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# Insight into Bulk Metallic Glass Technology Development Trajectory: Mapping from Patent Information Analysis

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## Abstract

Bulk metallic glasses (BMGs) having a completely amorphous structure possess many attractive properties, and several groups from academia and industry have conducted research to expand their application in the market. Although many efforts have focused on investigating scientific issues related to the mechanical and chemical properties of these amorphous alloys, very few studies have assessed the development trends of these amorphous materials, especially from the viewpoint of market application and R&D directions. Therefore, in this chapter, the development trajectory of BMG materials is summarized based on data extracted from patent bibliometric information. These data were used because the information on patent documents obtained from a commercial patent database, World Intellectual Property Service (WIPS 2.0), can provide the most comprehensive information on valuable R&D activities and market issues. The results summarize advances in technology based on various alloy categories and processing routes. Furthermore, the research interests are also analyzed according to different countries, companies, and research institutions. The patent information provided in this chapter can provide a clear direction to assist metallurgist/metallurgy engineers in further technology development forecasting and R&D plan management.

**Keywords:** metastable material, bulk glass metal, bibliometrics, patent analysis, technological forecasting

## 1. Introduction

Discovered by Klement et al. in the early 1960s, amorphous metallic glasses have attracted much attention for several decades due to their outstanding properties, such as excellent mechanical properties, good corrosion resistance, and unique physical and chemical characteristics. These metallic materials are suitable for application as a new class of advanced materials [1–3]. However, their tiny size, a result of their limited glass-forming ability (GFA), makes it difficult to use BMG materials in industry.

Therefore, over the past decades, three main directions have been followed in the development of higher-quality BMG materials with better properties. These directions are as follows: (1) new compositions of metallic alloys [4–6], (2) novel

processing routes [7–11], and (3) potential application fields [12–15]. In efforts to achieve new bulk metallic glasses (BMG) with high glass-forming ability (GFA), many studies have focused on establishing a relationship between the GFA and the chemical compositions of metallic materials. For example, in the Al-based metallic system, both types of metal elements, transition metal elements, and rare earth metal elements can increase the GFA of Al-based alloys [15, 16]. On the other hand, various processing routes, such as melt spinning [7], magnetron sputtering [8], pulsed laser quenching [9], and liquid splat-quenching [10] have also been developed to overcome the crucial constraint on the size and geometry of metallic glass samples. For instance, a high-throughput strategy, named the combinatorial approach via co-sputtering, has been developed for producing and characterizing substantial compositional libraries at the same time [11]. In addition, several studies have also focused on discovering potential fields of application, such as structural materials [3], hydrogen storage materials [12], soft magnetic materials [13], and biomaterials [14].

Although several research articles concerning metallic glass materials have been published, almost no studies have conducted patent analyses of metallic glass materials, to the author's best knowledge. Patent information is useful because it contains valuable research results for the researcher, business planner, R&D manager, and policymaker [17–20]. The reason is that a patent application is a costly and time-exhausting process; the willingness of the applicant to invest time, money, and effort in the process generally indicates that the patent can provide commercial benefits and technical contributions. Therefore, as pointed out by Daniel Gredel et al., patent documentation is the most comprehensive of all research resources. Nearly 70% of the technical information contained in these documents is not available in any other type of information source, and it can be used for detailed analysis [21]. For instance, patent data can be used to analyze competitors, track the evolution of technology, master crucial technologies, and identify the trends and conditions of patent development in different markets [22].

In the present research, patent data were analyzed to explore the technological development of metallic glass materials. The variations in numerous patents and assignees, technology life cycle, and categories of patents for metallic materials were studied. Furthermore, the top ten patent assignees and the trends of their patents filed, patent families, and patent citations were analyzed. The top five families and five most-cited patents are also explored in the present study.

The article is structured as follows. Section 2 presents the study methodology and the details of the information analysis. Section 3 presents an analysis of amorphous alloys patenting activity and possible explanations for the data. In Section 4, the final section, the implications and conclusions are presented.

## **2. Methodology**

### **2.1 Data extraction procedure**

In accordance with the suggestion of the WIPO Guide to Using Patent Information, the bibliographic records of patent documents were retrieved from a commercial database based on keywords and IPC codes related to amorphous and metallic glass alloys [23]. In the present study, we employed patent data to survey the development trends of amorphous alloy technology, as well as their technological impacts on the metallurgy industry. The patent information was gathered and analyzed by the following steps: (1) patent data retrieval, (2) patent data mining, and (3) patent data analysis.

