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Review

Effect of Binder on Oxidation Properties of Tungsten Carbides: A Review by a Conceptual Classification Approach

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Abstract: This study presents a conceptual classification scheme to review the literature on improving the oxidation resistance of tungsten carbide by modifying the binder. The first parts of the article are dedicated to the specification of the databases, the search method, and the description of the criteria chosen to classify the articles. Then, the data collected are presented in statistical graphs according to the proposed classification scheme. The data analyzed show that most of the significant improvements in oxidation resistance are achieved with advanced production processes, especially HIP and SPS, which eliminate porosity to a very high degree. In addition, statistical studies showed that the use of new replacement binders, Ni_3Al, Fe–based alloys, FeAl, and Al_2O_3, improved the oxidation properties in 75–100% of cases. Meanwhile, the use of high–entropy alloys (HEAs) as cermet binders may be the subject of future research for oxidation, given the recently published results of good mechanical properties.

Keywords: oxidation; tungsten carbide; binder; conceptual classification

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1. Introduction

Cemented carbides are one of the most widely used powder metallurgy products in the manufacture of wear–resistant materials. The reason for this is that these materials have a high correlation between hardness and toughness, compared to other materials such as diamond or high–speed steel [1–3]. Cemented carbides usually contain a mixture of hard carbide particles (WC, TiC, TiB_2, TaC, NbC) with soft and flexible metal bonds such as Co, Fe, and Ni [4–7]. During the sintering process, the metal melts and forms a liquid together with the hard carbide. As a result, the carbide particles in the liquid phase are surrounded by a capillary phenomenon and a relatively high density is achieved in the resulting cermet. The carbide particles in these cermets provide high hardness and wear resistance, while the binder phase improves fracture toughness [8,9]. Today, among the various types of carbides that have practical applications, cemented carbides with the initial phase of tungsten carbide (WC) are the most widely used hard materials in various industries [10–12]. A characteristic feature of this type of cermet is the possibility of obtaining a wide range of microstructures with different mechanical properties by choosing a suitable combination of hard carbide and binder phases and an optimal choice of hardening processing parameters [13]. Initially, tungsten–based cemented carbides were mainly used in wire drawing molds [1]. However, in recent years their applications have been extended to other areas, such as hot rolling, machining, forming, cutting tools, drilling, mining equipment, etc. [1,14]. One of the main challenges of using tungsten–based carbides in high–speed applications, especially compared to titanium–based carbides, is their resistance to oxidation. Depending on the cutting speed and other factors in specific applications, the cutting tool can reach temperatures in the range of 600 to 1050 °C [15–17]. This results in the formation of an oxidized product on the surface scale of the tool/material, which is often detached from the cermet surface, resulting in a reduction in mechanical properties. It is worth noting that oxidation also reduces the wear resistance of tungsten–based carbides. Therefore, the service life of tungsten–based carbide cutting tools is highly dependent on their resistance to oxidation at high temperatures [11,17]. The importance of the oxidation resistance of tungsten–based carbides has attracted increasing attention from researchers to understand their oxidation kinetics. An essential aspect of this class of cermets is the type of binder metal used. Over the years, cobalt (Co) has been the most common choice for bonding these materials, due to its hardness, wear resistance, and high toughness [15,17–20]. Despite these excellent properties, existing studies have shown that the use of cobalt as a binder can cause significant environmental and economic problems. The studies to date also show that long–term inhalation exposure to cobalt causes allergic reactions and cancer [5,14]. In addition, the poor corrosion and oxidation resistance of cobalt at temperatures above 600 °C and the poor mechanical properties of cobalt at high temperatures have led researchers to replace this element with other types of binder [2,4–6,13,16]. However, despite the undoubted importance of this subject, no reports have been published to classify the existing work on the oxidation resistance of tungsten carbide cermets and to interpret the data obtained from a statistical point of view. Therefore, a review is urgently needed to identify the achievements in the field of oxidation resistance and to highlight the future directions of research on tungsten–based carbides for high–speed applications. This review aims to provide the reader with an in–depth understanding of the effect of different binders on the oxidation resistance of tungsten–based carbides. For this purpose, a conceptual classification scheme is proposed to compare and explore the existing literature by defining appropriate criteria. This scheme systematically classifies publications into different categories based on a common criterion. In fact, a conceptual classification scheme (CCS) for reviewing the existing literature identifies the main content of the articles. The use of this method helps researchers to classify and summarize research findings and to identify research trends. Several review articles have been published using this classification method, which has the advantage of being published as a systematic article and analyzing the results, rather than referring to individual articles [21–24].

2. Survey Methodology

In this survey, the content analysis method is employed for the conceptual classification of studies in the context of oxidation of tungsten carbide compounds. Generally, a classification of literature based on content analysis includes two main steps: (1) defining the survey resources and search methods for the papers to be analyzed, and (2) determining the instrumental categories for classifying the selected documents. These steps are discussed as follows.

2.1. Step 1: Survey Resources and Methodology to Search for and Select the Relevant Papers

Only journal papers published up until December 2022 have been selected and evaluated for conceptual classification, while other sources, such as books, masters theses, Ph.D. dissertations, conference and workshop articles, etc., are excluded. Relevant publications are collected through computerized search using a list of appropriate terms and keywords such as: oxidation kinetics, oxidation behavior, oxidation resistance, tungsten carbide, metal binders, WC–Co, etc. Then, the references and cited articles for each selected paper are examined and new articles are gradually added to the survey analysis. To extract the relevant articles, major publishers such as ScienceDirect, Springer Link, John Wiley & Sons, EPMA, scientific.net, IJERT, IOP, and IPEN are considered.

2.2. Step 2: Classification of Extracted Papers

After the first stage, the selected articles are classified according to the following four criteria:

1. The number of papers according to the year of publication;
2. The title of journals, taking the number of relevant publications into account;
3. The names of the author and co–authors, taking into account the number of relevant publications;
4. Conceptual classification scheme for evaluating the extracted articles.

As seen in Table 1, to conceptually categorize the relevant articles extracted from step 1, six criteria for each selected paper should be assessed. These criteria, along with the possible related categories, are discussed in the following section.

Table 1. Questions and possible responses.

1. Among the papers that investigated oxidation properties, what production method was applied? *
(1.1) standard vacuum sintering (1.2) spark plasma sintering (SPS) (1.3) hot press (HP) (1.4) hot isostatic press (HIP) (1.5) not mentioned
2. Among the papers that investigated oxidation properties, which binder was used? **
(2.1) Co (2.2) Ni (2.3) Co + Ni (2.4) Cr (2.5) Mo (2.6) pure iron (2.7) Fe–based alloys (2.8) Ni_3Al (2.9) FeAl (2.10) Al_2O_3 (2.11) high–entropy alloys (HEAs)
3. What was the author's approach for modification of binder in oxidation studies on cemented carbides?
(3.1) use of new binder and comparison with previous study (3.2) investigating on the effect of various fraction of one binder (3.3) study on the effect of adding minor element to the binder (3.4) other
4. What was the oxidation outcome?
(4.1) considerable improvement (4.2) acceptable/minor improvement (4.3) reduction in oxidation resistance (4.4) no comparison with conventional WC–based cermets
5. Is the oxidation kinetics investigated? If yes, what type of equation is fitted?
(5.1) no (5.2) yes (5.2.1) parabolic equation (5.2.2) linear equation (5.2.3) linear/parabolic equation (5.2.4) other
6. How the wear properties of cermet change with oxidation properties?
(6.1) not investigated (6.2) both increased (6.3) both decreased (6.4) one increases and other decreases

* The methods listed here are derived from articles that have evaluated oxidation properties. Therefore, it is not claimed these are the only methods that have been used for the production of cemented carbides. ** The binders listed here are derived from articles that have evaluated oxidation properties. Therefore, it is not claimed these are the only binders that can be used in the composition of cemented carbides.

3. Questions and Possible Answers for Conceptual Classification of Selected Documents

In this section, the questions and possible answers for each one are analyzed.

3.1. Production Method

- **Standard vacuum sintering**
- The main idea behind this method is that cold pressing of ceramic powder and additives and producing an initial product (green body) and then sintering at high temperature is a simple and low–cost alternative for producing cermets or ceramic composites [25]. However, the most crucial challenge in this method is the porosity problem, which is a general challenge in methods based on powder compaction [26]. The cold isostatic press (CIP) increases the density of the component compared to the uniaxial press, and consequently enhances the hardness, strength, and corrosion resistance of cermets for this reason [27,28]. Furthermore, the difference in thermal expansion coefficients can show itself in the form of cracks or other defects during high–temperature sintering [29]. Among the articles that have dealt with the oxidation of tungsten carbide cermets and are reviewed in this research, various reports have used this method to produce the parts [7,8,10,11,13,15,16,19,28,30–44].
- Spark plasma sintering (SPS): This relatively new production method has been developed for sintering ceramic components in a short period with minimal porosity [45]. In this method, in addition to imposing mechanical pressure, plasma is formed between the powder particles by using direct and pulsed high currents passing through a conductive mold (which is usually made of graphite) [46,47]. The condition resulting from plasma formation and ion bombardment of powder particles enhances the particles' sintering efficiency and bond strength [48,49]. The high rate of heating, achieved by passing a high electric current, prevents particle growth and/or oxidation during the sintering process, which enables the production of nanostructured materials more easily [2,50]. Furthermore, this method can provide a density close to the theoretical one and almost complete elimination of porosity. It is worth mentioning that the SPS method has been extensively used to produce ceramic and metallic nanomaterials, composites and cermets, electronic materials, thermoelectric materials, biomaterials, etc. [45,49]. This method has also been used extensively in the research field of cemented carbides, and in particular some of the articles reviewed on the topic of oxidation have made tungsten carbide samples with this method [2,3,28,51–54].
- Hot press (HP): Hot press is a common method for densifying ceramic composites with powder raw material, which can be used both as a single method or in combination with other densification methods [55]. The main advantages of the hot press method are: (1) the concurrent use of temperature and pressure, which leads to products with low porosity, and (2) its lower equipment cost in comparison with the SPS method. In this press type, a more homogeneous structure can be achieved compared to the cold press [56]. Some articles dealing with oxidation have used this method to produce tungsten carbide [18,57–63].
- Hot isostatic press (HIP): In this method, the pressure is exerted uniformly from all directions through hydrostatic gas pressure at high temperatures. Therefore, complex components with homogeneous structures can be produced through this method [64]. Hot isostatic pressing is very efficient in removing any residual porosities, but it is a relatively expensive process [25]. In this densification method, the component after the sintering process can reach a density of 99.8% or even higher [65]. This method can be used for the production of cermets and ceramics, and even improving the mechanical properties of advanced alloys [66]. This method has been used to consolidate samples in research on tungsten carbide oxidation [67–72].

