ceramics

Review

Cermet Systems: Synthesis, Properties, and Applications

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Abstract: Cermet is an advanced class of material consisting of a hard ceramic phase along with a metallic binding phase with the combined advantages of both the ceramic and the metal phase. The superior properties of this class of materials are particularly useful in high-temperature, tribological, and machining applications. This review paper seeks to provide a comprehensive overview of the various cermet systems. More specifically, the most commonly used cermet systems based on tungsten carbide (WC), titanium carbide (TiC), titanium carbonitride (TiCN), and aluminum oxide (Al_2O_3) are discussed based on their development, properties, and applications. The effect of different metallic binders and their composition on the tribological and mechanical properties of these cermet systems is elaborated. The most common processing techniques for cermet systems, such as powder metallurgy (PM), reaction synthesis (RS), thermal spray (TS), cold spray (CS), and laser-based additive manufacturing techniques are discussed. The influence of the processing parameters in each case is evaluated. Finally, the applications and challenges of cermet systems are summarized.

Keywords: cermet; self-lubrication; cold spray; microstructure; wear resistance

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1. Introduction

Improvisation using existing materials and exploration of possibilities for the development of advanced materials capable of outperforming their predecessors by scientists and engineers is essential for advancement in science and technology. The properties and characteristics of materials determine the performance of the mechanical components. The need for advanced materials capable of performing under a variety of extreme conditions while demonstrating improved properties drives researchers to try new combinations of materials. Metals and ceramics have been used independently for a wide range of applications because of their excellent properties. However, while their unique properties contribute to many applications, they still possess some disadvantages, such as the poor oxidation resistance and high-temperature (HT) properties of metals, and the inherent brittleness of ceramics [1]. The development of composites enables the fabrication of materials with the combined advantages of the individual components.

A fundamental definition of the word 'cermet' is, "a composite that contains at least one ceramic and one metallic phase" [2]. Although the idea of a cermet is to produce a composite material with ceramic as the matrix and metals as the binder phase, there is still some ambiguity in the use of this word by researchers. The definition provided in the *Metals Handbook* [3] for cermet is "a powder metallurgy product consisting of ceramic particles bonded with metals". The main idea of a cermet is to produce material by combining ceramic and metal materials to achieve properties that are superior to those of ceramics and metals when used independently. Petzow et al. [4] include a wide variety of hard and brittle materials as ceramics in the definition of cermets. From this perspective, tungsten carbide (WC)-based, and cobalt (Co)-bonded cemented carbides or hard metals fall within the cermet category. The word 'cermet' has been applied historically to titanium carbide (TiC)-based hard metals. Among cutting tool specialists, the term 'cermet' is applied exclusively to tool materials based on titanium carbonitride (TiCN) with nickel (Ni) or cobalt (Co) as binders with possible carbide additives [5,6].

This review paper adopts a definition of cermet provided by Mari [5]. According to this definition, the meaning of the word 'ceramic' within the term cermet includes everything that has a high melting point or is refractory. Hence, cermets are a combination of high melting point material, along with a metal component to provide suitable ductility and heat conductivity to the material, making them insensitive to heat shock. A cermet (ceramic metal) is a structural material consisting of a hard ceramic phase, which constitutes approximately 15–85% of the material by volume, and a metal-binding phase [7]. Based on this definition, a wide range of composite materials fall under this category. It is appropriate to consider a cermet to be a ceramic-metal composite in which the dominant part is the ceramic phase including carbides, nitrides, oxides, and carbonitrides of titanium (Ti), molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V). The usual metallic binders for cermet systems include Ni, Co, and Mo. The above definition distinguishes cermets from metal matrix composites (MMCs) and ceramic matrix composites (CMCs). In both MMCs and CMCs, a ceramic phase is added as a reinforcement to a metallic or ceramic base material, whereas in cermets, in most cases, the metallic phase functions as a binder to improve the toughness alongside ceramic-like properties. These materials are generally refractory, hard, and chemically resistant [5]. Ceramic materials, in general, possess high-temperature resistance and hardness, while metals can deform plastically. Therefore, a cermet design aims to achieve the combined optimum properties of both ceramics and metals. Because of these combined properties, cermet materials are used in various applications, including machining and cutting tools, extrusion dies, wear-resistant coatings, high-temperature applications, etc. [8]. The metal binder content, mean free path of binder, distribution of ceramic particles, and average ceramic particle size are the characteristics that affect the tribological and mechanical properties of cermets [9].

Figure 1 classifies different cermet systems based on the ceramic phase. The selection of the metallic binder depends on the specific cermet system, the chemical and metallurgical properties of the ceramic-binder system, and the desired properties of the final cermet.

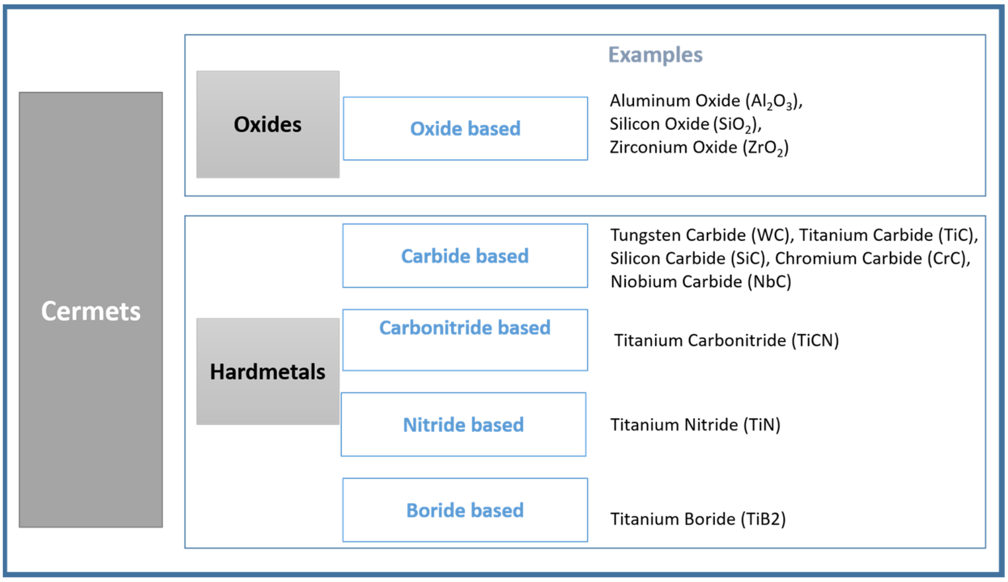

Figure 1. Classification of cermets based on ceramic phase.

The synthesis of cermets plays a pivotal role in achieving the desired properties for the fabricated component. The appropriate selection of synthesis route, the optimization of process parameters, the effect of the metallic binder, and the influence of the composition of both the ceramic and metallic phases in the cermet, are all critical factors determining the state of the final cermet product.

This paper reviews the development of cermets by considering various cermet systems. It is beyond the scope of the paper to discuss all possible cermet systems. This study classifies cermets based on the ceramic phase present in the system. The possible metallic binders and their influence on the mechanical and tribological properties of the cermet system are investigated. After discussing different cermet systems, various synthesis routes are explored by which cermets are fabricated. There are many methods that can be utilized for cermet fabrication. However, this paper reviews only a few relevant processes to give the reader an idea of the influence of the process parameters and various other factors that contribute to the final properties of the cermet. The unique microstructural features of cermets are discussed in one section. Finally, this review summarizes various applications and challenges in the application of cermets.

2. Cermet Systems

Over the last decade, various cermet systems that are of lightweight, high strength and toughness, and possess superior wear resistance and corrosion resistance were developed. Carbides, carbonitrides, nitrides, and borides are ceramics which are frequently used in cermets [10]. This section will cover developments in cermet systems that have occurred over the years. The first cermet ever produced was a WC-based cermet. The shortcomings of one system paved the way for the development of another system [11]. The following section discusses the most investigated cermet systems, which include:

1. WC-based cermets;
2. TiC-based cermets;
3. TiCN-based cermets;
4. Alumina (Al_2O_3)-based cermets.

This review paper considers systems that include various metal binders, carbides, and additives to explore improvements in the mechanical and tribological properties of cermets.

2.1. Tungsten Carbide (WC)-Based Cermets

Cemented WC is the most successful cermet developed so far. Cemented carbide development originated in 1923 at the Osram Lamp Works, and was introduced later in 1927 for use in cutting tools by Krupp AG in Germany under the trade name 'WIDIA' [12]. The unique combination of good strength and wear resistance of these materials made them suitable for a range of wear conditions [13]. WC attracted particular attention because of its high hardness and high melting point (2000 °C to 4000 °C). Due to poor oxidation resistance and high density, the use WC-based cermets as structural components at elevated temperatures was, however, limited. Nonetheless, the unique properties of these materials, such as high hardness, strength, and toughness, make this category of material suitable for wide application as cutting tools [14]. A shortage of tungsten and deficiency in certain physical properties, such as oxidation and corrosion resistance, has restricted the application of these materials [13].

The most common WC-based cermet system includes Co content as the binder phase from 4% to 30% by weight, with a grain size varying from 0.5 µm to 10 µm [15]. Depending on the composition, the hardness of WC-Co is 10% to 20% higher than tool steel, and it does not lose this advantage even at higher temperatures. The higher hardness of these materials results in increased wear resistance and improved tool life. However, compared to high-speed tool steel, WC-Co has lower toughness, which is a major disadvantage. An increase in carbide content leads to increased wear resistance but at the expense of Co content, which reduces the fracture toughness [15]. Another drawback of the WC cermet system is its poor oxidation resistance. Because of this, these materials are not usable as high-temperature materials. Nonetheless, its metallurgical structure has been a guiding principle for all cermet materials developed subsequently [1].