To find the patent information, we modified the search formula as follows: [ (“amorphous alloy\*” OR “metal\*glass\*” OR “glass\*alloy\*” ) ] (step 1). Furthermore, the IPC search expression, namely [C\*], was also included in the overall retrieval process. It should be emphasized that we performed keyword searches for the above formula appearing only in an independent claim to ensure that accurate patent information was found. Our intention was to exclude any information not involving the amorphous material industry. Patent data mining techniques were used in commercial software (WIPS 2.0) to quantify the patent information and analyze patent trends (step 2). In the final step, all the collected patent information was developed into various indicators and presented in tables or graphs plotted in commercial Microsoft software (step 3). Moreover, to avoid incorrect explanations of the trends, patents filed in 2016 and 2017 were not included in the present study, since most patents are not available before publication (i.e., for 18 months after the patent is filed). Therefore, the total number of patents that could be analyzed was 2857.

The commercial patent database WIPS 2.0 was selected for the overall search process because it includes full-text patents from 11 patent offices and abstract and bibliographic information from 75 countries. This commercial database also provides other advantages not included in other databases. For example, full-text translations of patents from Asian countries, such as China, Japan, and Korea, are provided, which facilitates complete search and analysis.

## 2.2 Detail of data analysis

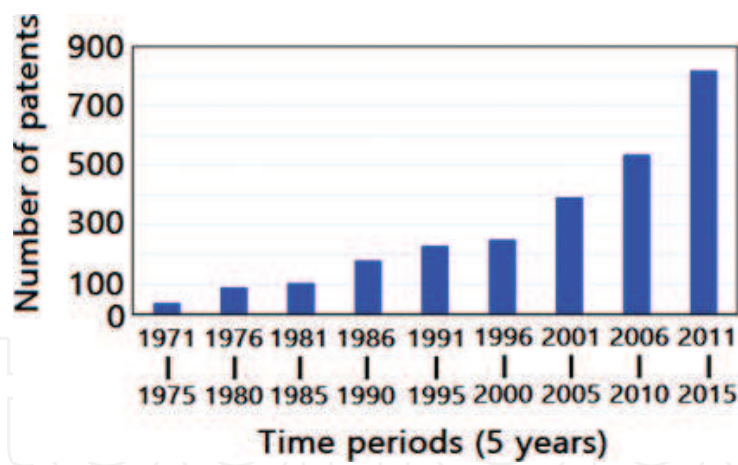
The analyzed indicators in the present study mainly included the progress of patent documents, percentages of various categories of amorphous alloys in the development of metallic alloy technology, patent activity in different countries, technology life cycle analysis, evolution of patents filed by different assignees and countries, analysis of top ten patent assignees, analysis of technological development of the top five patent families, and five most-cited patents. It should be emphasized that the numerical indicators analyzed here were based on suggestions from the field of quantitative research in science and technology and comments from experts in the field of amorphous materials [7, 12, 15].

All evolution indicators were plotted in periods of 5 years from 1971 to 2015. Furthermore, assignees' names were also unified carefully to avoid incorrect interpretation during patent-filing trends in different countries and analysis of the top 10 assignees. To evaluate the evolution of the amorphous alloys, all IPC codes were collected and analyzed as follows: Fe as the major constituent element (C22C 45/02), Ni or Co as the major constituent element (C22C 45/04), Be as the major constituent element (C 45/06), Al as the major constituent element (C22C 45/08), and Mo, W, Nb, Ta, Ti, or Zr as the major constituent element (C22C 45/10). We further named these classifications as follows: Fe-based alloys, Ni- or Co-based alloys, Al-based alloys, and Ti- or Zr-based alloys. However, the Be-based alloys were not included in the present analysis due to their rarity (only 8 patents found).