3.2. Type of Binder

- **Cobalt (Co)**: cobalt is the most important and widely used metal in tungsten carbide composites due to its suitable melting temperature and proper wettability. The use of cobalt results not only in excellent wettability and adhesion to tungsten carbide, but also in increased strength at room [73,74] and elevated temperatures [75,76]. Moreover, according to Basu and Sarin [15], to a certain extent, as the weight percentage of cobalt binder increases, the oxidation resistance of tungsten carbide improves. In some studies on improving the oxidation resistance of cemented carbides, cobalt was still used as a conventional binder [9,11,20,33–35,39,52,53,57,58,68,69,71,77,78]. The reasons for this are explained in the results and discussion section.
- **Nickel (Ni)**: The previous investigations showed that nickel can be a proper alternative to cobalt in the production of tungsten carbide cermets in terms of cost and availability [7]. According to Zhang et al. [73], using nickel results in creating a strong bond between tungsten carbide powder particles, proper resistance to oxidation at high temperatures, and resistance to wear in crucial condition. Therefore, in the oxidation research field, some articles worked on Ni–binder–containing cermets [13,16].
- **Cobalt–Nickel (Co–Ni):** In some cases, these two metals are employed together to use the advantages of both binders [8,9,16,30,42,67,69,79]. However, studies show that the oxidation resistance of nickel–cobalt binder is lower than that of cobalt binder [16].
- **Chromium (Cr)**: Using chromium as another substitute for cobalt improves oxidation and corrosion resistance. Moreover, using this element as a binder in cemented carbides increases the hardness [4].
- **Molybdenum (Mo)**: As another carbide–forming element like chromium, molybdenum is used as a binder in tungsten carbide composites. It should be noted that the oxidation resistance of tungsten carbide at high temperature reduces with increasing molybdenum [4]. A recent investigation shows that molybdenum in the form of secondary carbide (Mo_2C) also has a detrimental effect on the oxidation properties of cemented carbides [80].
- **Pure iron (Fe)**: Based on the price parameter, pure iron has been considered as a binder used in the consolidation of tungsten carbide powder [13,42,59]. Although iron is cheaper than nickel and cobalt, its oxidation resistance is not remarkable. In addition, the hardness and fracture toughness of the iron binder is equal to those of the cobalt binder [13].
- **Fe–based alloys**: Fe–based alloys have been given attention as substitutes for cobalt to overcome the shortcomings of pure iron [31,32,36,41,44,59,72,74]. Due to its high affinity to carbon, iron can be an obstacle to the growth of tungsten carbide particles during the sintering thermal cycle. Nickel can efficiently play an important role in stabilizing the austenite phase up to room temperature to overcome the above–mentioned limitations [5]. Therefore, a combination of these two elements as a binder increases hardness, resistance to oxidation, corrosion, and cracking compared to cermets with the cobalt binder [36]. On the other hand, along with limitations due to the price and toxicity of cobalt, since the most important reason for the replacement of cobalt has been the oxidation problem, stainless steels have also been considered as binders [31,72]. The use of stainless steel as a binder can enhance oxidation resistance and increase the fracture toughness and wear resistance concurrently [5]. Other Fe–based alloys with the combination of alloying elements such as manganese have also received increasing attention from researchers in the area of oxidation [32,81,82].
- **Nickel aluminide (Ni_3Al)**: The intermetallic compounds have captured significant attention from both academia and industry because of the limitation of oxidation resistance in cobalt binders [83,84]. Due to its excellent physical and mechanical properties, such as high hardness and outstanding oxidation resistance, nickel aluminide has attracted wide attention among intermetallic alloys as a substitute for cobalt in cemented carbides [5,51,85,86].

- **Iron aluminide (FeAl)**: Iron aluminide is a suitable alternative to cobalt, due to its resistance to oxidation and compatibility with better environmental conditions [2,7,40]. In this regard, increasing the amount of binder can reduce the hardness and increase the fracture toughness. In addition, WC–FeAl cermet has better behavior with respect to carbon trioxide, with a 30% longer lifetime than WC–Co [73]. The lower cost of FeAl than Ni_3Al, low density, high melting point, high thermal conductivity, and protective layer of alumina against high–temperature oxidation have increased the use of this type of binder [6].
- **Alumina (Al_2O_3)**: Alumina is also a cost–effective ceramic binder, with higher hardness, better corrosion/oxidation resistance, and higher chemical stability at high temperatures than cobalt, which has been used as the binder in oxidation investigations of tungsten carbides [54,61–63]. Furthermore, in contrast to metal binders, Al_2O_3 binder can not only facilitate the sintering process but also prevent the growth of tungsten carbide particles and the formation of W_2C [5].
- **High–entropy alloys (HEAs)**: The main feature of HEAs is that they provide the possibility of creating extraordinary properties by combining several different elements [87–90]. The use of HEAs as a binder in tungsten carbide compounds simultaneously increases the hardness and toughness of the product, and consequently can be a new and versatile binder compared to cobalt [5,91–94]. Regarding the attention which has been drawn to this type of binder in recent years, few articles with HEA binders have studied oxidation properties [3,95,96]. However, concerning the simultaneous improvement of hardness and toughness as two vital properties of tungsten carbide cermets, as it will be discussed in Section 4, this topic may be more researched in the coming years.

3.3. Binder Modification Approach in Oxidation Studies

- **Using new binder and comparison with previous studies:** In this procedure, while using a new binder to improve the oxidation resistance, the author compares the obtained results with previous ones, which are usually cermets with a cobalt binder;
- **Investigating the effect of various fractions of binder on tungsten carbide**: This type of research uses various percentages of a binder to investigate how the additional binder volume affects the oxidation properties of tungsten carbide;
- **Studying the effect of adding a small amount of an additive to the binder**: The author studies the effect of adding a small amount of a modifying additive to the binder. Note that the modifying additive in tungsten carbides is usually chromium.

3.4. Oxidation Outcome

- **Significant improvement:** This category includes research in which changing the binder has a beneficial effect on the oxidation resistance of tungsten carbide and reduces the oxidation rate;
- **Minor improvement**: This category includes binders with a small effect on reducing the oxidation rate of tungsten carbide;
- **Reduction in oxidation resistance**: In this category, the use of a binder other than cobalt has been identified as ineffective or destructive for oxidation resistance;
- **No comparison with conventional WC–based cermets**: In this category, the authors have not investigated the positive or negative effect of modification of the binder on the oxidation rate of tungsten carbide.

3.5. Temperature Range of Oxidation Tests

The relevant articles are classified into six different ranges of oxidation temperature. In this regard, temperature ranges from 300 °C to over 800 °C degrees are classified into five categories, while the sixth category is the case where the oxidation experiment was not performed in isothermal conditions or the temperature was not reported. It is a known fact that the oxidation rate of tungsten carbide compounds does not conform to an anomalous behavior and increases with increasing temperature [2]. However, it is necessary to examine the temperature range, which is more interesting by previous research.

3.6. Kinetics of Oxidation

Investigation of oxidation kinetics and modeling the mass increment per surface unit over time in tungsten carbide cermets has been carried out in some research work [2,8,11,16–20,33–35,39,43,51,52,57,63,67–69,71,79,97]. Equations that model the mass changes per surface unit are classified into parabolic, linear, a combination of linear and parabolic, etc. By determining the oxidation behavior, it is possible to obtain more precise estimates for the lifetime of components at high temperatures. As a consequence, the oxidation results are transformed from a qualitative comparison to an analysis based on quantitative information.

3.7. Changes of Wear Resistance in Connection with Alteration of Oxidation Resistance

Abrasion is surface damage that leads to the gradual removal of materials due to the relative movement between that surface and the material in contact. In most situations, enhancing wear resistance is desirable for increasing the lifetime of tools, components, and machine elements. This criterion checks how the change of binder for improving oxidation properties affects wear characteristics. Some researchers simultaneously explored changes in both oxidation and wear properties of tungsten carbides in one article [7,9,10,32,41,44,60,62,70,72,98]. These two properties together are the main properties in the surface characteristics of materials, especially at high temperatures. Therefore, the reviewed articles are classified into the following three categories:

- The wear properties increase as the oxidation properties increase;
- The wear properties reduce as the oxidation properties decrease;
- The wear properties reduce as the oxidation properties increases, or vice versa.

4. Statistical Discussion

The classification of the articles was performed according to the criteria presented in Table 1. A positive response to each criterion is denoted with a checkmark and presented in two parts in Tables 2 and 3. Also, in Table 4, the top researchers in terms of the number of articles in the field of tungsten carbide oxidation are presented based on the collected data. These data show that the distribution of the number of articles published among at least the first 20 researchers in the list is uniform, and they have published two or three articles in this field. However, the number of publications in the field of oxidation of tungsten carbides in top journals is not uniform. Table 5 represents data collected concerning top journals by considering the number of related publications. As can be seen, the *International Journal of Refractory Metals and Hard Materials* has much higher publications than other journals, due to the exact correspondence between the scope of the journal and the subject of tungsten carbide oxidation. The journals with the next highest number of articles are *Ceramics International*, *Materials Science*, and the *Journal of Alloys and Compounds*, which also publish articles related to cermets according to their scope.

Table 2. Classification of the papers according to the first four criteria mentioned in Table 1.