There have been constant efforts made by researchers to modify or replace WC with other carbides, such as TiC, silicon carbide (SiC), and niobium carbide (NbC), or by substituting the Co binder with other metals, such as nickel (Ni), iron (Fe), or chromium

(Cr) [16–20]. WC-Co-based cermets are the most studied and scientifically developed cermets compared to other cermet systems. Many studies have been conducted in WC-based cermet systems to explore the various mechanical and tribological properties of these materials and to enhance their properties. The composition, binder material, morphology, and synthesis route are some of the critical parameters used for determining the properties of these materials. Researchers have focused on three key issues when investigating cermet systems: (i) optimization of the microstructure and mechanical properties through structure processing and by altering the characteristics of starting materials using inhibitors [21–23], (ii) substitution of the Co binder with other metallic additives including high entropy alloys [24–26], and (iii) addition of additives and investigation of the influence of additives on the final material properties [27–30].

Ghazali et al. [31] explored the effects of addition of V and Ti to WC using an ultra-fast microwave heating process on the mechanical properties and microstructural features of the material. Crystalline phase identification confirmed the presence of the formation of carbide compounds of Ti and V. Microstructural analysis showed uniform dispersion of carbides and near full density was achieved with a higher sintering temperature. The authors concluded that the addition of Ti and V resulted in the in situ formation of a WC-based cermet with a very fine microstructure possessing superior mechanical properties.

The erosion properties and wear mechanisms are critical parameters in selecting cermet systems for specific applications. Wentzel et al. [32] investigated the erosion and corrosion resistance of WC-based cermets. They performed erosion-corrosion testing using silica-water slurry on a series of WC cermets with different binder phases and using combinations consisting of Co, Ni, and Cr. Binder combination variation was found to influence the properties and corrosion behavior of the cermets significantly, and influenced the erosion-corrosion action. The addition of Ni, which has inherent corrosion resistance properties, did not enhance the slurry erosion resistance of the cermets. However, a combination of Ni-Cr-Co grades showed improved erosion-corrosion behavior compared to Co-binder-based cermets.

Aw et al. [33] investigated the influence of the binder on the corrosion resistance of WC-based cermets. They deposited WC-17 Ni and WC-17 Co combinations onto mild steel and stainless steel (SS) substrates using a high-velocity oxy-fuel (HVOF) process and calculated the porosity of the obtained coatings. The cermet system with WC-17 Ni had lower porosity and acted as an efficient barrier in preventing corrosion attack when coated on the mild steel substrate. To study the influence of additives on the mechanical properties of WC-Co cermets, Lin et al. [34] added varying amounts of aluminum nitride (AlN) to the WC-Co cermet system. The presence of AlN led to the refinement of the WC grains and reinforcement of the cermet. Higher hardness and transverse rupture strength were observed for a cermet system with 1 wt.% AlN compared to a pure cermet. A 2 wt.% AlN addition improved the oxidation resistance of the cermet system to nearly 1.9 times that of the pure cermet. It was observed that, by incorporating AlN, the mechanical properties and oxidation resistance of the WC-Co system were enhanced.

Kim et al. [35] studied a WC-based cermet with Ni as the binder phase. They were able to produce WC-Ni-based cermets with a density of 98% using high frequency induction heated sintering (HFIHS). The sample had a WC grain size of 300 nm after sintering. The measured hardness values were significantly higher than for conventionally sintered WC-Co and WC-Ni systems without any appreciable decrease in fracture toughness. Chen et al. [36] investigated WC-based cermet systems using a novel approach. They produced WC-multi-element alloys with different ratios and studied the material properties. The multi-element alloy represented as $Al_{0.5}CoCrCuFeNi$ was a new novel metal material produced having high hardness, good high-temperature strength, and anti-oxidation characteristics. Multi-metal powders were prepared by blending different pure metal powders using mechanical alloying. WC and multi-element alloys were mixed and alloyed together, resulting in homogeneously dispersed WC particles in a ductile multi-element alloy without any second phase formation. As a result, the hardness of the sintered cermet was (200 HV–300 HV) higher at room temperature and 200 HV higher at 900 °C than the traditional WC-Co sintered system. In addition, the authors observed an enormous improvement in the material properties of the WC-multi-element system compared to the traditional system. Table 1 summarizes the investigated systems referred to in this review paper.

Table 1. Effect of binder composition and synthesis on the properties of WC-based cermets.

Binder (Weight %)	Synthesis Route	Properties	Reference
Co 5% + (V, Ti) 5%	Ultrafast microwave heating	Improved mechanical properties (Bending strength- 981 ± 10 MPa, Hardness- 24.7 ± 0.1 GPa Fracture toughness- 8.6 ± 0.1)	[31]
Ni (10%), Ni+ Cr+ Co (10%)	Powder metallurgy	No effect on erosion resistance Improved erosion resistance	[32]
Ni (17%), Co (17%)	High-velocity oxy-fuel process	Better corrosion resistance with Ni binder compared to Co binder	[33]
Ni (10%)	High-frequency induction heated sintering	Higher hardness compared to conventional route along with comparable toughness (HV 1810 kg/mm^2)	[35]
$Al_{0.5}$CoCrCuFeNi (20%)	Powder metallurgy	Improved hardness and fracture toughness compared to traditional WC-Co system	[36]

The development of WC-based cermet systems has paved the way for rigorous studies of cermet systems based on other ceramic materials. The following sections discuss further developments in other cermet systems, focusing on studies of the mechanical and tribological properties.

2.2. Titanium Carbide (TiC) Based Cermets

The shortage of tungsten and the inadequate corrosion resistance and oxidation associated with WC-based cermets has led to the development of TiC-based cermets [37]. TiC-based cermets possess some advantages compared to WC-based cermets due to their higher oxidation resistance and lower friction resistance [38]. Even though both WC and TiC-based materials have found applications in critical operating conditions, such as aircraft landing gear and wing flap tracks, the much lower density of TiC (4.93 g/cm^3) than WC (15.63 g/cm^3) represents a significant advantage for TiC-based cermets [7,39]. Generally, however, TiC-based cermets also possess certain disadvantages, such as low strength and inadequate abrasive and erosion resistance. However, developments in processing routes have resulted in substantial improvement in the performance of this type of system.

The cermets described are important structural materials in wear-resistant and tool applications because of properties such as HT hardness, good thermal deformation resistance, and excellent chemical stability. The wear properties of these materials are related to their hardness and toughness, with the optimum wear performance achieved when these properties are at an appropriate level [40]. However, the brittleness of TiC-based cermets is increased by the metal binders due to the poor wettability of TiC, which limits their application. Various studies have found that the toughness could be improved by using Ni, Mo, and Ni-Mo as binders in TiC-based cermets [41]. Furthermore, the mechanical properties of TiC-based cermets are often improved by the addition of transition metal carbides in the binder chemical composition [42–44]. Several elements (e.g., Fe, Cr, Ni, Co, Mo, Ni-Mo) can be considered for use as a binder in TiC-based cermets, with the choice made based on the desired properties for specific applications [45–48].

The factors that influence the properties and performance of each cermet system are almost the same. Researchers have focused on analyzing the effect of these variables in optimizing the properties of the cermet system. Rajabi et al. [41], demonstrated that the grain size and the chemical composition of binders are critical factors in improving the toughness of TiC-based cermets. Their study reported the advantages of various binders in the cermet system. Using Ni as a binder increased the density, decreased crack growth during sintering, and prevented ball abrasion during milling. The low wettability of Ni binders with ceramic particles remained a drawback. However, Mo as a binder metal appeared to have good wettability with the ceramic phase. In another study, Rajabi et al. [49] determined that the chemical composition, microstructure, grain size, and sintering temperature were important parameters for increasing the toughness of TiC-based cermets. Among various additives, TiN proved to be more effective in achieving improved toughness of cermets because of the similar crystal structure and low hardness. Using TiN nanoparticles produced advantages, such as high densification, lack of easy dislocation movement, control of micro-crack propagation during wear, and control of grain growth. These factors can improve the performance of cermets. Having nanoparticles in the composition of cermets can create some challenges in relation to the contamination of nanoparticles by oxygen. This can result in degradation in the mechanical properties of cermets due to a reduction in wettability between the nanoparticles and the binders. This limitation can be controlled to some extent with vacuum heat treatment.

The effect of Ni and Fe as binders on the wear performance of TiC-based systems in metal-forming operations was studied by Roosaar et al. [13]. They observed that the surface failure of these cermets during adhesion tended to start from the binder phase. With equal carbide volume, an Fe binder-based TiC system showed advantages compared to TiC-based cermets with an Ni binder with respect to wear conditions. The authors postulated that resistance to local plastic strain controls the performance of carbide-based cermets in wear conditions, primarily depending on the amount and properties of the binder.

The feasibility of using a heat-treatable binder phase in TiC-based cermets was studied by Gaier et al. [50]. They analyzed the effect of heat treatment on the properties of a TiC-based cermet with a ductile binder of precipitation-hardenable steel (PH 17-4 grade) compared to a TiC-based cermet with a non-heat-treatable steel (316L) binder. The comparison was made using systems with 30 vol.% of steel phase in both cases. A significant improvement in the Vickers hardness was found for heat treatment of 1150 °C/4 h of the system. Further observation indicated that the scratch resistance improved significantly. The study demonstrated that the mechanical properties of the cermet could be enhanced by incorporating heat-treatable steel grades as metallic binders.