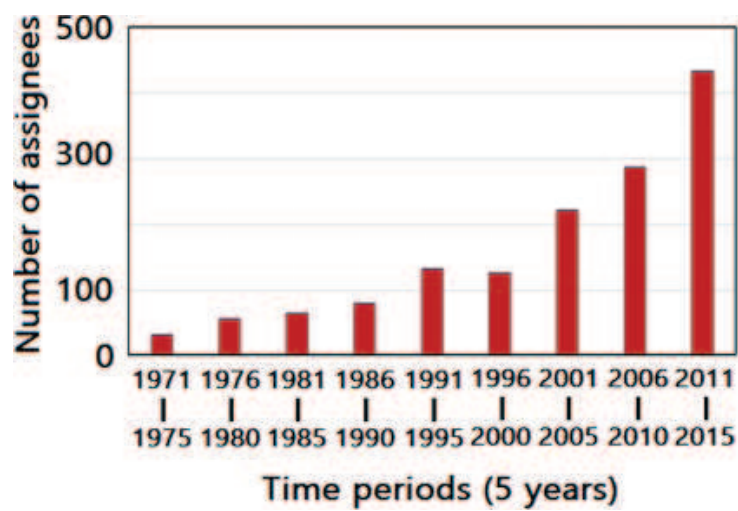
## 3. Results and discussion

### 3.1 Amorphous alloy development: evolution of patent application

The evolution of the number of patents and assignees in every decade since the 1970s is shown in **Figures 1** and **2**, respectively. Both figures show obvious increments in the numbers of both patents and assignees after 1990. From subsequent analysis, it was found that the first apparent growth in the number of patent



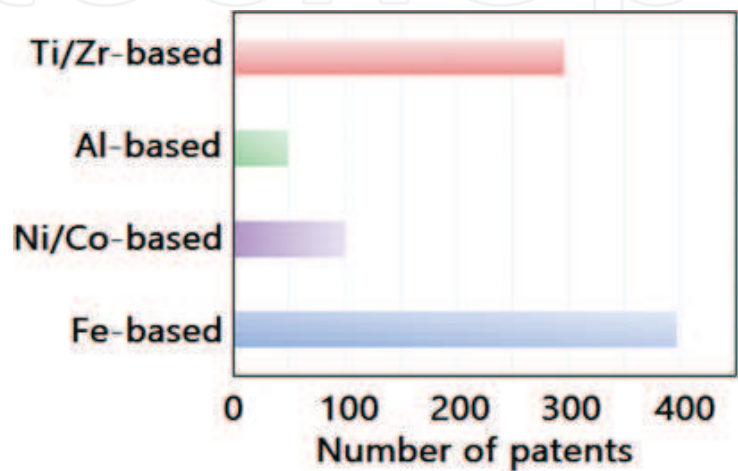
**Figure 1.**  
*Evolution of the number of patents.*



**Figure 2.**  
*Evolution of the number of assignees.*

applications/assignees was indicated by an increase in the number of patents filed in Japan in 1990. The second surge in patent applications/assignees occurred in 2000 as a consequence of patent filings from China.

The trend of patenting different categories of amorphous alloys is shown in **Figure 3**. Fe-based amorphous alloys had the most active patenting activity in the



**Figure 3.**  
*Patenting activity for different amorphous alloys.*



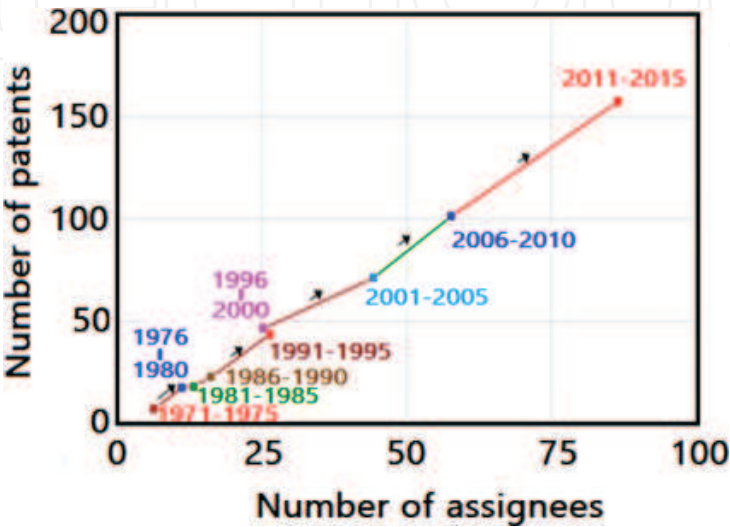
period of investigation. These Fe-based patents were filed by mostly Japanese corporations and research institutes mainly due to their magnetic properties, which can be exploited in the technology fields of electric/magnetic devices, energy storage devices, and some semiconductor devices [24, 25]. On the other hand, more than Ni-/Co-based and Al-based amorphous alloys, Ti-based and/or Zr-based amorphous alloys occupied the second role of patenting activity because these amorphous alloys possess superior mechanical properties and biocompatibility and can be widely used in the biomedical industry, even though applications in electronic and energy conversion devices were also widely found [26, 27].