	Production Method						**Binder of Composite**												**Author's Approach**				**Oxidation Outcome**			
Paper	**Spark Plasma Sintering (SPS)**	**Hot Press (HP)**	**Cold Press (CP) + Sintering**	**Hot Isostatic Press (HIP)**	**Cold Isostatic Press (CIP)**	**Not Mentioned**	**Co**	**Ni**	**Co + Ni**	**Cr**	**Mo**	**Pure Iron**	**Fe–Based Alloys**	**Ni_3Al**	**FeAl**	**Al_2O_3**	**$TiC_{0.4}$**	**High–Entropy Alloys (HEA)**	**Using New Binder and Comparing with Pervious Study**	**Investigating on the Effect of Various Fraction of One Binder**	**Study on the Effect of Adding Minor Element to the Binder**	**Other**	**Considerable–Improvement**	**Acceptable/Minor Improvement**	**Reduction In Oxidation Resistance**	**No Comparison with Conventional WC–Based Cermets**
Penrice [98]						√				√	√								√				√			
Upadhyaya and Bhaumik [42]			√						√			√							√	√				√	√	
Bhaumik et al. [69]				√			√		√										√				√	√		
Ogwu and Davies [85]			√											√	√							√	√			
Sikka et al. [86]						√								√					√				√			
Mari and Gonseth [77]						√	√															√				√
Lofaj and Kaganovskii [19]			√				√													√						√
Basu and Sarin [15]			√				√													√						√
Voitovich et al. [16]			√							√	√								√					√	√	
Subramanian and Schneibel [7]			√												√				√	√			√			
Gille et al. [41]			√										√							√			√			
Casas et al. [17]						√	√													√			√		√	

Table 2. *Cont.*

Paper	Production Method						Binder of Composite												Author's Approach				Oxidation Outcome			
	Spark Plasma Sintering (SPS)	Hot Press (HP)	Cold Press (CP) + Sintering	Hot Isostatic Press (HIP)	Cold Isostatic Press (CIP)	Not Mentioned	Co	Ni	Co + Ni	Cr	Mo	Pure Iron	Fe–Based Alloys	Ni_3Al	FeAl	Al_2O_3	$TiC_{0.4}$	High–Entropy Alloys (HEA)	Using New Binder and Comparing with Pervious Study	Investigating on the Effect of Various Fraction of One Binder	Study on the Effect of Adding Minor Element to the Binder	Other	Considerable–Improvement	Acceptable/Minor Improvement	Reduction In Oxidation Resistance	No Comparison with Conventional WC–Based Cermets
Tavare et al. [58]		√					√														√		√			
Aristizabal et al. [8]			√						√										√	√	√		√			
Barbatti et al. [33]			√				√														√		√			
Del Campo et al. [34]			√				√														√					√
Fernandes et al. [59]		√										√	√							√	√		√		√	
Shon et al. [13]			√					√				√							√				√		√	
Aristizabal et al. [67]				√					√										√	√	√		√			
Aristizabal et al. [70]				√					√												√		√			
Jianxin et al. [9]						√	√															√				√
Barbatti et al. [31]			√										√						√	√			√			
Chen et al. [20]						√	√															√	√			
Hwang and Lee [35]			√				√														√				√	

Table 2. *Cont.*

Paper	Production Method						Binder of Composite												Author's Approach				Oxidation Outcome			
	Spark Plasma Sintering (SPS)	Hot Press (HP)	Cold Press (CP) + Sintering	Hot Isostatic Press (HIP)	Cold Isostatic Press (CIP)	Not Mentioned	Co	Ni	Co + Ni	Cr	Mo	Pure Iron	Fe–Based Alloys	Ni_3Al	FeAl	Al_2O_3	$TiC_{0.4}$	High–Entropy Alloys (HEA)	Using New Binder and Comparing with Pervious Study	Investigating on the Effect of Various Fraction of One Binder	Study on the Effect of Adding Minor Element to the Binder	Other	Considerable–Improvement	Acceptable/Minor Improvement	Reduction In Oxidation Resistance	No Comparison with Conventional WC–Based Cermets
Aly et al. [57]		√					√															√				√
Chang and Chen [36]			√										√						√				√			
Chen et al. [10]			√															√	√	√			√			
Dong et al. [61]		√														√					√					√
Chen et al. [39]			√				√															√	√			
Furushima et al. [40]			√												√					√						√
Furushima et al. [38]			√												√						√					√
Furushima et al. [37]			√												√				√	√				√		
Huang et al. [43]			√				√														√		√			
Li et al. [51]	√													√					√				√			
Schubert et al. [32]			√										√						√						√	
Chen et al. [11]	√						√															√				√

Table 2. *Cont.*

Paper	Production Method						Binder of Composite												Author's Approach				Oxidation Outcome			
	Spark Plasma Sintering (SPS)	Hot Press (HP)	Cold Press (CP) + Sintering	Hot Isostatic Press (HIP)	Cold Isostatic Press (CIP)	Not Mentioned	Co	Ni	Co + Ni	Cr	Mo	Pure Iron	Fe–Based Alloys	Ni_3Al	FeAl	Al_2O_3	$TiC_{0.4}$	High–Entropy Alloys (HEA)	Using New Binder and Comparing with Pervious Study	Investigating on the Effect of Various Fraction of One Binder	Study on the Effect of Adding Minor Element to the Binder	Other	Considerable–Improvement	Acceptable/Minor Improvement	Reduction In Oxidation Resistance	No Comparison with Conventional WC–Based Cermets
Emanuelli et al. [79]						√			√													√	√			
Oh et al. [54]	√															√				√			√			
Lin et al. [71]				√			√														√		√			
Mottaghi and Ahmadian [60]		√													√				√		√		√			
Aly et al. [18]		√					√															√				√
Ezquerra et al. [30]			√						√												√		√			
Karimi et al. [2]	√														√				√				√			
Shoufa [68]				√			√															√			√	
de Oro Calderon et al. [44]			√										√					√	√			√	√			
Su et al. [62]		√														√					√		√			
Tarraste et al. [72]				√									√						√		√		√			
Wang et al. [53]	√						√														√				√	

Table 2. *Cont.*

Paper	Production Method						Binder of Composite												Author's Approach				Oxidation Outcome			
	Spark Plasma Sintering (SPS)	**Hot Press (HP)**	**Cold Press (CP) + Sintering**	**Hot Isostatic Press (HIP)**	**Cold Isostatic Press (CIP)**	**Not Mentioned**	**Co**	**Ni**	**Co + Ni**	**Cr**	**Mo**	**Pure Iron**	**Fe–Based Alloys**	**Ni_3Al**	**FeAl**	**Al_2O_3**	**$TiC_{0.4}$**	**High–Entropy Alloys (HEA)**	**Using New Binder and Comparing with Pervious Study**	**Investigating on the Effect of Various Fraction of One Binder**	**Study on the Effect of Adding Minor Element to the Binder**	**Other**	**Considerable–Improvement**	**Acceptable/Minor Improvement**	**Reduction In Oxidation Resistance**	**No Comparison with Conventional WC–Based Cermets**
Karimi and Hadi [28]	√		√		√										√				√				√	√	√	
Basyir et al. [52]	√						√														√		√			
Luo et al. [3]	√																	√	√				√			
Wu et al. [97]						√	√															√				√
Hui et al. [63]		√														√			√				√			

Table 3. Classification of the papers according to the last three criteria mentioned in Table 1. (Here, P stands for a positive answer to the questions listed in Table 1).

Paper	Oxidation Temperature						Oxidation Kinetics					Wear Properties of Cermet			
	300–500 °C	500–600 °C	600–700 °C	700–800 °C	>800 °C	Not Mentioned or Non–Isotherm Test	No	Parabolic Equation	Linear Equation	Linear/Parabolic Equation	Other	Not Investigated	Both Increased	Both Decreased	One Increases and Other Decreases
Penrice [98]						P	P						P		
Upadhyaya and Bhaumik [42]					P		P					P			
Bhaumik et al. [69]					P							P			
Ogwu and Davies [85]						P	P					P			
Sikka et al. [86]												P			
Mari and Gonseth [77]						P	P					P			
Lofaj and Kaganovskii [19]												P			
Basu and Sarin [15]			P	P	P				P			P			
Voitovich et al. [16]		P	P	P						P		P			
Subramanian and Schneibel [7]					P		P						P		
Gille et al. [41]						P	P						P		
Casas et al. [17]				P					P			P			
Tavare et al. [58]	P						P					P			
Aristizabal et al. [8]				P	P					P					P
Barbatti et al. [33]			P	P						P		P			
Del Campo et al. [34]	P	P	P	P						P		P			
Fernandes et al. [59]						P	P					P			
Shon et al. [13]					P		P					P			
Aristizabal et al. [67]				P						P		P			
Aristizabal et al. [70]				P	P		P						P		
Jianxin et al. [9]			P				P								P
Barbatti et al. [31]					P		P					P			
Chen et al. [20]						P			P			P			
Hwang and Lee [35]				P	P			P				P			
Aly et al. [57]				P	P				P			P			
Chang and Chen [36]					P		P					P			
Chen et al. [10]					P		P						P		
Dong et al. [61]					P		P					P			
Chen et al. [39]		P						P				P			
Furushima et al. [40]						P	P					P			
Furushima et al. [38]						P	P					P			
Furushima et al. [37]						P	P					P			
Huang et al. [43]	P	P	P	P	P			P				P			
Li et al. [51]			P	P	P				P			P			
Schubert et al. [32]						P	P							P	
Chen et al. [11]		P	P						P			P			
Emanuelli et al. [79]			P	P				P				P			
Oh et al. [54]						P	P					P			
Lin et al. [71]				P					P			P			
Mottaghi and Ahmadian [60]			P				P						P		
Aly et al. [18]						P		P				P			
Ezquerra et al. [30]				P			P					P			
Karimi et al. [2]				P	P					P		P			
Shoufa [68]		P	P	P						P		P			
de Oro Calderon et al. [44]						P	P						P		
Su et al. [62]			P				P						P		
Tarraste et al. [72]						P	P						P		
Wang et al. [53]	P	P	P				P					P			
Karimi and Hadi [28]		P					P					P			
Basyir et al. [52]					P					P		P			
Luo et al. [3]			P	P					P			P			
Wu et al. [97]		P	P	P				P				P			
Hui et al. [63]			P	P				P				P			

Table 4. Top researchers by considering the number of related publications.