2.3. Titanium Carbonitride (TiCN)-Based Cermet

Cermets are considered the most promising materials in the cutting tool industry due to their superior HT hardness, low to moderate reactivity with steel and other metals, and higher thermal conductivity. TiC-based and TiCN-based cermets are currently the most used systems in the industry. Of these two, TiCN-based cermets are superior to TiC cermets. This is due to their higher HT hardness, transverse rupture toughness, superior oxidation resistance, and thermal conductivity. Apart from these factors, due to the finer grains of the hard phase in TiCN-based cermets, they possess better HT creep deformation than TiC-based cermets. A comparison of these properties at elevated temperatures is shown in Table 2 [51].

Table 2. Comparison of properties of TiC and TiCN.

Cermet System	Microhardness ($kgf \cdot mm^{-2}$)	Strength (MPa)	Thermal Conductivity (W/m°C)
TiC-based	500	1050	24.7
TiCN-based	600	1360	42.3

Ti(C, N) is a category of cermet material having high hardness, strength, good toughness, excellent wear properties, low density, and high thermal conductivity. This material can potentially replace WC-based materials in many applications [52]. TiCN-based cermets were first developed in 1931. The main applications for TiCN-based cermets are in the machining industry. The property enhancement of TiCN-based cermets has contributed to their effectiveness under various conditions. Wear resistance is a crucial parameter in determining these materials' service time as a cutting tool during machining. During machining, sliding wear, fretting wear, erosive wear, crater wear, creep, etc., are associated with TiCN-based cermets. The improved HT machining characteristics of TiCN-based cermets are achieved through the proper selection of cermet composition. Secondary additives, such as WC, TaC, NbC, or Al_2O_3 are added to enhance the high-temperature strength and hardness of TiCN-based cermets. Table 3 summarizes the effect of the addition of secondary carbides on the mechanical properties of TiCN-based cermets. The optimum value of composition and variation of properties based on composition is also reported.

Table 3. Effect of secondary carbide addition on the mechanical properties of TiCN-based cermets.

Secondary Carbide	Composition	Hardness	Bending Strength (MPa)	Toughness (MPa. $m^{1/2}$)	Reference
WC	15 wt.%	93.4 HRA	1500	-	[53]
	20 wt.%	91.6 HRA	2100	-	[54]
	10 wt.%	91.2 HRA	1800	-	[54]
Mo_2C	5 wt.%	-	1580–1820	17.9–18.4	[55]
	10 wt.%	93.5 HRA	~1300	-	[53]
NbC	3 mol.%	1631–1835 HV	700–1100	3.5–5.5	[56]
TaC (Tantalum Carbide)	7 wt.%	93.0 HRA	-	1580	[53]
Cr_2C_2	7 wt.%	93.5 HRA	-	1490	[57]
VC	1 wt.%	1749 HV	-	1204.6	[58]

Fretting wear is defined as the material removal from two contacting surfaces arising from relative oscillatory movement (of amplitude less than 30 μm) [59]. Considering the fretting wear behavior of TiCN-based cermets, each carbide has a unique role in the wear resistance of the cermet. The addition of NbC or WC aids in decreasing the wear of TiCN-based cermets, whereas TaC has little or no influence on the resistance to plastic deformation. A controversy exists concerning the influence of the addition of hafnium carbide (HfC) to TiCN cermets. Some researchers assume that the addition of HfC will degrade the toughness of the TiCN-based cermet, thereby reducing wear resistance [60]. However, other researchers believe HfC addition creates harder Hf oxides, which can improve the wear resistance of TiCNNi-based cermets by the formation of a thick tribo-layer on the counter face [61]. The addition of WC hampers the wear and abrasion resistance of TiCN-based cermets. This may be because of tungsten oxide volatilization followed by its diffusion through the tribo-layer in cermets. With increase in the amount of WC added, the wear mechanism of TiCN-Ni changed from spalling-induced micro-cracking and abrasion to adhesive and tribo-chemical wear [62]. Meng et al. [63] studied the friction and wear behavior of TiCN-based cermets with different compositions at HT. Two systems comprising TiCN-Ni-Mo and TiCN-Al2O3-Ni-Mo were manufactured. Compared to the former system, the latter exhibited more friction and less wear. At low temperature, the worn surface of TiCN-Ni-Mo was rough and showed serious damage as micro-fractures, whereas the other system had a relatively smooth surface. At 600 °C, tribo-oxidation, along with formation and deterioration of the tribo-layer, were observed to be the dominating wear mechanisms for TiCN-based cermets. In a similar study conducted by Zheng et al. [64], the authors focused on the influence of WC addition and variation in composition on the mechanical, friction, and wear behavior of TiCN-based cermets. A TiCN, WC-Mo2C-TaC-(Ni, Co), with varying WC from 5.77 wt.% to 19.68 wt.% was examined. It was observed that with increase in the WC content, a higher fraction of the white core phase occurred, along with a rise in hardness of about 10%, accompanied by a decline in toughness of 20%. Furthermore, a decreased wear rate of about 80% was noticed in the system with higher WC content at both 25 °C and elevated temperatures (400 °C and 750 °C).

The effect of carburization on the wear behavior of TiCN-based cermets with various secondary carbides was studied by Wang et al. [65]. The findings indicated strong graphite precipitation because of solid carburization. Activated carbon atoms in the cermet matrix were consumed, either by rearrangement followed by precipitation as graphite, or by combination with metal atoms, followed by precipitation to form carbides or carbonitrides. Precipitation as carbide or carbonitrides increased the rim thickness. Carburization resulted in a noticeable degradation in the mechanical properties because of the presence of graphite and ceramic particle coarsening. However, the presence of graphite had an effect in improving the coefficient of friction of the cermet owing to its good lubrication properties. Varma et al. [66] studied the influence of binders and ternary carbides on the friction and wear properties of a TiCN-based cermet system. SEM analysis showed a typical core-shell microstructure for all the studied samples. TaC addition to a TiCN-WC-Ni/Co cermet system resulted in the highest Vickers hardness and fracture toughness. TaC addition, along with both Ni and Co, led to improved plastic flow which reduced the wear. Tribo-layer formation was the reason behind the lower coefficient of friction (COF) and wear in the studied system.

2.4. Aluminum Oxide (Al_2O_3)-Based Cermet Systems

Aluminum oxide (alumina)-based ceramics have remarkable physical and chemical properties, along with good mechanical resistance and good thermal and electrical insulation properties [67]. Despite their excellent properties, their applications are limited due to their highly fragile nature. This characteristic property makes them very sensitive to minute levels of defects in their microstructure which can act as possible crack initiation sites. Even though there is relevant research being carried out to improve the properties of alumina by the addition of tough metal binders, the development of oxide-based cermets is still very limited. The presence of a dominant ceramic phase suppresses the effect of the metallic binder. This is mostly because of the poor bonding at the oxide/metal interface [68]. However, there are still clear advantages of oxide-based cermets for oxidation and chemical resistance for high-temperature applications. Al_2O_3-based cermets, along with binders such as Ni, Ni_3Al, Al, or Cr, or along with TiC and Ni alloy binders, are used as wear parts functioning at high temperatures. Miranda et al. [69] studied the synthesis, microstructure, and mechanical properties of alumina-based cermets with different metals, including Al, Fe, and Ti as metallic binders. They adopted a powder metallurgy (PM) synthesis route with pressureless sintering. The microstructural observation revealed the equal distribution of metallic particles in alumina with Al and Fe as binders. However, the system with Ti as a binder was characterized by a metallic network, which was interconnected with the matrix. The incorporation of a metallic binder in the alumina matrix improved the toughness of the system. The authors of the study proposed the probable toughening mechanism to be crack-bridging resulting from a homogenous distribution of ductile metal in the cermet matrix.

Eric et al. [70] investigated Al-Al_2O_3 cold spray coating formation and its properties. The influence of Al particle size, Al_2O_3 mass fraction, and various process parameters on the deposition efficiency (DE) was studied. The observed DE increased for systems having a larger Al particle size. However, the coatings with larger Al particle sizes were harder than the smaller Al powder system. The reason may have been the larger peening effect of larger Al particles on the substrate. The DE was influenced by the ceramic content in the powder and an optimum efficiency was achieved with 30% Al_2O_3 in the system. In a similar study conducted by Sova et al. [68], the influence of ceramic powder size on the cold spray of the cermet system was investigated. The authors investigated the properties, including the DE, of Al_2O_3 with Al and Cu binders. A specially designed nozzle enabling separate injection of ceramic and metal powders was used to carry out the cold spray process. The DE of the coating increased significantly with finer binder particle size. Furthermore, the coarser particles increased the erosion effect and considerably reduced the coating deposition efficiency. Fernandez and Jodoin [71] also conducted a study on Al-Al_2O_3 cermets synthesized using the cold spray process. They focused on the effect of alumina content on the properties of the cermet system. The study investigated three possible mechanisms suggested in previously published literature for the DE increase in the cermet system in the cold spray process. The mechanisms discussed were

1. Improvement of DE by the peening effect of ceramic particles due to impact,
2. The mechanical adherence of metallic particles due to asperities created by ceramic particles.
3. Adherence of metallic particles to the oxide-free surface created by ceramic particle impact.

Through experimental and numerical studies, it was concluded that the probability of improving DE by the first mechanism was negligible. However, the other two mechanisms were shown to have a significant influence in improving the DE of the system. The DE of the coating was found to be maximal with 30% Al_2O_3 ceramic content in the spray system.