**Figure 4** shows the technology life cycle curve for amorphous alloys in the present study. Grasping the technology life cycle curve is critical for researchers and R&D managers in assessing further trends in technological development. As pointed out by Trappey et al., a typical technology life cycle curve can be divided into four stages: (1) introductory, (2) growth, (3) maturity, and (4) decline [28]. In the introductory stage, the number of patents and assignees are extremely low because very few corporations have invested in the field. In the following years, more and more assignees become involved in the prospective technology field due to a reduction of uncertainty in the market and technology outlook, which also leads to a gradual increase in patent applications as the life cycle moves into the growth stage. On the other hand, if the number of patents and the number of assignees begin to decrease, the stage is classified as technological maturity. Only a few corporations are willing to invest in such a technology.

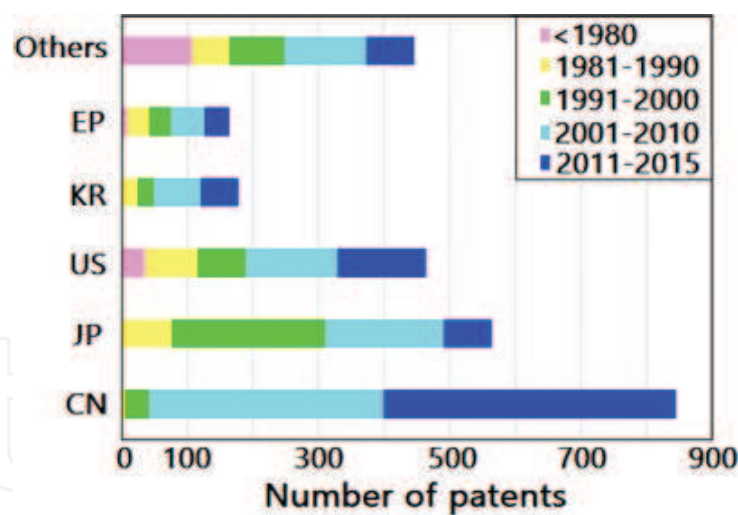
Therefore, in the present study, the rapid increase in the numbers of patents and assignees after 2000 indicated that the technology had entered the growth stage. The average numbers of patents and assignees, respectively, increased from 47 and 52 in 2000 to 157 and 86 in 2015. The characteristic of this growth stage is the absence of technical problems and market uncertainty, which leads to more companies becoming involved in developing related products for the market. This stage is a possible explanation for the surge in patenting in China.

3.2 Amorphous alloy development: analysis by country and assignee nationality

**Figure 5** shows the number of patent application in various countries and their evolutionary trends. As shown in the figure, China, Japan, the United States, Korea, and Europe were the top five patent-filing countries/regions, indicating their potential market attraction. For example, the total number of patent applications in China was



**Figure 4.**  
*Technology life cycle.*



**Figure 5.**  
*Number of patents and its evolution by country.*

844, which implies the commercial value of bulk metallic glasses in the Chinese market. Another interesting event in the same figure is the R&D investment transfer from the United States and Japan to China. Discovered in the United States and further exploited in Japan, the number of patents related to metallic glass alloys in Japan in the last three decades gradually decreased from 233 (1991–2000) to 181 (2001–2010) and then to 73 (2011–2015). In contrast, unlike those in other countries, the patents filed in China increased by a wide margin, from 35 (1991–2000) to 358 (2001–2010) and then 444 (2011–2015). The above surge in patent filing in China, often called China’s patent boom, occurred not only in amorphous alloy technology but also in other technological areas. As pointed out by several research teams, a decrease in the cost of filing a patent and the initiation of a subsidy program for patent applications were two major causes of the explosion in patent applications in China [29, 30].

Like that in China, patenting behavior in the United States shows a similar trend of progressive increases in the numbers of patents filed over the past three decades: from 72 (1991–2000) to 140 (2001–2010) and finally to 135 (2011–2015). In Korea and Europe, however, the number of patents filed has declined since 2011. The explanation of phenomenon is still unclear and will require further study.