Author	Affiliation/Country	Documents
Aristizabal, M.	CEIT and TECNUN, Paseo Manuel de Lardizábal 15, 20018, San Sebastián, Gipuzkoa, Basque Country, Spain	3
Chen, L.	School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China	3
Furushima, R.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	3
Hosokawa, H.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	3
Katou, K.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	3
Liu, H.	School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China	3
Matsumoto, A.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	3
Shimojima, K.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	3
Yi, D.	School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China	3
Zhu, S.	College of Mechanical Engineering, Donghua University, Shanghai 201620, PR China	3
Aly, S.T.	The Center of Scientific Research, The Ministry of Military Production, Cairo, Egypt	2
Barbatti, C.	Max–Planck–Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany	2
Bhaumik, S.K.	Department of Metallurgical Engineering, Indian Institute of Technology, 208 016, Kanpur, India	2
Brito, P.	Max–Planck–Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany	2
Garcia, J.	Helmholtz–Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany	2
Hadi, M.	Materials Engineering Group, Golpayegan College of Engineering, Isfahan University of Technology, Iran	2
Ibarreta, F.	FMD CARBIDE S.A.L., Zorrozaurre 35, 48014, Bilbao, Spain	2
Karimi, H.	Materials Engineering Department, Malek Ashtar University of Technology, Shahin Shahr, Iran	2
Martinez, R.	FMD CARBIDE S.A.L., Zorrozaurre 35, 48014, Bilbao, Spain	2
Mikami, M.	National Institute of Advanced Industrial Science and Technology, 2266–98 Anagahora, Shimoshidami, Moriyama–ku, Nagoya 463–8560, Japan	2
Pyzalla, A.R.	Helmholtz–Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany	2
Rodriguez, N.	CEIT and TECNUN, Paseo Manuel de Lardizábal 15, 20018, San Sebastián, Gipuzkoa, Basque Country, Spain	2
Sánchez, J.M.	CEIT and TECNUN, Paseo Manuel de Lardizábal 15, 20018, San Sebastián, Gipuzkoa, Basque Country, Spain	2
Shon, I.J.	The Research Center of Advanced Materials Development, Chonbuk National University, Chonbuk 561–756, Republic of Korea	2
Schubert, W.D.	Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Austria	2
Upadhyaya, G.S.	Department of Metallurgical Engineering, Indian Institute of Technology, 208 016, Kanpur, India	2
Wang, B.	School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China	2

Table 5. Top journals considering the number of related publications.

Journal Title	Number of Papers	Percentage
International Journal of Refractory Metals and Hard Materials	20	37.73
Ceramics International	9	16.98
Materials Science	5	9.43
Materials Science and Engineering A	4	7.55
Journal of Alloys and Compounds	3	5.66
Corrosion Science	3	5.66
Wear	2	3.77
Advanced Materials Research	1	1.89
Engineering Research and Technology	1	1.89
Intermetallics	1	1.89
Materials Research Express	1	1.89
Materials shaping technology	1	1.89
Powder Metallurgy	1	1.89
Thermal Analysis and Calorimetry	1	1.89

After collecting the data presented in the above tables, to obtain a better insight into the trend of investigations, these data are illustrated as the abundance distribution in each criterion by programming in Python.

Figure 1 indicates the distribution of published articles in the domain of binder effect on oxidation resistance from the production method point of view. The high frequency of the "standard vacuum sintering" method in Figure 1 shows that, even in articles with the aim of binder modification for improving the oxidation properties, this production method has been preferred by researchers. This will be more important considering that it is most likely that the cold press and sintering method has been used in articles where the production method is not mentioned. In this condition, the share of cold press and sintering production methods reaches 47.3%. This shows that, despite the important achievements of advanced production methods such as SPS, most researchers have utilized conventional ones to investigate the role of the new binder. The reasons for this fact are: (1) the standard vacuum sintering production method is significantly cheaper and more accessible due to rapid industrialization; (2) in investigating the effect of changing the binder, researchers usually prefer to keep the other factor, i.e., the production method, constant, so that the effect of the variable factor can be examined more clearly.

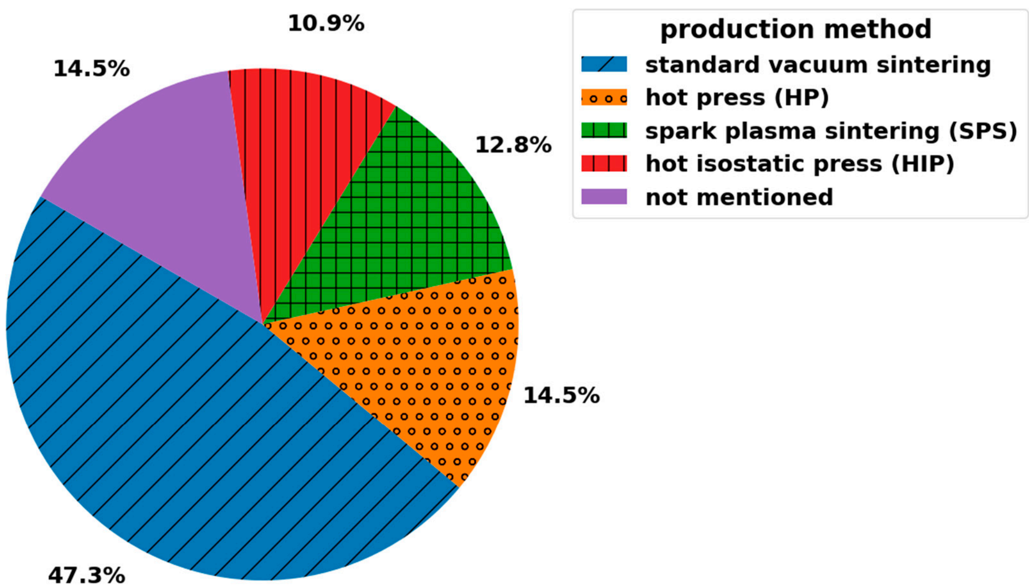

Figure 1. Distribution of the reviewed papers according to production method.

Figure 2 depicts the distribution of published articles on the oxidation of tungsten carbide cermets from the binder–type point of view. From this figure, a total of 65.6% of the articles written in the field of improving the oxidation of tungsten carbide cermets have pursued this goal by replacing the cobalt binder with alternative binders. This value is the sum of the percentages of binders other than cobalt in Figure 2. Also, it is remarkable from Figure 2 that the typical binders of cobalt and cobalt–nickel, which are extensively used in industrial production of tungsten carbide cermets, have the most extensive contribution to oxidation literature. Nevertheless, cobalt has been regarded as one of the high–risk metals from the standpoint of environmental consequences by some studies and reports, such as [99]. It is worth mentioning that the high use of cobalt as a binder in articles related to improving oxidation properties might be the consequence of researchers' approach to enhancing the oxidation properties of tungsten carbide. Therefore, considering Figure 3 is sound for interpreting this high usage. Figure 3 illustrates the frequency of the relevant articles from the research approach perspective. As can be seen from the figure, binder changes to improve oxidation properties make a contribution of 33.8% to the literature. In many of these articles, it is necessary to compare the properties of modified cermets with those of cermets with a cobalt binder. Because every binder used in the reviewed articles has been counted in the classification procedure, this has increased the number of articles that have been used.

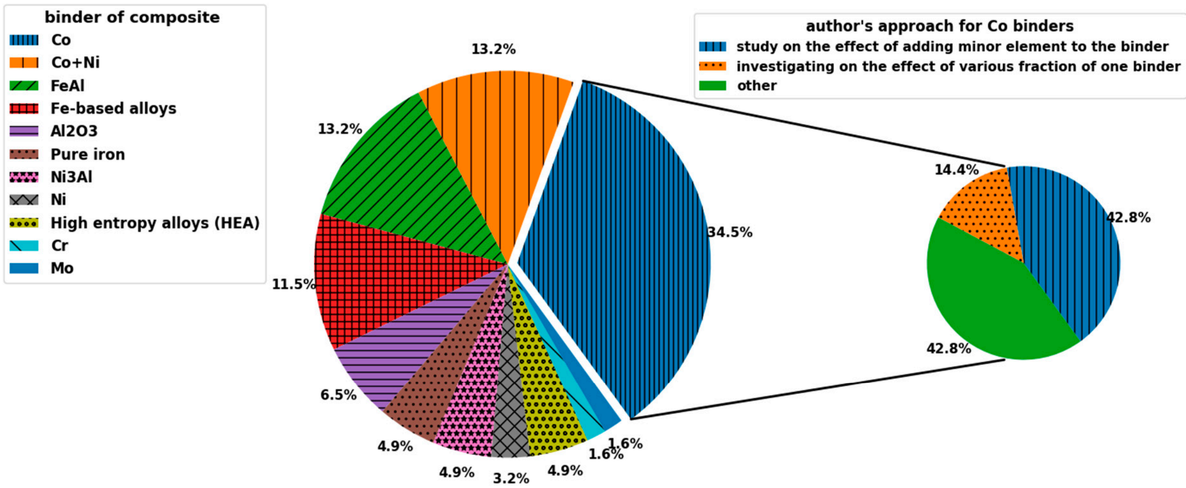

Figure 2. Distribution of the surveyed papers according to binder of composite and author's approach.

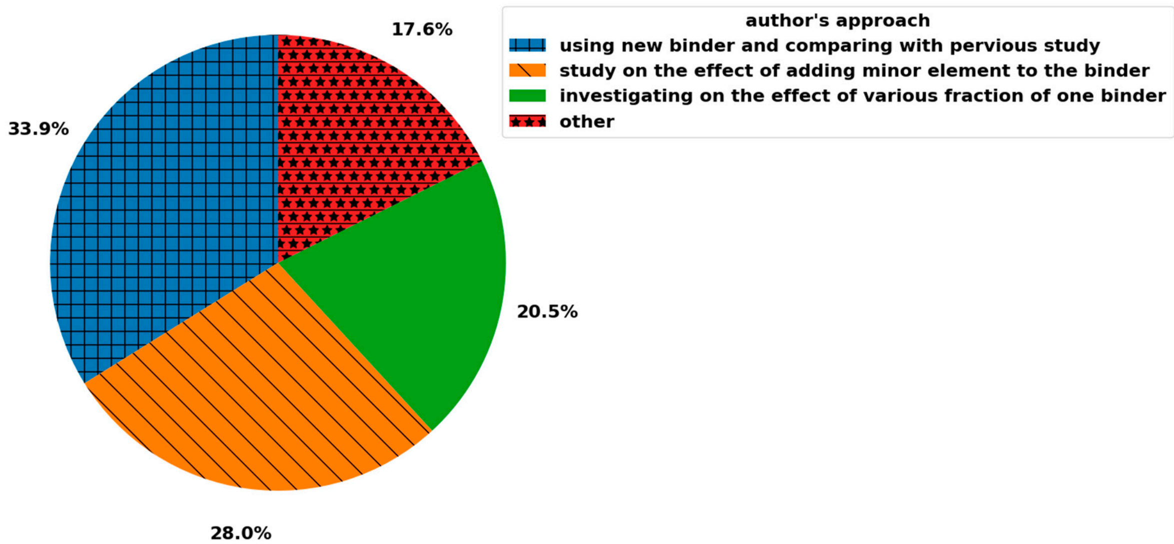

Figure 3. Distribution of the reviewed articles in terms of the author's approach.

In addition, numerous types of research have been carried out to improve the oxidation properties by adding minor elements. In such studies, cermet with a cobalt binder is considered the initial state, and the effect of adding minor elements is compared with this state.