3. Synthesis of Cermets

The fabrication of cermets is a cumbersome task faced by both scholars and engineers. The synthesis route of cermets plays a predominant role in influencing the properties of the cermet system. There are limitations associated with each method used, and researchers are still seeking to identify the best possible means of producing cermets with the desired properties. The processing parameters significantly affect the final property and microstructure of the cermet system. This suggests the need to choose the appropriate synthesis route. The following section discusses various conventional and modern techniques used to fabricate cermets. There is constant development of new fabrication techniques, but, within the scope of this paper, only a few selected methods, for which a considerable amount of study on the cermet fabrication process has been undertaken, are reviewed. This section aims to provide the reader with an understanding of previous and existing techniques in cermet synthesis, the effect of process parameters, and the advantages and disadvantages associated with each method described.

3.1. Powder Metallurgy (PM)

The most common methods of cermet fabrication involve PM techniques. The main steps involved in PM processes are the mixing of powder, milling of the powder mix to obtain proper intermixing and the desired particle size, compaction, and sintering. The powders of ceramic and metal particles are thoroughly mixed and further milled in ball mills or attritors. To prevent the agglomeration of the powder and oxidation, a wetting organic lubricant, such as polyglycol or paraffin wax, is added along with the mixture. The milling process facilitates the uniform distribution of ceramic grain sizes and embeds the ceramic particles with metal, which aids in the sintering process. The formed slurry is dried to expel the solvent, and, eventually, the powder forms as spherical granules with dimensions in the range of 0.1 mm–0.5 mm [5]. The milling process is followed by the powder compaction step. The part is formed into the required shape during this step. Cold pressing is the most commonly used method for relatively simpler shapes. Complex shapes can be achieved by PM injection molding, cold isostatic pressing, or extrusion slip casting.

In many cases, an additional shaping operation is required to obtain the final shape. The cold compacted product is then sintered with fully dense cermets obtained using a high-temperature PM process. This is generally performed in ovens under an inert atmosphere, vacuum, or in hydrogen. Depending on the ceramic-metal system, liquid or solid-phase sintering is performed. The liquid-phase sintering enhances densification by rearranging particles, grain coarsening, and solution precipitation [72]. Following the sintering process, hot isostatic pressing (HIP) may be carried out to eliminate residual porosities. The solid-state sintering process achieves bonding and densification by applying heat below the melting point of the materials. Solid-state sintering processes, such as powder-rolling and warm extrusion, are utilized to produce wires or slabs. Figure 2 depicts the steps involved in the PM processing of cermets. The sintering process leads to building up of the microstructure, morphology, and phases of the cermet.

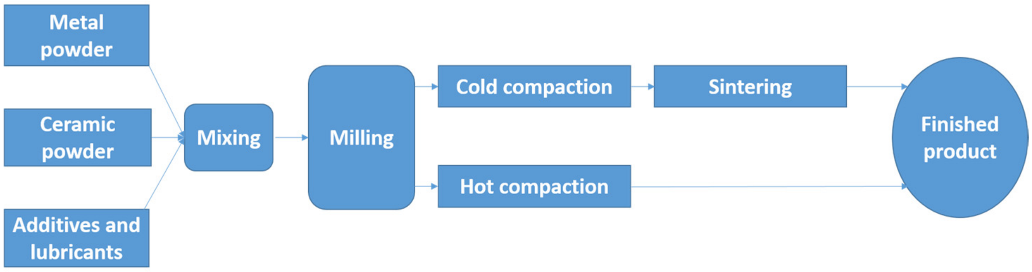

Figure 2. Powder metallurgy process steps for cermets.

In most cases, the cermets possess a typical core-shell morphology. The core consists of the undissolved particles, whereas the shell is produced by sintering through reaction and precipitation. The core and shell possess identical crystal orientations. The ceramic particles join each other and form a continuous network during the sintering process to minimize surface energy. A similar interconnected network formation also occurs with metallic binders. The metallic binders in this constrained state exhibit features different from those of the free metal [73]. The distribution of the network of metallic binders and the formation and characteristics of ceramic particles within the cermet system greatly influence the final properties of the system.

Liquid-phase sintering is effective when there is good wettability and solubility of the hard phase in the liquid. The absence of such a mechanism in most cermet systems requires other processes, such as pressure-assisted sintering (hot uniaxial or isostatic pressing) to obtain pore-less materials in non-wetting systems, such as oxide cermets. These techniques are carried out at relatively low temperatures to eliminate the formation of undesirable phases. Spark plasma sintering is a recent development for sintering at relatively low temperatures within a short period. The infiltration of molten metal into the ceramic is another development in the synthesis of cermet systems. This method overcomes the limitation of the excessive shrinkage associated with liquid-phase sintering and produces accurate dimensions in complex shapes. The infiltration system is most effective with a wetting system where it penetrates the matrix by capillary action. A pressure-assisted infiltration system is employed for metal matrix composite fabrication, and can be utilized in the fabrication of cermets, but the high-volume content of ceramic in the matrix makes this process difficult. The infiltration technique can also be applied to fabricate functionally graded cermets.

The polymer-derived ceramic (PDC) composites are an interesting category of materials with unique properties compared to conventional ceramic materials. The transformation of polymer to ceramic helps in achieving significant breakthroughs in ceramic technology. The composites find applications in wide areas, including aerospace, nuclear, and defense industries, where the oxidation resistance and high-temperature properties of PDC are beneficial [74–76]. The capability to fabricate complex shapes with the PDC enhances the application areas for this processing route. The advancements in this area have been in obtaining PDC as coatings, fibers, reinforcements, or ceramics which are stable at ultra-high temperatures (up to 2000 °C). However, the synthesis of cermets through the PDC route is viable and can be further investigated in the future.

3.2. Reaction Synthesis (RS)

The reaction synthesis process, owing to its ability to produce CMCs with desired microstructural features and tailored properties, has recently attracted much attention as a fabrication technique for CMCs. The various reaction synthesis processes, including directed metal oxidation (DMO), reactive metal penetration (RMP), reaction bonding (RB), reactive hot pressing (RHP) and reactive forging (RF) can be used to fabricate cermets with a typical three-dimensionally interconnected ceramic reaction product with some metallic content. An alumina ceramic matrix with residual Al metal can be achieved with the DMO approach. The DMO process has been implemented successfully for several cermet systems, including carbides, nitrides, borides, and oxides of Al, Ti, Zr, Hf, and Si [77–80].

Single and multiphase materials with oxide and non-oxide ceramics, intermetallics, and metals can be synthesized using RHP. The powder preformed in the porous starting condition is transformed into desirable phases involving reactions such as reduction reactions, displacement reactions, and elemental precursors reactions [81]. Cermets that include Al_2O_3/Ni and Al_2O_3/Nb are synthesized with this method. LaSalvia et al. [82] have successfully synthesized TiC-30% Ni and studied the effect of varying the Mo addition on its microstructural and mechanical properties.

3.3. Thermal Spray (TS)

Thermal spray (TS) processes are growing rapidly and represent an important surface modification technology [83]. They have become an important modern industrial tool capable of producing customized surface properties for a range of industrial applications, which include thermal barrier coatings for turbine blades, erosion-resistant coatings for boiler tubes, and so on [84]. Like most coating techniques, TS coating helps in combining the advantages of the core with increased hardness, resistance to abrasive wear, and heat resistance [85]. TS is one of the most frequently used protective coating technologies. The TS technique is carried out by partially or completely melting the spraying material for milliseconds, then propelling it onto the surface to be coated with highly accelerated velocities [86]. The microstructure and properties of the thermally sprayed components depend on the powder characteristics and processing parameters [87].

The TS coating is performed by melting materials, which are in wire stock or particulate form, and accelerating the partially melted or fully melted particle droplets towards a substrate. As the droplets strike the substrate, they expand out radially to form a "splat". With continued deposition of these splats, they eventually interact and combine to form a continuous coating. High particle velocities or high temperature during the impact can improve the bonding between these splats and the removal of pores. Various processes have varying thermal and kinetic energy contents [88]. TS can produce metallic, ceramic, carbide, and cermet coatings with any phase composition on a properly prepared base. In general, TS coatings possess good adhesion strength with various substrates. They have good wear resistance and low corrosion rates. Typically, these are applied to weaker underlying materials to ensure improved wear properties, thereby increasing the life of the components [89].

There are several types of thermal coating techniques which are utilized to produce cermet coatings, including high-velocity plasma spraying (HVPS), high-velocity oxygen fuel (HVOF) spraying, and the detonation gun (D-Gun) method [90]. Among them, HVOF spraying is the most effective technique for cermet coatings. The following section explains the properties, advantages, and disadvantages of HVOF spraying for the coating of cermets.

High-Velocity Oxygen Fuel (HVOF) Spraying

HVOF is a TS coating technique that can produce coatings with a very dense and compact structure and good adhesion to the substrate. Recent advancements in HVOF spraying have made it possible to produce coatings with lower porosities and decarburization [91]. The HVOF technique produces an efficient deposit of composite coatings with higher density, good bond strength, and comparatively lower decarburization. This is because of the high particle velocities and relatively lower temperature during deposition. In the HVOF process, the fuel and oxygen are intermixed and burnt in the combustion chamber at higher flow rates of up to 1000 L/min, and with a pressure range of up to 12 bars. This produces a high-speed gas jet. Powder particles with a size in the range of

5–70 µm are injected into the high-speed gas jet and accelerated towards the substrate. The heated powders are deposited on the substrate at 600–650 m/s. Upon impact, they form lenticular splats and adhere strongly to each other and the substrate. Raster movement of the HVOF gun in several passes achieves the required coating thickness [92].