### 3.3 Analysis by top ten patent assignees

Analysis of the patent assignees from the original patent data pool can help researchers to understand the technological development strategies and product development trajectories of large companies. Therefore, the top ten patent assignees with a focus on the development of amorphous alloys are summarized in **Table 1**. The top ten patent assignees were mainly from Japan (7), China (2), and the United States (1). Moreover, the assignee from the United States was an academic institution, whereas those from Japan and China were mostly corporations and research institutions.

The number of patent families and average number of countries where patents were filed are also shown in **Table 1**. The variation in patent families was related to the total number of patents; that is, the patent families increased monotonically in conjunction with the number of patent applications. The top assignee, California Institute of Technology (CIT), was associated with 633 patent families, which is obviously higher than those of the other assignees. The reason for this large difference in the number of patent families could be attributed to the fact that CIT filed its patents in many countries (an average of 7). In contrast, Chinese assignees generally filed patents only in their home country, which explains the similarity between the number of patents and patent families.

Assignee (nationality)	Total number of patents	Patent families	Average cited times	Average Number of application countries
California Inst. Techn. (US)	96	633	16.0	7
Hitachi Metals LTD (JP)	76	376	4.7	5
BYD Company LTD (CN)	68	134	2.1	2
Univ. Tohoku (JP)	67	221	2.0	3
Nippon Steel Corp. (JP)	67	270	3.5	4
YKK Corp. (JP)	62	252	4.1	4
ALPS Electric Co. LTD (JP)	59	192	3.9	3
Japan Science & Tech Corp. (JP)	45	103	6.9	2
Inst. Metal Res. Chinese Acad. Sc. (CN)	35	48	1.9	1
JFE Steel KK (JP)	29	93	3.5	3

**Table 1.**  
*Top ten patent assignees.*

**Table 1** also presents the average number of citations of each assignee’s patents; this number can be used to assess the quality of a patent [31, 32]. A weak relationship was found to exist between the average number of citations and the total number of patents/patent families. Therefore, a high number of citations indicate that more related inventions followed, which usually implies a higher economic value of the patent. In addition, patents filed by CIT got the most attention. They had the highest number of citations (16.0), which was considerably higher than those of other assignees. In contrast, patents owned by China were rarely cited, which could be associated with their short filing periods (**Table 2**).

**3.4 Technological development strategy analysis: analysis of the top five patent families**

The analysis of the top five patent families is shown in **Table 3**. The first patent family, US2009236017A1 [33], proposes an apparatus and method comprising

Assignee (number of active years)	1981 ~1990	1991 ~2000	2001 ~2010	2011 ~2015	Total
California Inst. Techn. (20)	-	18	31	43	92
Hitachi Metals LTD. (27)	3	16	32	18	69
BYD Company Limited (9)	-	-	46	22	68
UNIV. Tohoku (12)	-	-	51	14	65
Nippon Steel CORP. (22)	5	24	35	3	67
YKK CORP (15)	3	51	8	-	62
ALPS Electric Co. LTD. (15)	11	45	3	-	59
Japan Science & Tech. Corp. (13)	-	16	29	-	45
Inst. Metal Res. Chinese Acad. Sc. (14)	-	1	14	12	27
JFE Steel KK (10)	-	23	-	5	28

**Table 2.**  
*Trend of the patent applications for top ten patent assignees.*



Patent number [reference]/ assignee (nationality)	Title	Patent Families
US2009236017A1 [33]/Cal. Inst. Tech. (US)	Forming of metallic glass by rapid capacitor discharge	57
US7323071B1 [34]/Bechtel BWXT Idaho, LLC. (US)	Method for forming a hardened surface on a substrate	33
US5628840 [35]/Allied Signal INC. (US)	Metallic glass alloys for mechanically resonant surveillance systems	29
US6183568B1 [36]/Fuji Photo Film Co. LTD (JP)	Method for preparing a magnetic thin film	25
US8529712B2 [37]/Cal. Inst. Tech. (US)	Tough iron-based bulk metallic glass alloys	21