Furthermore, it can be concluded from the "Author's approach for Co binders" part within Figure 2 that in all studies related to cobalt binder, in 42.9% of the studies the effect of adding new minor elements to this binder has been considered, while 14.3% have investigated different volume fractions of cobalt binder.

On the other hand, the main part of Figure 2 demonstrates that, regardless of whether the research approach has been based on examining the effect of changing the binder or not, a total of 52.5% of publications on oxidation context have not used cobalt or cobalt–nickel binders. This percentage confirms the high tendency of researchers to use new and alternative binders for improving oxidation resistance. It is clear from Figure 3 that only 20.6% of the published articles in the area of oxidation of cemented carbides have had their focus on modifying the properties by changing the volume percentage of cobalt. In other words, a great deal of attention has been directed to the use of new replacement binders or binders modified with minor elements and their comparison with conventional binders.

The effect of the production method and binder type on oxidation outcome has been demonstrated in Figure 4. It can be seen in Figure 3 that a significant improvement has been reported in 55.7% of the oxidation articles, as well as a minor improvement in oxidation resistance in 8.2% of the published articles. This finding also indicates that from employing advanced production methods and changing the binder a positive effect on improving the oxidation properties of WC cemented carbides can emerge. The difference between HIP and SPS methods and other production methods that have improved oxidation resistance can be seen in the production method sub–graph in Figure 4. These two methods have excellent efficiency in removing porosity, due to the application of isostatic pressure at high temperatures (in HIP), and plasma formation during sintering (in SPS). Previous studies have shown the direct role of porosity reduction in increasing oxidation resistance [2] and wear resistance [28] in cemented carbides. However, according to the production method sub–graph in Figure 4, a lower number of studies that have improved the oxidation resistance belong to standard vacuum sintering. It should be pointed out that replacing Co with new binders has been addressed by many studies that have used new sintering methods such as SPS or HIP. As a result, the effect of these two factors may have led to higher efficiency in such studies. However, the impact of porosity reduction on improving oxidation resistance that occurs in advanced production methods such as SPS and HIP has been confirmed in independent studies [67,100]. However, since the selection of specific sintering methods is often used to investigate the effect of new binders, based on the obtained data it is not possible to recommend with certainty a change of production method to improve oxidation resistance.

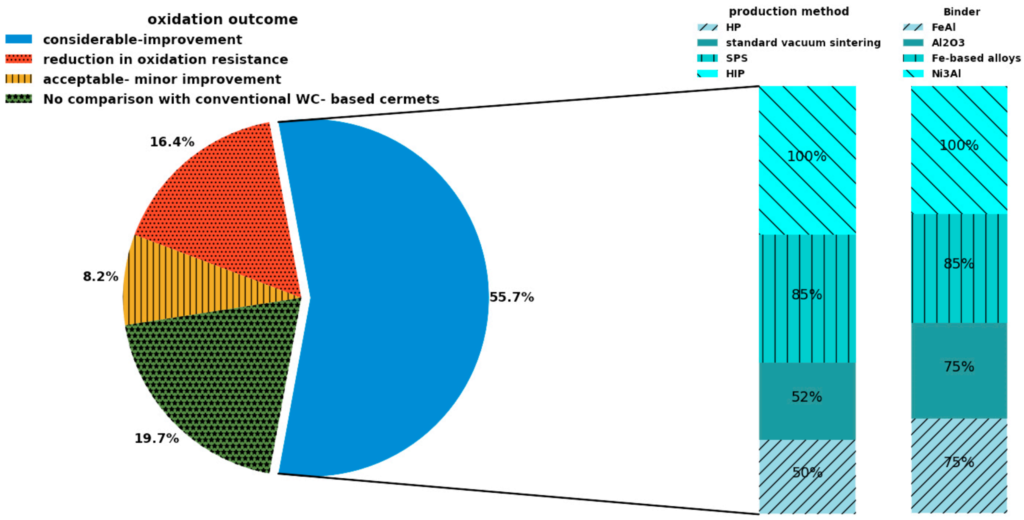

Figure 4. Distribution of explored articles from the perspective of oxidation outcome, with sub–graphs of binder composition and production method.

The outcome of binder change on the improvement of oxidation resistance is shown in another sub–graph of Figure 4. It is remarkable from this sub–graph that numerous studies that have used alternative binders based on intermetallic compounds such as Ni_3Al and FeAl in WC cemented carbide composition found an improvement in oxidation resistance. Previous studies on aluminide–based intermetallic compounds have shown that an oxide phase of Al_2O_3 is formed in the oxide scale of these compounds at high temperatures, which results in high oxidation resistance due to reduction in the penetration of anion ions (O–) and cation (metal) ones [83,101]. Reducing the diffusion coefficient of elements is equivalent to decreasing the possibility of an oxidative reaction and consequently reducing the oxidation rate.

By using these compounds as binders in cemented carbides, a modified oxide scale and complex Al–based compounds such as $FeAlO_3$ are created, which reduces penetration within the surface layer [2]. Note that one of the best alternatives from an oxidation point of view is FeAl binder. Karimi et al. [2] evaluated the mass gain during oxidation in WC–FeAl and WC–Co cermets at temperatures of 700 °C to 900 °C over time, and uncovered that the oxidation resistance obtained with FeAl binder is higher than that of cobalt binder at all temperatures. They showed that the oxide scale in WC–FeAl cermet contains $FeWO_4$, $FeAlO_3$ phases, and WO_3 phase, which reduces the diffusion of oxygen and consequently decreases the oxidation rate [2]. It can also be concluded that, in addition to intermetallic compounds, in most cases, changing the cobalt binder to iron–based alloys and Al_2O_3 ceramics has led to the enhancement of oxidation resistance. In such changes, modification of the oxide scale is the main factor in reducing the carbide oxidation rate. In fact, in the typical case (WC–Co cermets), oxidation can start from low temperatures such as 500 °C [102]. In addition, the passivation capability in the oxide layer containing tungsten oxide is small, and cobalt independently has a low oxidation resistance and is easily oxidized at high temperatures [2,51,63]. Consequently, changing the binder can improve oxidation. As mentioned earlier, in recent years, various investigations have been conducted regarding the use of high–entropy alloys as binders. However, in most of these studies, improving mechanical properties other than oxidation resistance has been more considered [3].

The distribution of the relevant studies in the context of the oxidation of cemented carbides in terms of the temperature range of the oxidation experiment is depicted in Figure 5. It is obvious from Figure 5 that a high percentage of the isothermal oxidation experiments on WC–cemented carbides have been conducted in the temperature range above 500 °C. According to previous studies, the reason behind this is that the oxidation of WC–based compounds begins at a temperature above 500 °C, while the oxidation rate significantly increases at higher temperatures [102].

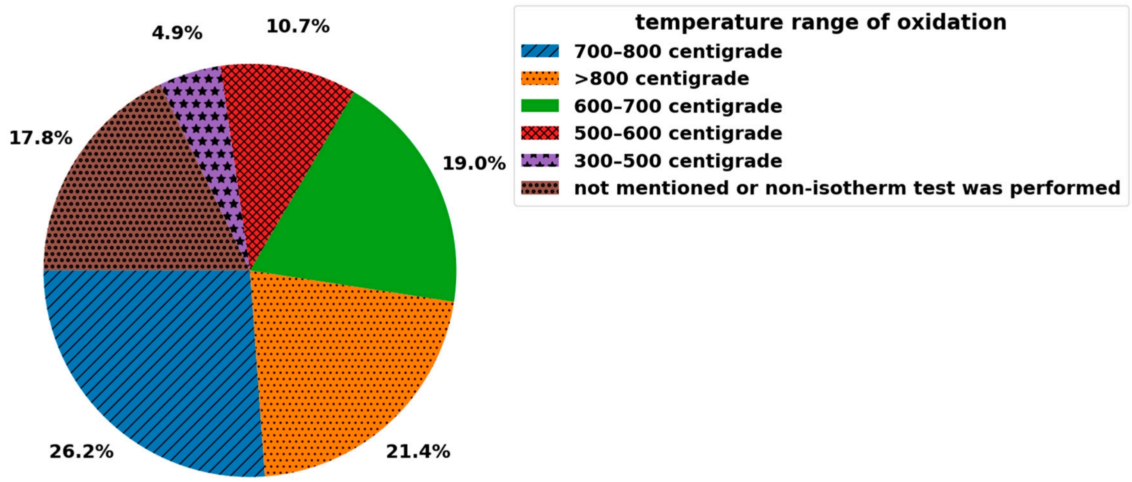

Figure 5. Distribution of the surveyed papers according to the temperature range of oxidation experiments.

On the other hand, according to the recent applications of cemented carbide, the investigation of oxidation behavior at higher temperatures has been increasingly highlighted by researchers. The results also show that the experiments carried out at a temperature above 800 °C and within the range of 700–800 °C have had almost the same frequency which is followed by experiments at a temperature of 600–700 °C. A possible reason for this is that, in the studies conducted based on changing the binder to improve oxidation behavior, a temperature increment makes it easier to compare the binders' efficiency on oxidation resistance by intensifying the oxidation kinetics.

Figure 6 shows the distribution of the selected articles in terms of oxidation kinetics. As can be seen from the figure, the percentage of studies that have modelled the oxidation kinetics is a little less than half. Among these studies, the accordance of mass gain versus time by a parabolic function has a percentage of 15.1% [18,19,35,39,43,63,79,97]. Meanwhile, 15.1% of the articles have approximated the oxidation behavior of WC–cemented carbides linearly [3,11,17,20,51,69,71]. As illustrated in Figure 6, in 15.1% of the reviewed articles, the trend of mass changes over time has been estimated by a combination of linear and parabolic functions [2,8,16,33,34,52,57,67,68]. Note that under a parabolic approximation based on the experimental results, the general mass gain–time equation ($\Delta m^n = kt$) converts to the parabolic function $\Delta m^2 = kt$, while we have $\Delta m = k't$ for the linear behavior case. Obviously, the linear equation indicates a higher oxidation rate, which means that the oxide layer does not have a sufficient passivation capability [2]. Under the parabolic equation, the oxidation resistance of the substrate is higher, and the diffusion rate of cations and anions from the oxide layer controls the oxidation transformation [55]. In this case, it will be worthwhile to compare the obtained values of n and k to measure the oxidation resistance under different conditions (for example, changing the binder).

