are more related to Materials Development, Powder Production and AM Production, focusing on the development and production of materials capable of working at high temperatures in harsh conditions. Moreover, Post AM processes of Ni-based alloys are also considered to reduce internal defects and to modify microstructures and mechanical performances of the components. Finally, Ti-based alloys patents focus efforts on AM Production, Materials Development and Powder Production and show the relevance of health and aerospace applications in the AM field.

This review can help industries involved in metal AM to identify appropriate economic growth strategies and can also be of interest to research for a greater understanding of the most relevant issues affecting the applicability of these technologies.

## Funding

Open access funding provided by Politecnico di Torino within the CRUI-CARE Agreement.

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