The spraying of WC-based cermet coatings is one of the most significant applications of the HVOF method because of the reduced carbide transformation due to the low temperature received by the particles. High particle velocities are attained using a converging-diverging de Laval nozzle design and high gas pressures. Solid particle erosion (SPE) plays a critical role in the degradation of materials. Cermet systems based on WC and chromium carbide (CrC) coated by HVOF have shown impressive erosion behavior [93,94]. Kumar et al. [95] experimented on WC and CrC-based HVOF thermally sprayed cermet coatings to study their erosion behavior and investigated their effectiveness in the application of pulverized coal burner nozzles (PCBN) to mitigate SPE. It was observed that the coatings failed to sustain the erosion attacks and exposed the substrate. One possible reason for this was the larger particle velocity and the flux incorporated to mimic the PCBN conditions. It is still possible for the coatings to sustain particles moving in low velocities but they fail to do so in applications involving high velocity together with high particle flux. Wood et al. [96] investigated the tribology of thermally sprayed WC-Co coatings. They observed a more than 50% improvement in erosion resistance for HVOF coatings after parameter optimization compared to coating achieved with a conventional D-gun with similar nominal composition. The abrasive resistance of these coatings was comparable to sintered cermets having the same composition. The coating was found to have relatively high dry sliding and wet sliding wear resistance with a COF ranging from 0.2 to 0.5. The friction and wear appeared to be influenced by the oxide presence on the binder.

Wayne et al. [97] analyzed the microstructure, mechanical, and wear properties of thermally sprayed and sintered WC-Co cermet systems with two different types of binder content. The influence of cobalt content was not significant in the wear resistance to diamond abrasion of the thermally sprayed cermet. However, it showed a greater effect in controlling the wear resistance due to particle erosion. The abrasion wear and erosion wear resistance of the studied cermet system mainly depended on the porosity, mean free path, and carbide grain size of the binder. It was evident from the observations that, for coatings, the porous structure resulted in poor intersplat bonds, which further reduced the hardness and fracture toughness. These observations are in contrast to those of other researchers because of the difference in the tribological conditions used.

3.4. Cold Spray

Cold spraying (CS) or cold gas dynamic spraying is a process where solid powders are deposited on a substrate using a de Laval nozzle. To explore specific properties, CS can effectively deposit various materials, including metals, ceramics, polymers, and composites. As the particle's impact velocity exceeds a threshold limit, it undergoes plastic deformation and adheres to the substrate [98]. Because of the low gas temperatures arising due to the rapid gas expansion in the nozzle, the feedstock powders stay solid throughout the complete travel of the nozzle [71]. The CS technique can form very dense coatings with very low oxygen content without grain growth, residual tensile stresses, or phase changes. The deposition of some materials can even produce grain refinement at the nanoscale. These properties make CS suitable for the deposition of a set of advanced materials. This is an efficient and novel technique to produce surface coatings with several advantages over TS. It uses the particle's kinetic energy instead of thermal energy for deposition. Through this, oxidation, undesired chemical reactions, and tensile residual stress can be eliminated [99]. The low temperatures in CS lead to the occurrence of unique characteristics. The CS technique can retain the microstructure and properties of the feedstock powders and avoid oxide formation and undesirable structural changes. This helps in improving the durability of the coating. CS coatings are used to deposit not only metals, as was its initial purpose, but also polymers, ceramics, and advanced composites. As the particles contact the substrate, they experience severe plastic deformation due to the kinetic energy released. They are adhered to the substrate by mechanical anchoring. If there is sufficient plastic deformation, metallurgical bonding facilitates adherence [98,100,101]. In the conventional case of cold spraying of metals on metallic substrates, the adhesion between the substrate and the metal occurs due to the combined effect of metallurgical bonding and interlocking via the adiabatic shear instability (ASI) mechanism [98].

There are two types of CS systems: high-pressure cold spray (HPCS) and low-pressure cold spray (LPCS) systems. In the HPCS system, particles are injected ahead of the nozzle throat from a high-pressure gas supply. In contrast, in the LPCS system, the powder particles are injected into the diverging section of the nozzle by a low-pressure gas supply. In high-pressure cold spraying (Figure 3), a preheated high-pressure gas (up to 1000 psi), either nitrogen or helium, is forced through a converging-diverging de Laval nozzle. The nozzle converts enthalpy into kinetic energy by expansion and accelerates the gas flow to a supersonic region (1000 m/s), causing a temperature reduction. The powder is supplied axially into the gas stream before reaching the nozzle throat. The gas carries the powder particles with sufficient acceleration and impacts the substrate. The particle's kinetic energy is sufficient to induce a mechanical or metallurgical bond between particles and the substrate [99,102].

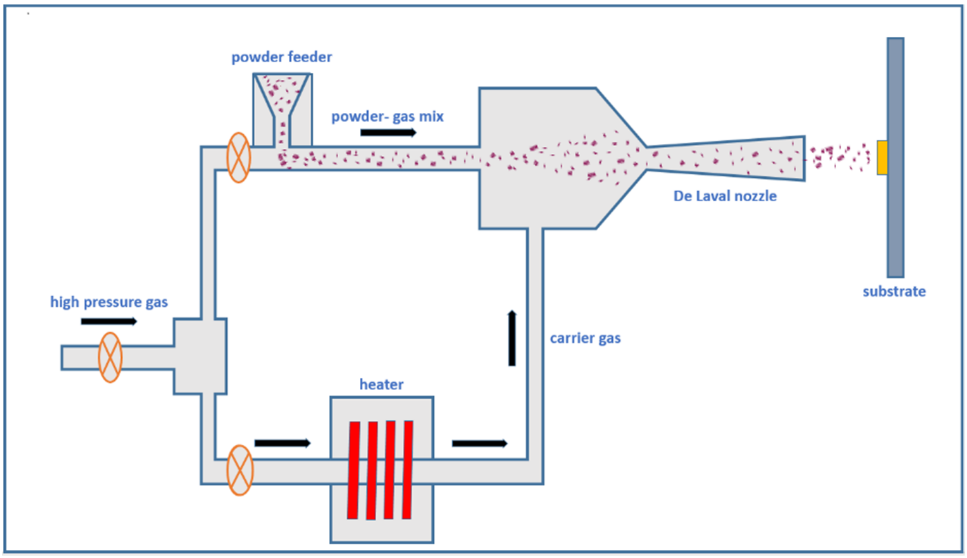

Figure 3. The high-pressure cold spray process.

In low-pressure cold spraying (Figure 4), air or nitrogen is used as the carrier gas with relatively low-pressure values (80–140 psi). The preheated gas is forced through a de Laval nozzle and accelerated to 600 m/s. Then, the powder is supplied into the nozzle's diverging section (downstream) and accelerated towards the substrate [103].

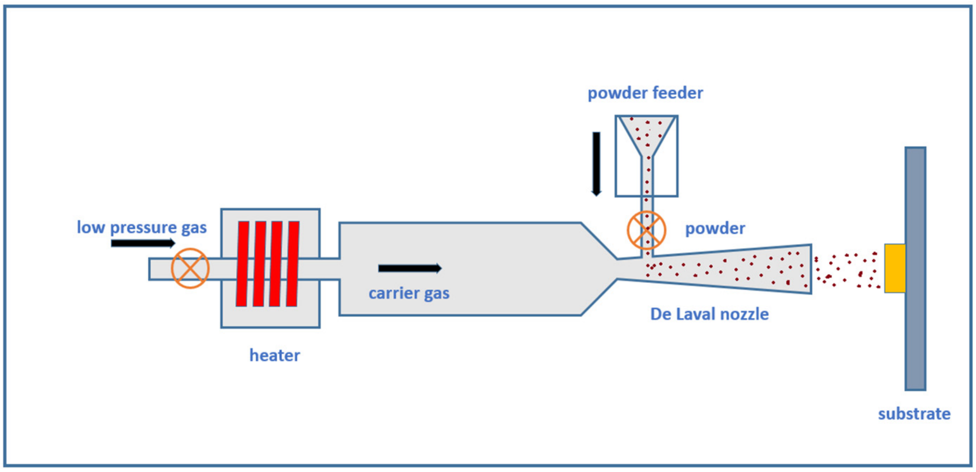

Figure 4. The low-pressure cold spray process.

The cold spraying of cermets is performed by mixing the reinforcement particles with the ductile metallic feedstock powders. Materials such as ceramics, oxides, and so on, in their pure form, cannot produce a coating on any surface without causing surface erosion. However, numerous studies have reported the possibility of depositing already prepared cermet mixtures on different substrates [68,104–106]. By this method, metal coatings with ceramic inclusions can be produced. Only a limited amount of the reinforcement particles are retained in the final coating. The process does not induce severe plastic deformation to the hard reinforcement particles as is the case with ductile materials, but rather leads to more plastic deformation in ductile materials. These particles embed themselves in the coating, producing cermets [68,70].

Several ceramic-metal coating combinations have been successfully obtained using the CS technique [70,107,108]. The intended properties and applications of these coatings are almost the same as in the case of TS techniques. These mainly include wear resistance, high hardness, and high-temperature hardness. The addition of ceramic particles is the main reason for enhancing these properties. It also influences the deposition process behavior. There are three main theories that have been proposed to explain the influence of ceramic particles on the coating and deposition properties. One proposed mechanism involves the peening or impingement effect of ceramic particles [109]. It is proposed that, as the spraying happens, the hard ceramic particles behave like shot balls, which peen the softer particles in front of them, causing more deformation. This, in turn, increases the DE of softer metallic particles. This mechanism has also been described in several other studies [107,110].