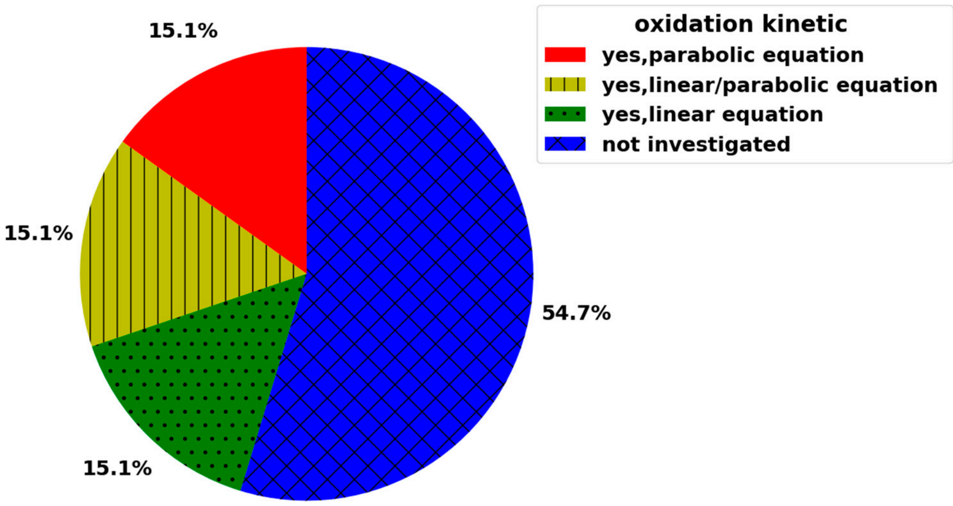

Figure 6. The frequency of reviewed articles from the perspective of oxidation kinetics.

Another factor that is usually considered during kinetic modeling in oxidation studies is the oxidation activation energy (Q), which indicates the required energy barrier for starting the oxidation process. To calculate this quantity, isotherm tests are usually performed at least at three temperatures. The value of Q is obtained by measuring the slope parameter $\ln(k_p)$ in equation $k_p = k_0 \exp\left(\frac{-Q}{RT}\right)$ in terms of $\left(\frac{1}{T}\right)$. Note that Q is expressed in terms of $\frac{\text{cal}}{\text{mol}}$, while R denotes the gas constant in terms of cal/(K.mol), k_0 is a pre–exponential value, and T is the temperature (K). Exploring tungsten carbide oxidation articles showed that the Q value was calculated around 230 kCal/mol in at least nine studies [16,35,43,51,57,63,67,97].

On the other hand, wear resistance plays an essential role in cemented carbide applications. Figure 7 evaluates the relationship between the oxidation resistance increment and wear resistance, considering the published literature in the context of oxidation of cemented carbides. As can be seen from this figure, a high percentage of the published articles in the oxidation context have neglected to focus on wear resistance. This may be because the investigation of wear behavior and its associated factors can be investigated separately from the oxidation properties. Another reason for less attention being paid to wear in articles related to oxidation is that high hardness guarantees high wear resistance to a very large extent [103,104]. The figure also shows that, from the total of 22.7% of the articles that concurrently conducted wear and oxidation tests, 17.0% reported an increase in both oxidation and wear resistance. Concerning the relationship between hardness and wear resistance, it can be concluded that a similar correlation between the factors of improving the production method (by reducing the porosity) and changing the binder (binders harder than cobalt) with the hardness parameter is also valid for wear resistance, which leads to improving oxidation and wear resistance concurrently. It should be pointed out that the aforementioned new binders (such as FeAl, Ni_3Al, and HEAs) have a higher hardness than cobalt. Consequently, since the hardness of two–phase materials is affected by the hardness of both phases, the hardness increment of the binder leads to an increase in the total hardness of the cermet.

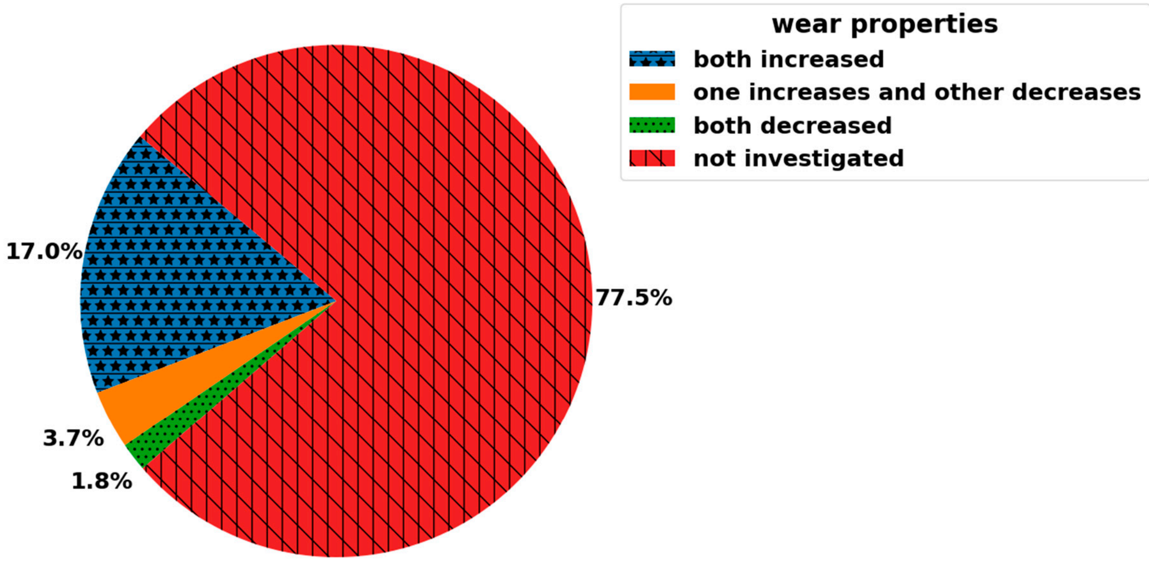

Figure 7. Distribution of the reviewed papers in terms of wear properties.

5. Assessment of Statistical Analysis with Published Data

The fact that the type of binder influences the oxidation properties of tungsten carbide is one of the most important findings from the classification of oxidation studies. The results obtained showed that, statistically speaking, the use of Al_2O_3, Ni_3Al, and FeAl binders had the greatest impact on the improvement of the oxidation properties. Figure 8 compares the values of the mass increase per unit area due to oxidation for these three types of binder from three different articles. As can be seen from the figure, using Al_2O_3 binder instead of Co at 600–800 °C for 1 h significantly reduced the oxidation rate of the cermet. This figure also shows that when Ni_3Al binder is used the mass increase due to oxidation is reduced over a relatively long period. It should be noted that the results of oxidation tests have shown that the use of Ni_3Al binder results in a significant reduction in the amount of oxidation. Finally, this figure shows that when FeAl binder is used the amount of oxidation decreases. However, the effectiveness of this binder in oxidation reduction was not as high as that of the Al_2O_3 and Ni_3Al binders.

Previous studies have shown that the change in oxide scale composition is the main reason for the reduction in oxidation rate after binder modification. The study of the scale structure of WC–Co cermets has shown that the compound containing WO_3 provides many pathways for oxygen to penetrate through the formation of cracks, which increases the oxidation rate. The reason for the formation of these cracks is the release of gases such as CO and CO_2 because of oxidation reactions. On the other hand, in cermet with FeAl binder, for example, the oxide layer contains $FeAlO_3$ and $FeWO_4$ compounds, which make the oxide layer denser and less porous, thus reducing the oxidation rate [2].

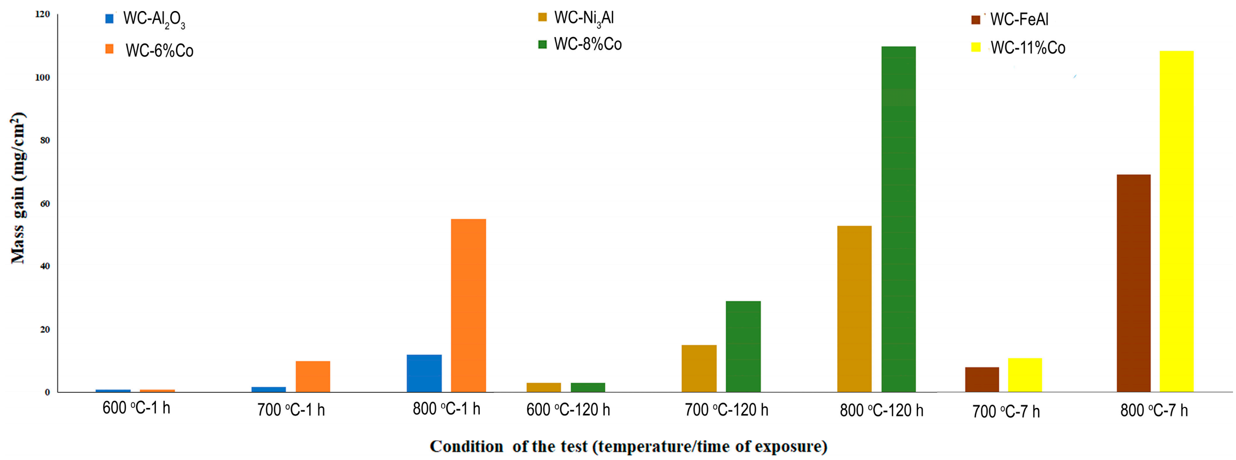

Figure 8. The values of the mass increase per unit area for three types of binders from three different articles [3,105–115].

The classification of papers also shows that the use of high–entropy alloys as binders has become very popular in recent years. Figure 9 provides an overview of the literature published in the field of cobalt binder replacement with HEAs. This figure summarizes six types of different alloy compositions that have been used in recent years, together with the main results obtained. As can be seen in the figure, the binders used are based on the addition of the new quaternary element CoCrFeNi. This figure shows that despite significant successes in using HEA binders to reduce size, improve hardness, and increase the strength and fracture toughness of cermets, only one paper addressed the modification of oxidation resistance. Therefore, considering the numerous achievements in the field of HEA binders and the research trend on tungsten carbide, a more complete investigation of the tribological properties, including wear and oxidation resistance, of HEA binders may be a possible direction for future studies.