**Table 3.**  
*Top five patent families.*

uniform heating, rheological softening, and thermoplastic forming of metallic glasses rapidly into a net shape using a rapid capacitor discharge forming (RCDF) tool. The RCDF method utilizes a discharge of electrical energy stored in a capacitor to uniformly and rapidly heat a sample or charge of metallic glass alloy to a predetermined “process temperature” between the glass transition temperature of the amorphous material and the equilibrium melting point of the alloy on a time scale of several milliseconds or less. Once the sample is uniformly heated such that the entire sample block has a sufficiently low process viscosity, it may be shaped into high-quality amorphous bulk articles by any number of techniques, such as injection molding, dynamic forging, stamp forging, and blow molding, in a time frame of less than 1 s. The second patent family, US7323071B1 [34], discloses a metallic glass coating formed over a metallic substrate. After the formation of the coating, at least a portion of the metallic glass can be converted into a crystalline material having a nanocrystalline grain size. The third patent family, US5628840 [35], relates to a glassy metal alloy consisting essentially of the formula  $\text{Fe}_a\text{Co}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f\text{C}_g$ , where “M” is at least one member selected from the group consisting of molybdenum, chromium, and manganese. The notations “a–g” are in atom percent, “a” ranges from about 30 to about 45, “b” ranges from about 4 to about 40, “c” ranges from about 5 to about 45, “d” ranges from about 0 to about 3, “e” ranges from about 10 to about 25, “f” ranges from about 0 to about 15, and “g” ranges from about 0 to about 2. The alloy can be cast by rapid solidification into a ribbon or otherwise formed into a marker that is especially suited for use in magneto-mechanically actuated article surveillance systems. Advantageously, the marker is characterized by relatively linear magnetization response in the frequency regime wherein harmonic marker systems operate magnetically. Voltage amplitudes detected for the marker are high, and interference between surveillance systems based on mechanical resonance and harmonic re-radiance is virtually eliminated. The fourth patent family, US6183568B1 [36], proposes a soft magnetic thin microcrystalline film of  $\text{Fe}_a\text{B}_b\text{N}_c$  (at %) where B is at least one of Zr, Hf, Ti, Nb, Ta, V, Mo, and W, and  $0 < b \leq 20$  and  $0 < c \leq 22$ , except for the range of  $b \leq 7.5$  and  $c \leq 5$ , show low coercivity  $H_c$  of  $80\text{--}400\text{ Am}^{-1}$  (1–5 Oe), which is stable upon heating at elevated temperature for glass bonding. This film is produced by crystallizing an amorphous alloy film of a similar composition at  $350\text{--}650^\circ\text{C}$  to a crystal grain size of up to 30 nm to provide uniaxial anisotropy and increased magnetic permeability at the higher frequency. It can also provide low magnetostriction of around  $\lambda_s = 0$ . The composite magnetic head is made using this thin film. A diffusion-preventive  $\text{SiO}_2$  layer disposed between the ferrite core, and this thin film in the magnetic head prevents an interdiffusion layer and suppresses beats in the output signal. The fifth

patent family, US8529712B2 [37], relates to an iron-based bulk metallic glass alloy and more particularly to a family of the iron-based phosphor-containing bulk metallic glass alloys exhibiting low shear moduli. The independent claim specifies an Fe-based metallic glass composition comprising at least Fe, Mo, P, C, and B, where Fe comprises an atomic percent of at least 60, Mo comprises an atomic percent of 2–8, P comprises an atomic percent of 5–17.5, C comprises an atomic percent of 3–6.5, and B comprises an atomic percent of 1–3.5, wherein the composition has a shear modulus (G) of less than 60 GPa and a glass transition temperature ( $T_g$ ) of less than 440° C, and the composition is capable of forming a bulk amorphous object having a critical thickness of at least 2 mm.

### 3.5 Technological exploitation analysis: five most-cited patents

In most scientific publications, patents are rarely cited in SCI papers. For example, only about 1.5% of US patents are cited in SCI journals [38]. Similarly, in most technology fields, most of the prior art cited within patents are also patent documents, not scientific papers, which could be a sign of the few connections between academia and industry [38, 39]. However, the technological value of patents can provide important information to subsequent researchers and thus is worthwhile to refer to, especially in the case of patents with a high number of citations. Therefore, like a scientific paper, a high number of citations represent the high technological value of a patent, which might indicate that high commercial profit can be expected. In the present study, the five most-cited patents were extracted from the original patent pool (Table 4), and their technological contents are reviewed as follows.