Irissou et al. [70,111] proposed another mechanism for the improved DE of the CS technique. They observed that as the ceramic content in the feedstock powder mixture increases, the roughness of the interface between the coating and the interface increases. The increase in roughness is attributed to the grit blasting action of the impacting ceramic particles. In addition, they suggest that the asperities formed during this process help to bond more particles, thereby improving the DE due to mechanical anchoring. The third mechanism suggested is related to the oxide cleaning action of ceramic particles on metallic particles or substrates. The ceramic particles, upon impacting the metallic particles or substrates, remove the oxide films, thereby exposing the fresh surface of the material for the further impact of metallic particles. This creates favorable bonding sites. The same effect can be achieved by the pure deformation of the brittle oxide layer, shredding from the surface, and improving the DE [112,113]. The optimization of parameters serves a crucial role in producing quality CS materials. Couto et al. [114] experimented with studying the wear and corrosion properties of WC-based cermets with two distinct binder proportions (WC-7Co and WC-12Co) coated on an Al 7075-T6 aluminum substrate using the CS technique. They optimized the critical parameters influencing the properties of the deposited coating, including the temperature, spraying angle, spraying distance, gas pressure, and gas medium. They were successful in producing a dense and well-bonded coating on the substrate. Significant features of the processing route included that the coating obtained after spraying had no microstructural changes, decarburization, or any unwanted phase formation, indicating that the bulk properties of the feedstock powder were preserved. It was observed that higher temperature resulted in denser and thicker coatings on both occasions for the WC-Co cermet.

Dosta et al. [115]] conducted a similar study of the wear and corrosion resistance of WC-25Co cermet cold sprayed on carbon steel and Al7075-T6. They measured the bonding strength of the coating by adhesion testing based on ASTM C633-08. Sliding and abrasive resistance were also measured. The main objective of this study was to optimize the spraying conditions of the cermet system and the CS system to obtain good quality coatings. Dense and thick coatings on both substrates were obtained using the CS technique. The coating obtained had no decarburization, microstructural change, or unwanted phases. The CS technique is promising and can produce better coatings than the TS coating technique. A major concern associated with ceramic particles in the CS technique is the erosion that might occur to the metallic particles or substrate. The influence of particle size on the properties of cermet coatings was studied experimentally by Sova et al. [68]. They experimented with a specially developed nozzle with a separate metal powder and ceramic injection into the gas stream. They observed a strong activation effect and better coating for spraying soft metals (Al, Cu) while incorporating them with fine ceramic powders (Al_2O_3 and SiC). This also led to an increase in the DE of the metal component of the mixture compared to the deposition of pure metal alone. The coarser ceramic powders negatively influenced the process by creating a strong erosion effect, which considerably reduced the deposition efficiency of the metal over the substrate. The deposition behavior and DE for several Al-Al_2O_3 cermet systems were investigated by Fernandez et al. [71]. They used different Al-Al_2O_3 feedstock powders to analyze the deposition behavior and influence of the ceramic content on deposition efficiency. An increase in DE was observed, with a peak value obtained with 30 wt.% of ceramic content, followed by a gradual decrease, and eventually no deposition at 100% Al_2O_3. The experiment demonstrated the positive impact of the presence of ceramic particles in improving the DE of Al coating.

3.5. Laser-Based Additively Manufactured Cermets

The conventional fabrication methods of cermets are based on excessive usage of precursors and involve the use of complex equipment. However, it is impossible to fabricate advanced geometric structures with these methods. Additive manufacturing (AM) has emerged as a promising method capable of eliminating most of the limitations of conventional production routes. The development of additive manufacturing techniques has significantly influenced the production of complex and intricately shaped materials. AM methods are defined as the "process by which metals are joined, usually layer by layer, to make objects from three-dimensional (3D) model data, rather than the formative manufacturing and subtractive manufacturing methodologies" [116,117]. Because of the unique processing routes of additive manufacturing, it is possible to produce objects having complex geometry which otherwise would not be possible with conventional methods [118]. The most common AM methods (also called 3D printing methods) include stereolithography (SLA), selective laser sintering (SLS), selective laser melting (SLM), fused deposition modeling (DM), and robocasting/direct ink writing (DIW) [119]. The fabrication of cermets using AM-based techniques has significant limitations, such as low density, higher porosity, and poor mechanical properties of the finished components. Much research has been based on AM-based techniques for manufacturing cermet parts with improved mechanical properties and enhanced densities; however, the understanding of the correlation between the microstructure of additively manufactured materials with their mechanical properties is limited. The following section reviews some of the most popular AM-based techniques for the fabrication of cermets. The development of the microstructure during AM process of cermets is briefly discussed. Based on the feedstock, AM-based processes are classified as solid-based, liquid-based and powder-based techniques [120,121]. The current most commonly used processes for AM of cermets are selective laser sintering/melting (SLS/SLM), laser engineering net shaping (LENS), binder jet (3D printing), direct laser deposition (DLD), and robocasting [122–126]. There is a scarcity of reports in the literature on the fabrication of cermets using the AM technique. Most of the studies are based on conventional hard metal (WC) production with various binders. As a promising futuristic technique for the fabrication of cermets, gaining fundamental insights regarding the different AM methods, their advantages, disadvantages, and scope of improvement will enable the design and development of new and existing techniques.

3.5.1. Selective Laser Melting (SLM)

SLM is an AM fabrication technique that combines powder metallurgy and laser technology. The components are produced according to a 3D CAD model of the final part by the selective fusion of a powder layer in an argon gas environment [127]. Using a high-energy laser beam, the powder material from which the component is to be made is heated and fused, followed by rapid solidification of the molten pool [128]. The powder properties, composition, morphology, size, purity, and size distribution uniformity are critical factors that can affect the microstructural and mechanical properties of the SLM [129]. Few studies have reported the fabrication of cermets using SLM techniques. Almost all the published papers agree on certain points regarding the formation of cracks with different compositions and decarburization causing the degradation of mechanical properties.

In a study carried out by Khmyrov et al. [130], the evolution of phase during fabrication of WC with variation in Co wt.% is reported. The authors observed a complete dissolution of WC in all samples except one which contained 6 wt.% of Co. They noted the dissolution of WC by the formation of different carbides and the eventual reduction of carbon content in SLM samples. Two specimens with 75 wt.% and 50 wt.% of Co were prepared to obtain crack-free WC-Co samples. The SLM fabrication was carried out with a hatching distance of 100 µm, power of 50 W, and a scan speed of 100 mm/min. The formation of brittle W3Co3C was recognized as the prime reason for cracks occurring in samples with 50 wt.% Co.

However, the specimen with 75 wt.% Co had no cracks. The study also correlated the size of carbide particles and ceramic-metal composite after the SLM technique. Studies conducted by Grigoriev et al. [131] and Campanelli et al. [132] assume that the crack formation in manufactured specimens with WC as a brittle phase is due to the considerable difference in the thermal expansion coefficients and the melting points of WC and the binder. Investigation of the evolution of the microstructure and mechanical response of WC-2% co-produced by SLM process has been undertaken by Domashenkov et al. [133] using conventional powder particles and nanoparticles. Their paper reports that W2C and W2Co4C occur because of the decarburization of WC during melting and solidification. Hardness measurement was performed to analyze the effect of the size of carbides in both samples, and it was observed that higher hardness was found with samples having finer carbides.

3.5.2. Selective Laser Sintering (SLS)

SLS is an AM technique similar to the SLM process used for 3D printing cermets. SLS and SLM have similar process parameters and powder preparation routes [134]. Process parameters have a significant role in the properties of cermets. Hence, the optimization of process parameters for each material is necessary. Normally, the cermets produced by the SLS technique will undergo post-production. Few studies have reported SLS manufactured cermets undergoing further field infiltration [135]. The presence of porosities can drastically affect the mechanical properties of SLS cermets. The infiltration process, as a post-processing technique, is considered to increase the density and mechanical properties of the parts. Wear tests on WC-Co-based cermets, with and without bronze, performed by Kumar et al. [136] showed enhanced mechanical properties for the infiltrated samples. The infiltrated SLS parts showed high wear resistance, suitable for cutting tool production.

Kumar et al. [137] studied the influence of preheating of the powder bed and the effect of various parameters, including scan speed and power, on the mechanical properties and microstructural evolution of the SLS cermet samples. It was evident from the observations that the porosities reduced with increase in input energy density no matter the condition of preheating of the powder bed. An increase in input energy and preheating of the powder bed resulted in restructuring of large connected cracks to form small hairline cracks. This phenomenon was assumed to improve the mechanical properties of the system. SLS samples with preheated powder beds also aided in a more uniform hardness variation than SLS without preheating.