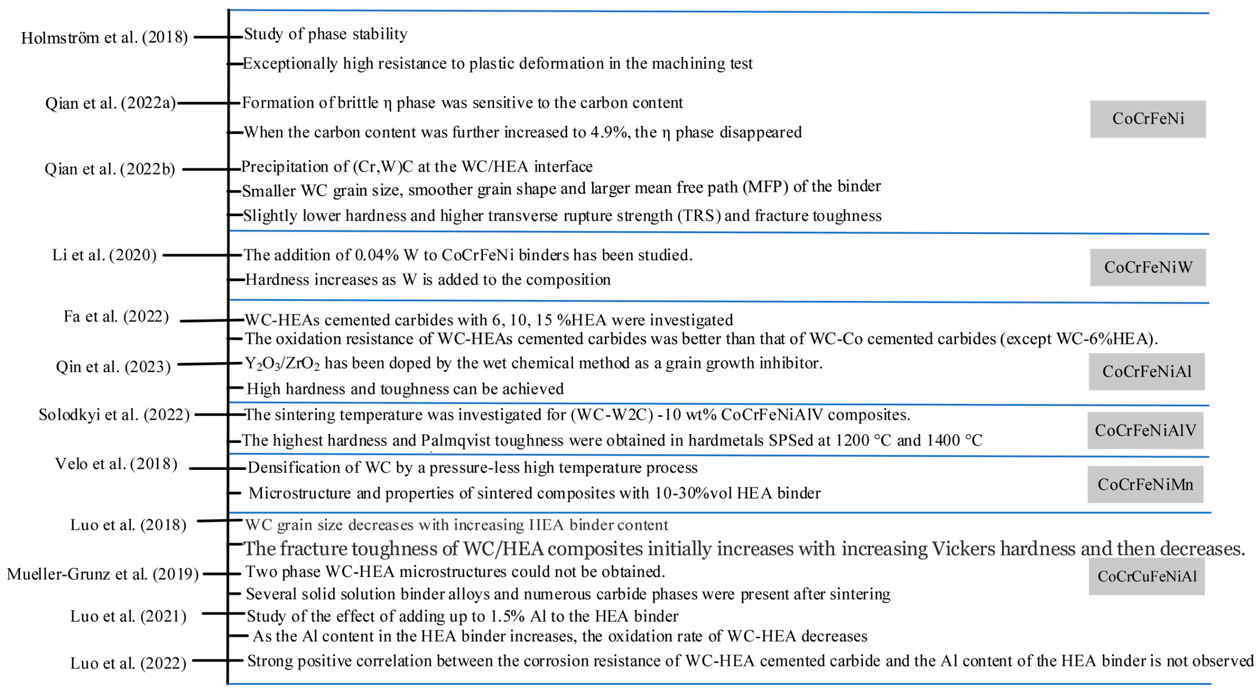

Figure 9. A summary of publications in the field of cobalt binder substitution using high–entropy alloys (HEAs) [3,105–115].

6. Conclusions and Directions for Future Research

The findings of this survey are listed as follows:

1. Oxidation resistance is a crucial characteristic for tungsten carbide cermets, especially for processes with high machining speed. The findings of this survey showed that the studies that are conducted to improve the properties of this type of cermet do not all necessarily lead to the improvement of oxidation properties. It was indicated that a significant improvement of oxidation properties has been obtained in only 65.6% of the articles that changed the binder of WC–Co cemented carbides;
2. Among the production methods reported in the reviewed articles regarding oxidation resistance, the most frequent method with a frequency of 47.3% belongs to the standard vacuum sintering technique. However, employing advanced production methods such as hot press (with a frequency of 14.5%), hot isostatic press (with a frequency of 10.9%), and spark plasma sintering (with a frequency of 12.7%) can lead to a success rate between 80 and 100 percent in oxidation improvement;
3. Reviewed articles in the field of oxidation revealed that more than half of investigations (65.6%) used new binder in order to enhance oxidation resistance. It is also concluded that changing cemented carbide binders from cobalt to intermetallic compounds of Ni_3Al, FeAl, Fe–based alloys, and Al_2O_3 accounts for the most extensive proportion of the articles that reported oxidation improvement. In recent years, replacing cobalt binders with high–entropy alloys (HEAs) for improving mechanical properties has attracted the attention of both manufacturers and researchers. However, only 4.9% of the reviewed articles focused on enhancing oxidation properties. Hence, investigation of the oxidation properties of tungsten carbide cermets with a binder of HEAs may be a potential direction for future studies;
4. The results of this research showed that the oxidation behavior of tungsten carbide cermets is reported in three modes, including parabolic, linear, and parabolic–linear, with almost the same frequency. This means the equation and trend of mass gain depend on the composition of the binder used. Furthermore, the oxidation activation energy of these cermets is reported to be around 230 kCal/mol;
5. It is proved from this survey that changing the binder to improve oxidation resistance can often maintain or improve wear resistance. From 22.7% of the articles in the field of oxidation that also examined wear resistance, 17% reported the improvement of both wear resistance and oxidation properties;
6. This survey focused on tungsten carbide as the main constituent of cermets. Several other studies have been performed to achieve higher mechanical properties using secondary carbides such as TiC, TaC, Mo_2C, and VC in recent years. Meanwhile, some studies have been conducted on using some new addition such as graphene to improve mechanical properties. Furthermore, the use of cermets based on (Ti,W)(C,N) has been the subject of many studies, especially for conditions where the oxidation problem affects the cermet application. Although these three approaches were outside our survey topic, they have provided the prospect of achieving better properties, and future research in the field of oxidation may be carried out on these cermets.

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References

1. García, J.; Ciprés, V.C.; Blomqvist, A.; Kaplan, B. Cemented carbide microstructures: A review. *Int. J. Refract. Met. Hard Mater.* **2019**, *80*, 40–68. [CrossRef]
2. Karimi, H.; Hadi, M.; Ebrahimzadeh, I.; Farhang, M.R.; Sadeghi, M. High-temperature oxidation behaviour of WC-FeAl composite fabricated by spark plasma sintering. *Ceram. Int.* **2018**, *44*, 17147–17153. [CrossRef]
3. Luo, W.; Liu, Y.; Liu, X.; Zhou, Z. Oxidation behavior of ultrafine WC-based cemented carbides with AlxCoCrCuFeNi high-entropy alloy binders. *Ceram. Int.* **2021**, *47*, 8498–8509. [CrossRef]
4. Penrice, T. Alternative binders for hard metals. *Carbide Tool J.* **1988**, *20*, 12–15. [CrossRef]
5. Sun, J.; Zhao, J.; Gong, F.; Ni, X.; Li, Z. Development and application of WC-based alloys bonded with alternative binder phase. *Crit. Rev. Solid State Mater. Sci.* **2019**, *44*, 211–238. [CrossRef]
6. Vilardell, A.; Cinca, N.; Tarrés, E.; Kobashi, M. Iron aluminides as an alternative binder for cemented carbides: A review and perspective towards additive manufacturing. *Mater. Today Commun.* **2022**, *31*, 103335. [CrossRef]
7. Subramanian, R.; Schneibel, J. FeAl–TiC and FeAl–WC composites—Melt infiltration processing, microstructure and mechanical properties. *Mater. Sci. Eng. A* **1998**, *244*, 103–112. [CrossRef]
8. Aristizabal, M.; Rodriguez, N.; Ibarreta, F.; Martinez, R.; Sanchez, J. Effect of the binder phase content and decarburization phenomena on the oxidation and wear resistance of WC-CoNiCr materials. In Proceedings of the EuroPM2009 Congress and Exhibition, Copenhagen, Denmark, 12–14 October 2009; EPMA: Shrewsbury, UK, 2009; pp. 299–306.
9. Jianxin, D.; Hui, Z.; Ze, W.; Yunsong, L.; Jun, Z. Friction and wear behaviors of WC/Co cemented carbide tool materials with different WC grain sizes at temperatures up to 600 C. *Int. J. Refract. Met. Hard Mater.* **2012**, *31*, 196–204. [CrossRef]
10. Chen, C.-S.; Yang, C.-C.; Chai, H.-Y.; Yeh, J.-W.; Chau, J.L.H. Novel cermet material of WC/multi-element alloy. *Int. J. Refract. Met. Hard Mater.* **2014**, *43*, 200–204. [CrossRef]
11. Chen, L.; Yi, D.; Wang, B.; Liu, H.; Wu, C. Mechanism of the early stages of oxidation of WC–Co cemented carbides. *Corros. Sci.* **2016**, *103*, 75–87. [CrossRef]
12. Erenkov, O.Y.; Yavorskii, D.; Kalenskii, A.; Lopushanskii, I.Y. Turning of Thermoplastics Using Ceramic Cutting Tools. *Glass Ceram.* **2020**, *77*, 194–196. [CrossRef]
13. Shon, I.-J.; Jeong, I.-K.; Ko, I.-Y.; Doh, J.-M.; Woo, K.-D. Sintering behavior and mechanical properties of WC–10Co, WC–10Ni and WC–10Fe hard materials produced by high-frequency induction heated sintering. *Ceram. Int.* **2009**, *35*, 339–344. [CrossRef]
14. Ojo-Kupoluyi, O.; Tahir, S.; Baharudin, B.; Azmah Hanim, M.; Anuar, M. Mechanical properties of WC-based hardmetals bonded with iron alloys—A review. *Mater. Sci. Technol.* **2017**, *33*, 507–517. [CrossRef]
15. Basu, S.; Sarin, V. Oxidation behavior of WC-Co. *Mater. Sci. Eng. A* **1996**, *209*, 206–212. [CrossRef]
16. Voitovich, V.; Sverdel, V.; Voitovich, R.; Golovko, E. Oxidation of WC-Co, WC-Ni and WC-Co-Ni hard metals in the temperature range 500–800 °C. *Int. J. Refract. Met. Hard Mater.* **1996**, *14*, 289–295. [CrossRef]
17. Casas, B.; Ramis, X.; Anglada, M.; Salla, J.; Llanes, L. Oxidation-induced strength degradation of WC–Co hardmetals. *Int. J. Refract. Met. Hard Mater.* **2001**, *19*, 303–309. [CrossRef]
18. Aly, S.; Hamad, K.; Salam, N.A.; Abdel-Hamid, S. Oxidation Kinetics of Tungsten Carbide-20cobalt Composite using Non-Isothermal Thermal Analysis. *Int. J. Eng. Res.* **2018**, *7*. [CrossRef]
19. Lofaj, F.; Kaganovskii, Y.S. Kinetics of WC-Co oxidation accompanied by swelling. *J. Mater. Sci.* **1995**, *30*, 1811–1817. [CrossRef]
20. Chen, L.; Wang, B.; Yi, D.; Liu, H. Non-isothermal oxidation kinetics of WC–6Co cemented carbides in air. *Int. J. Refract. Met. Hard Mater.* **2013**, *40*, 19–23. [CrossRef]
21. Hachicha, W.; Ghorbel, A. A survey of control-chart pattern-recognition literature (1991–2010) based on a new conceptual classification scheme. *Comput. Ind. Eng.* **2012**, *63*, 204–222. [CrossRef]
22. Kolbe, R.H.; Burnett, M.S. Content-analysis research: An examination of applications with directives for improving research reliability and objectivity. *J. Consum. Res.* **1991**, *18*, 243–250. [CrossRef]
23. Maleki, M.R.; Amiri, A.; Castagliola, P. Measurement errors in statistical process monitoring: A literature review. *Comput. Ind. Eng.* **2017**, *103*, 316–329. [CrossRef]
24. Maleki, M.R.; Amiri, A.; Castagliola, P. An overview on recent profile monitoring papers (2008–2018) based on conceptual classification scheme. *Comput. Ind. Eng.* **2018**, *126*, 705–728. [CrossRef]
25. Jose, S.A.; John, M.; Menezes, P.L. Cermet Systems: Synthesis, Properties, and Applications. *Ceramics* **2022**, *5*, 210–236. [CrossRef]
26. Liu, G.; Guo, S.; Li, J.; Chen, K.; Fan, D. Fabrication of hard cermets by in-situ synthesis and infiltration of metal melts into WC powder compacts. *J. Asian Ceram. Soc.* **2017**, *5*, 418–421. [CrossRef]
27. Akimov, G.Y. Cold isostatic pressing as a method for fabricating ceramic products with high physicomechanical properties. *Refract. Ind. Ceram.* **1998**, *39*, 283–287. [CrossRef]
28. Karimi, H.; Hadi, M. Effect of sintering techniques on the structure and dry sliding wear behavior of WC-FeAl composite. *Ceram. Int.* **2020**, *46*, 18487–18497. [CrossRef]
29. Omanović-Mikličanin, E.; Badnjević, A.; Kazlagić, A.; Hajlovac, M. Nanocomposites: A brief review. *Health Technol.* **2020**, *10*, 51–59. [CrossRef]
30. Ezquerra, B.L.; Lozada, L.; van den Berg, H.; Wolf, M.; Sánchez, J.M. Comparison of the thermal shock resistance of WC based cemented carbides with Co and Co-Ni-Cr based binders. *Int. J. Refract. Met. Hard Mater.* **2018**, *72*, 89–96. [CrossRef]