The most-cited patent in Table 4, US5288344, is about beryllium-bearing amorphous metallic alloy formed with a low cooling rate [40]. In this patent, the proposed technology suggests an alloy containing beryllium in the range of 5–52 atomic percent and at least one early transition metal in the range of 30–75 atomic percent and at least one late transition metal in the range of 2–52 atomic percent. A preferred group of metallic glass alloys has the formula  $(Zr_{1-x}Ti_x)_a(Cu_{1-y}Ni_y)_bBe_c$ . A preferred embodiment is a class of alloys which form metallic glass upon cooling below the glass transition temperature at a rate of less than  $10^3$  K/s, which is far below the normal cooling rate,  $10^4$  to  $10^6$  K/s. The second most-cited patent, US5735975, describes at least quinary alloys that form metallic glass upon cooling below the glass transition temperature at a rate of less than  $10^3$  K/s [41]. Such alloys comprise zirconium

Patent number [reference]/ assignee (nationality)	Title	Times Cited/ (Patent family)
US5288344 [40] / Cal. Inst. Tech. (US)	Beryllium bearing amorphous metallic alloys by low cooling rates	290 / (12)
US5735975 [41] / Cal. Inst. Tech. (US)	Quinary Metallic glass alloys	220 / (7)
US5368659 [42] / Cal. Inst. Tech. (US)	Method of forming beryllium bearing metallic glass	204 / (12)
US5618359 [43] / Cal. Inst. Tech. (US)	Metallic glass alloys of Zr, Ti, Cu, and Ni	169 / (7)
US6325868 [44] / Univ. Yonsei Seoul (KR)	Nickel-based amorphous alloy compositions	157 / (4)

**Table 4.**  
*Top five patent families.*

and/or hafnium in the range of 45–65 atomic percent, titanium and/or niobium in the range of 4–7.5 atomic percent, and aluminum and/or zinc in the range of 5–15 atomic percent. The balance of the alloy composition comprises copper, iron, cobalt, and nickel. The composition is constrained such that the atomic percent of iron is less than 10%. Furthermore, the ratio of copper to nickel and/or cobalt is in the range of 1:2 to 2:1. Therefore, the alloy glass can be formed at a reduced critical cooling rate without any beryllium addition. The third most-cited patent, US5368659, discloses an invention similar to the above most-cited patent; the alloy forms metallic glass containing beryllium in a narrower range of 2–47 atomic percent, at least one early transition metal in the range of 30–75 atomic percent, and at least one late transition metal in the range of 5–62 atomic percent [42]. Furthermore, the critical cooling rate to achieve the amorphous structure can be reduced to 1–100 K/s or lower. Patent US6325868, the fifth most-cited patent, discloses a nickel-based amorphous alloy composition, particularly a quaternary nickel-based amorphous alloy containing nickel, zirconium, and titanium as the main constituent elements and additive Si or P [44]. The quaternary nickel-zirconium-titanium-phosphorus alloy compositions comprise nickel in the range of 50–62 atomic percent, zirconium and titanium in the range of 33–46 atomic percent, and phosphorus in the range of 3–8 atomic percent, represented by the general formula  $\text{Ni}_d(\text{Zr}_{1-y}\text{Ti}_y)_e\text{P}_f$ . The nickel-based amorphous alloy compositions have a superior amorphous phase-forming ability, and bulk amorphous alloy having a thickness of 1 mm can be produced by general casting methods.

#### 4. Conclusion

This study focuses on the analysis of patent data to explore the technological developments of metallic glass materials. The primary findings of this study can be summarized as follows:

1. Two obvious increments in patent applications occurred in 1990–2000 and 2000–2015. The former primarily arose from the increased number of patent applications filed in Japan. The latter is mainly attributed to patent applications filed in China.
2. Patents related to iron-based alloys are the main category of metallic glass materials for which patents were applied. The reason is that iron-based metallic materials can be used in several applications, especially in the soft magnetic fields.
3. According to the analysis of the present study, metallic glass materials are in the growth stage of the technology life cycle, which implies that increasing amounts of resources will be invested in the metallic glass field for the development of commercial products.
4. All of the top ten assignees were from the United States, China, and Japan. The US assignees were from an academic institution, whereas most of their Japanese and Chinese counterparts were from commercial businesses or research institutions.
5. Patents filed by the California Institute of Technology were cited the most frequently, with an average of 16.0 citations, implying their high technological value.

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