3.5.3. Laser Engineered Net Shaping (LENS)

The laser-engineered net shaping (LENS) technology is a category of AM technologies for the direct fabrication of material parts. This technique is widely used to fabricate cermet components and as a surface treatment technique [120]. The outstanding features, including high cooling/solidification rates, rapid prototyping, and proper control over material geometry, make this process a favorable processing technique. A few highlights of LENS are the improved material structure, good thermal and mechanical properties, and better manufacturing efficiency than conventional methods. In this process, the material powder is injected into a molten pool on the surface of the solid substrate. The high-energy laser beams create the molten pool. A review on the AM of cermets by Aramiana et al. [120] identified the process parameters which influence microstructural evolution during the LENS process as laser power, powder feeding rate, working distance, and laser beam traverse speed. Shorter working distances have been shown to enhance the uniformity of the microstructure and cause marginal density improvement of the final product. High laser power or powder feed rate or reduced traverse speed can maintain the larger layer thickness. An investigation by Xiong et al. [122] on the LENS process reported variation in mechanical properties with height of the specimen. This was correlated with the change in the cooling rate of WC-10% Co cermets. The observed hardness value was least for layers close to the top surface. In addition, it was observed that optimizing process parameters was crucial for the LENS method to achieve crack-free, thin-walled specimens. Xiong et al. [138] observed a reduction in the concentration of Ni content during the production of (Ti, W) C-Ni cermets via the LENS process because of the evaporation of Ni during the process. The researchers did not observe the typical core/rim microstructure for this material.

3.5.4. Binder Jet 3D Printing (BJ3DP) Technique

This is an AM technique capable of producing complex cemented carbide parts. This process includes SLM and electron beam melting. The process uses powder and a binder. The binder is in liquid form and acts as an adhesive film that bonds the powder layer at low temperatures. The binder is sprayed over the powder and the parts are heated to 2000 °C and sintered. This curing process improves strength. The volume change associated with the transformation from a green to a fully consolidated part contributes to the main disadvantage of the process. This can be improved with infiltration of the porous specimen, though a compromise needs to be made between strength and component design. Enneti et al. [123] described the tribological behavior of WC-12% Co cermets produced by the BJ3DP technique. Cermets fabricated via this route exhibited lower volume loss than conventionally fabricated cermets. In addition, the wear resistance of WC cermets was enhanced due to the dual grain-sized microstructure of BJ3DP material. Some investigations have concerned the infiltration of molten metal on the cemented carbide materials fabricated with BJ3DP [120]. Observations from these investigations indicated that this approach resulted in fully dense cermet parts with high fracture toughness and hardness comparable to that of conventional cermets. However, this technique also faces major AM challenges, such as cracks, porosities, and shrinkage [139,140].

4. Microstructural Features of Cermets

Cermets are characterized based on their unique core-shell type microstructure. Cermets mainly consist of three phases: a hard phase, metal binder, and a surrounding phase. Since most of the literature focuses on the TiCN system, this section is exclusively dedicated to the microstructural features of TiCN-based cermets. Based on the descriptions in various studies [56,141,142], TiCN-based cermets consist of a core-rim structure. The rim may consist of two parts—an outer rim and an inner rim. Normally, the core composition (hard phase) in TiCN-based cermets is believed to be TiCN or TiC, which is considered to be the residue of undissolved raw materials. The phase that surrounds the core, called the rim, is a complicated (Ti, W, Nb) (C, N) solution with a similar crystalline structure to that of the core, but which contains much heavier metal atoms compared to the core [56,142]. The observation made in the scanning electron microscope (SEM) in back-scattering electron (BSE) mode is that the core is mostly black, and the rim is grey. It is also known that the white bright observation in SEM-BSE mode indicates a higher content of heavy elements [141]. Figure 5 shows a schematic of a commercial cermet microstructure imaged using SEM.

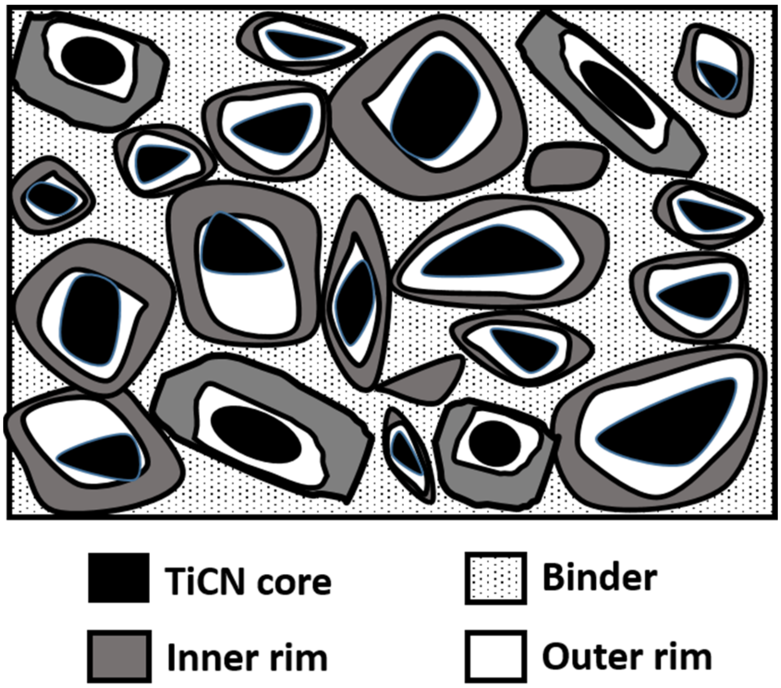

Figure 5. Schematic of a commercial cermet microstructure imaged using SEM.

The core-rim structure of the TiCN-based cermet depends on the various constituents, which include C, N, secondary carbides, other additives, and binder metals (Ni, Co, Mo, etc.). In TiCN-based cermets, the binder phase is mostly composed of either Ni or Co. The solid solution hardening of this binder phase has a critical role in cermet applications. In the TiCNNi-Mo system, additional Ni metal content improves bending strength and causes a reduction in hardness [143,144]. The addition of Co into the TiCN-based cermets results in improved toughness and oxidation resistance due to the higher toughness of Co compared to Ni and the better wettability of Co in the hard phase in the cermet. However, the TiCN-based cermets with Co have inferior corrosion resistance compared to those with Ni. Mo has a much larger atomic radius compared to Ni; adding Mo into TiCN-based cermets will reduce the solid solubility of Ti in Ni, hence promoting a stable carbonitride [145]. The rim of a TiCN cermet rich with Mo can suppress the recrystallization by holding up the TiCN grain growth [146]. This will, in effect, improve the relative density, resistance to plastic deformation, and strength of cermets [147,148]. The Mo content in the cermets should be optimum, or else it will lead to a steep decrease in the fracture toughness and bending strength of the cermets [146]. The influence of the core-rim structure on the properties of TiCN-based cermets is reported in several studies. Based on these studies, the common assumption is that the wettability of the hard phase with the binder and the bond of the two phases is improved by the presence of the surrounding phase, which enhances the toughness of the cermets [149,150].

Cardinal et al. studied the influence of the addition of various metal binder compositions and TiN on the microstructural properties of TiCN-based cermets. Cermets with varying wt.% of TiN and Ni were studied. The microstructure analysis was carried out by SEM in BSE mode. The presence of a typical core-rim structure embedded into the metal binder was distinguishable from the grey levels of the image (Figure 5). With the addition of TiN (cermets in Figure 6), the rim thickness and binder phase percentage increased, and the initial Ni percentage did not influence this change.

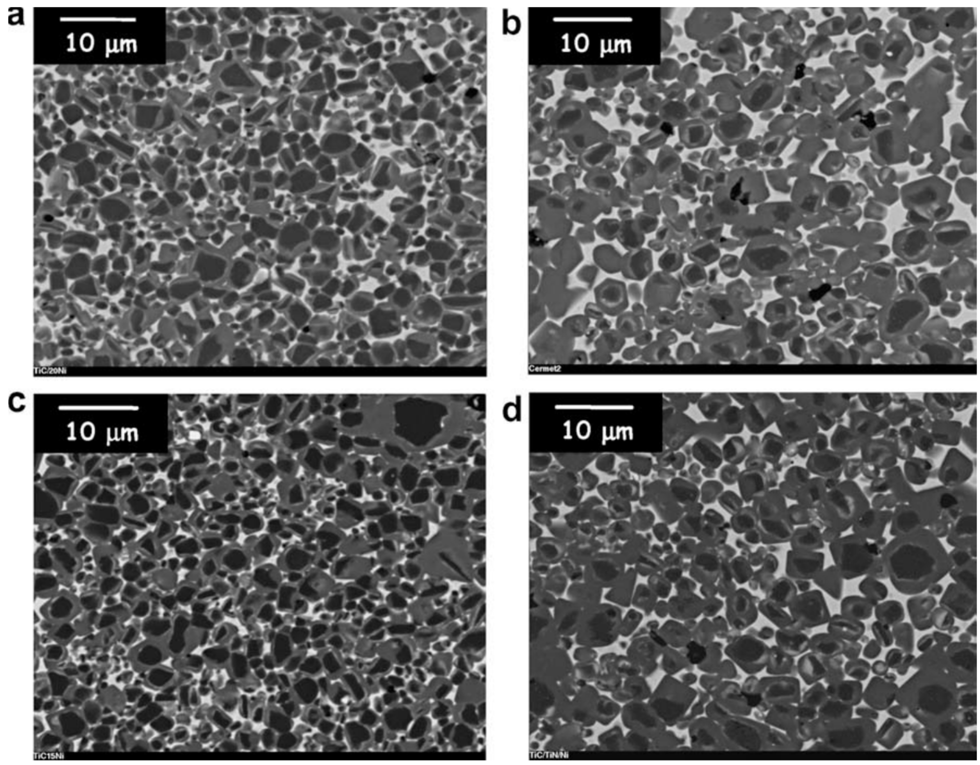

Figure 6. SEM image of cermet surface, (**a**) 0% TiN, 20% Ni, (**b**) 10% TiN, 20% Ni, (**c**) 0% TiN, 15% Ni, (**d**) 10% TiN, 15% Ni. Reprinted with permission from [48]. Copyright 2009 Elsevier.

Andren [151] studied the microstructural developments during the sintering and heat treatment of cermets and reported the formation mechanisms of the core and rim structure of the cermets. The formation of the inner rim stems from the solid-state sintering, where the solid binders dissolve part of the hard phase. These dissolved atoms are carried by diffusion and then re-precipitated onto the undissolved hard grains (cores), forming the inner rim with the composition attained by equilibrium conditions. The liquid phase sintering assists the formation of the outer rim through further dissolution and re-precipitation. The outer rim surrounds the core. Equilibrium conditions in the material determine the composition. The small core dissolution and outer rim growth result in grain growth. Several researchers have studied the influence of binder composition on the microstructural evolution of different cermet systems. There is often a relationship based on the binder composition and the grain growth of the cermet microstructure. Yu et al. [152] conducted a study on the influence of vanadium (V) content on the microstructural properties of the Mo2FeB2 cermet system. They obtained the smallest grain size with the addition of 2.5 wt.% of V. The role of TiCN particle size on the microstructure of the TiCN-WCNi-based cermet system was investigated by Jeon et al. [153]. They observed enhanced structural homogeneity and a larger volume fraction of the rim phase within the core-rim structure with ultrafine grade TiCN compared to the coarse TiCN cermets. With the influence of the composition of binder and hard phase in the cermet on the microstructure known, there have been few attempts to enhance the properties by incorporating nano-sized materials in the microstructure. Li et al. [52], studied the effect of a multilayer core-shell microstructure on the mechanical properties of a TiCN-based cermet system (Ti (C, N)/Mo-Co-Ni/CaF_2 in Al_2O_3). They successfully developed a multilayer core-shell microstructure with nanosized CaF_2 core, with Al_2O_3 as the intermediate layer, and a metal phase (Ni, Co, Mo) as the shell. The formation mechanism of the multilayer core-shell structure is shown in Figure 7. CaF_2 nano-sized powder was mixed with Al_2O_3 by a homogenous nucleation mechanism, and the multilayer core-shell structure was achieved by the liquid phase diffusion of metal binders. The optimum mechanical properties were obtained with a 10% volume addition of CaF_2 in Al_2O_3. The study also compared (Ti (C, N)/Mo-Co-Ni) to evaluate the effect of the multilayer core-shell microstructure. The authors observed that the fracture toughness and hardness increased by 31.83% and 24.25%, respectively.

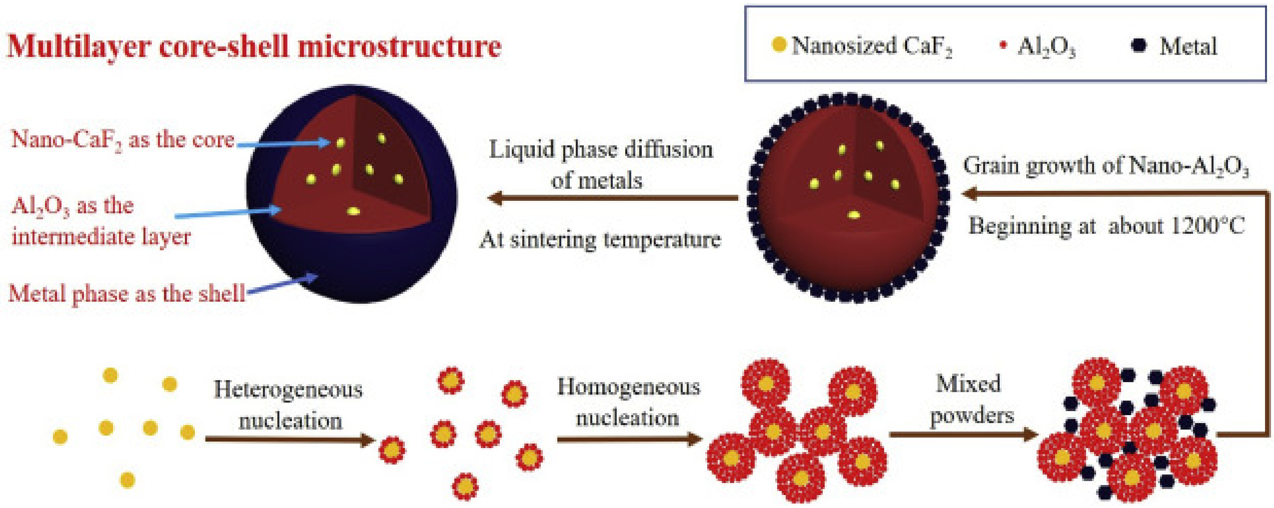

Figure 7. Formation of multilayer core-shell microstructure of TiCN-based cermet system. Reprinted with permission from Ref. [52]. Copyright 2020 Elsevier.

5. Applications and Challenges

The exceptional properties of cermets have led to various applications in diverse fields. One of the important application areas for cermets is the cutting tool industry. Several features constitute the exceptional cutting performance of cermets, including high cutting speeds at moderate chip thickness, the excellent surface finish of machined work-pieces, excellent wear properties, high edge sharpness and strength, and so on [6]. Cermets are used in all types of wear applications, such as sliding wear, abrasive wear, and erosive wear. Applications of WC-based cermets include cutting tools, earth and rock drilling tools, sheet metal forming and drawing tools and dies, wear components (plunges, nozzles, etc.), and other engineering applications, such as structural components (e.g., boring bars, mechanical seals) [38].

WC-based cermets find their application mainly in the field of cutting tools. The broad use of these materials as cutting tools is due to their excellent combination of desired properties, such as high hardness, deformation resistance, high strength, and wear resistance. One of the advantages of WC cutting tools over high-speed steel cutting tools is the higher hardness, resulting in much higher wear resistance [13].

The main applications for TiCN-based cermets are in the machining industry. Cutting tools made of these materials are applied for finishing and semi-finishing operations of SS and carbon steel at high speed [154]. They are also utilized for machining and milling of alloy steels, cast iron, and normal carbon steels [6]. In addition, they find application as refractory parts for jet engines, turbine engines, diesel engines, and commercial gasoline engines because of their low density and excellent high-temperature properties [155]. The exceptional wear resistance of this kind of material makes them useful in producing gauges, wire-drawing dies hot rolls, and bearings [156]. Apart from the aforementioned applications, TiCN could even be used as functionally gradient materials [157], and coating materials [158].

Cermets' physical and mechanical properties can be altered within certain limits according to the required cutting task.

The excellent properties of Ti(C,N) based cermets, such as very low friction coefficient against metals, superior wear resistance, and resistance to thermal deformation, find applications in wear-resistant materials, such as bearings and mechanical faces [159,160]. The high corrosion resistance and thermal stability at HT of the cermets of ternary borides, such as Mo2FeB2-Fe, WCoB-Co, and Mo2NiB2-Ni, are considered promising materials for wear-resistant applications [161,162]. Furthermore, the higher oxidation resistance and lower frictional resistance of TiC and TiCN-based cermets find applications in critical operating conditions, such as wing flap tracks, aircraft landing gear, etc. [7,39].

Self-lubricating cermets are an interesting category of materials that possess several advantages. The superior wear resistance and good HT properties of cermets make them a viable choice for high-temperature applications. The inability of oil and grease lubricants to provide effective lubrication creates a need for solid lubricants for these extreme condition applications [163]. Incorporating solid lubricants in cermets to obtain self-lubricating cermets generates several possible applications. Many studies have been conducted to produce self-lubricating cermets with different lubricating mechanisms [52,164,165]. The micro-pores of cermets act as lubricant reservoirs in wet sliding conditions, providing significant advantages in wear processes [166].

The main challenges associated with cermet systems include obtaining a combination of a hard-phase and binder phase with the required composition, and synthesis in the appropriate proportion without any phase transformation or evolution of any new phase. The evolution of various phases and improper or inadequate distribution of binder metals in the cermets will deteriorate the cermet properties. Optimization of the processing parameters, and selection of the proper composition and particle size of ceramic and metal particles, significantly influence the characteristics of the final cermet system.

6. Conclusions

Cermets are a class of materials that possess the combined advantages of both the ceramic phase and the metallic binder and limit the disadvantages of the ceramic and the metals. The historical progress in the development of the cermets was elucidated. Cermet systems were classified and studied based on the ceramic part. The influence of binders, additives, and composition on various mechanical and tribological properties was elaborated, along with applications of each cermet system's relevance. Various synthesis routes for the fabrication of cermets and the effect of processing routes and processing parameters studied by various researchers were reported. Several parameters influence the final properties of the cermet system. Proper selection of the composition of material and processing routes ensures achievement of the optimum properties from the cermets. The synthesis of cermets presents certain challenges, and researchers are constantly trying to perfect existing processing techniques and develop new techniques. The inherent difficulties of fabricating components with both metal and ceramic phases have been, to an extent, solved by advanced technologies with good final properties.

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Abbreviations

ASI	Adiabatic Shear Instability
HPCS	High-Pressure Cold Spray
LPCS	Low-Pressure Cold Spray
HIP	Hot Isostatic Pressing
DIW	Direct Ink Writing
TICN	Titanium Carbonitride
SLS	Selective Laser Sintering
SLM	Selective Laser Melting
FDM	Fused Deposition Modeling
BJ3DP	Binder Jet 3D Printing
LENS	Laser Engineered Net Shaping
HVOF	High-Velocity Oxygen Fuel
WC	Tungsten Carbide
TIC	Titanium Carbide
DE	Deposition Efficiency

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