31. Marques, B.; Fernandes, C.; Senos, A. Sintering, microstructure and properties of WC-AISI304 powder composites. *J. Alloys Compd.* **2013**, *562*, 164–170. [CrossRef]
32. Schubert, W.; Fugger, M.; Wittmann, B.; Useldinger, R. Aspects of sintering of cemented carbides with Fe-based binders. *Int. J. Refract. Met. Hard Mater.* **2015**, *49*, 110–123. [CrossRef]
33. Barbatti, C.; Garcia, J.; Brito, P.; Pyzalla, A.R. Influence of WC replacement by TiC and (Ta, Nb) C on the oxidation resistance of Co-based cemented carbides. *Int. J. Refract. Met. Hard Mater.* **2009**, *27*, 768–776. [CrossRef]
34. Del Campo, L.; Pérez-Sáez, R.; González-Fernández, L.; Tello, M. Kinetics inversion in isothermal oxidation of uncoated WC-based carbides between 450 and 800 °C. *Corros. Sci.* **2009**, *51*, 707–712. [CrossRef]
35. Hwang, Y.S.; Lee, D.B. High-temperature Oxidation of WC-20% TiC-10% Co Carbides. *Adv. Mater. Res.* **2013**, *811*, 93–97. [CrossRef]
36. Chang, S.-H.; Chen, S.-L. Characterization and properties of sintered WC–Co and WC–Ni–Fe hard metal alloys. *J. Alloys Compd.* **2014**, *585*, 407–413. [CrossRef]
37. Furushima, R.; Katou, K.; Shimojima, K.; Hosokawa, H.; Mikami, M.; Matsumoto, A. Changes in constituents and FeAl composition with oxygen content in WC–FeAl composites. *Int. J. Refract. Met. Hard Mater.* **2015**, *50*, 298–303. [CrossRef]
38. Furushima, R.; Katou, K.; Shimojima, K.; Hosokawa, H.; Matsumoto, A. Control of WC grain sizes and mechanical properties in WC–FeAl composite fabricated from vacuum sintering technique. *Int. J. Refract. Met. Hard Mater.* **2015**, *50*, 16–22. [CrossRef]
39. Chen, L.; Yi, D.; Wang, B.; Liu, H.; Wu, C.; Huang, X.; Li, H.; Gao, Y. The selective oxidation behaviour of WC–Co cemented carbides during the early oxidation stage. *Corros. Sci.* **2015**, *94*, 1–5. [CrossRef]
40. Furushima, R.; Katou, K.; Shimojima, K.; Hosokawa, H.; Mikami, M.; Matsumoto, A. Effect of η-phase and FeAl composition on the mechanical properties of WC–FeAl composites. *Intermetallics* **2015**, *66*, 120–126. [CrossRef]
41. Gille, G.; Bredthauer, J.; Gries, B.; Mende, B.; Heinrich, W. Advanced and new grades of WC and binder powder–their properties and application. *Int. J. Refract. Met. Hard Mater.* **2000**, *18*, 87–102. [CrossRef]
42. Upadhyaya, G.; Bhaumik, S. Sintering of submicron WC-10wt.% Co hard metals containing nickel and iron. *Mater. Sci. Eng. A* **1988**, *105*, 249–256. [CrossRef]
43. Huang, S.; Xiong, J.; Guo, Z.; Wan, W.; Tang, L.; Zhong, H.; Zhou, W.; Wang, B. Oxidation of WC-TiC-TaC-Co hard materials at relatively low temperature. *Int. J. Refract. Met. Hard Mater.* **2015**, *48*, 134–140. [CrossRef]
44. de Oro Calderon, R.; Edtmaier, C.; Schubert, W.-D. Novel binders for WC-based cemented carbides with high Cr contents. *Int. J. Refract. Met. Hard Mater.* **2019**, *85*, 105063. [CrossRef]
45. Chuvildeev, V.; Panov, D.; Boldin, M.; Nokhrin, A.; Blagoveshchensky, Y.V.; Sakharov, N.; Shotin, S.; Kotkov, D. Structure and properties of advanced materials obtained by Spark Plasma Sintering. *Acta Astronaut.* **2015**, *109*, 172–176. [CrossRef]
46. Weston, N.; Thomas, B.; Jackson, M. Processing metal powders via field assisted sintering technology (FAST): A critical review. *Mater. Sci. Technol.* **2019**, *35*, 1306–1328. [CrossRef]
47. Shchegoleva, N.; Evdokimov, S.; Modin, S.Y.; Karachevtsev, F. Investigation of the Properties of SiC–ZrB_2-Based Ceramic Composite Materials Obtained by Spark Plasma Sintering. *Glass Ceram.* **2018**, *75*, 253–257. [CrossRef]
48. Suárez, M.; Fernández, A.; Menéndez, J.; Torrecillas, R.; Kessel, H.; Hennicke, J.; Kirchner, R.; Kessel, T. Challenges and opportunities for spark plasma sintering: A key technology for a new generation of materials. *Sinter. Appl.* **2013**, *13*, 319–342.
49. Mamedov, V. Spark plasma sintering as advanced PM sintering method. *Powder Metall.* **2002**, *45*, 322–328. [CrossRef]
50. Guillon, O.; Gonzalez-Julian, J.; Dargatz, B.; Kessel, T.; Schierning, G.; Räthel, J.; Herrmann, M. Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments. *Adv. Eng. Mater.* **2014**, *16*, 830–849. [CrossRef]
51. Li, X.; Zhang, M.; Zheng, D.; Cao, T.; Chen, J.; Qu, S. The oxidation behavior of the WC–10 wt.% Ni_3Al composite fabricated by spark plasma sintering. *J. Alloys Compd.* **2015**, *629*, 148–154. [CrossRef]
52. Basyir, A.; Izzuddin, H.; Hermanto, B.; Sudiro, T. Remarkable improvement in high temperature oxidation resistance of WC-12Co by the addition of $CrSi_2$. *Int. J. Refract. Met. Hard Mater.* **2021**, *96*, 105497. [CrossRef]
53. Wang, Z.; Liu, Y.; Liu, K.; Wang, B. Mechanical properties and microstructure of spark plasma sintered WC-8 wt.% Co-VC-cBN ultrafine grained cemented carbide. *Ceram. Int.* **2019**, *45*, 23658–23665. [CrossRef]
54. Oh, S.-J.; Kim, B.-S.; Yoon, J.-K.; Hong, K.-T.; Shon, I.-J. Enhanced mechanical properties and consolidation of the ultra-fine WC–Al_2O_3 composites using pulsed current activated heating. *Ceram. Int.* **2016**, *42*, 9304–9310. [CrossRef]
55. Karimi, H.; Ghasemi, A.; Hadi, M. Microstructure and oxidation behaviour of TiAl(Nb)/Ti_2AlC composites fabricated by mechanical alloying and hot pressing. *Bull. Mater. Sci.* **2016**, *39*, 1263–1272. [CrossRef]
56. Erdem, O. Comparative study of hot and cold press and their effect on superconducting properties of coronene added bulk MgB_2. *Phys. C Supercond. Its Appl.* **2019**, *565*, 1353508. [CrossRef]
57. Aly, S.; Amin, S.K.; El Sherbiny, S.; Abadir, M. Kinetics of isothermal oxidation of WC–20Co hot-pressed compacts in air. *J. Therm. Anal. Calorim.* **2014**, *118*, 1543–1549. [CrossRef]
58. Tavares, E.; Costa, F.A.; Acchar, W. Mechanical characterization of alumina-doped tungsten carbide. *Mater. Sci. Forum* **2003**, *414–416*, 616–620. [CrossRef]
59. Fernandes, C.; Popovich, V.; Matos, M.; Senos, A.; Vieira, M. Carbide phases formed in WC–M (M= Fe/Ni/Cr) systems. *Ceram. Int.* **2009**, *35*, 369–372. [CrossRef]
60. Mottaghi, M.; Ahmadian, M. Comparison of the wear behavior of WC/(FeAl-B) and WC-Co composites at high temperatures. *Int. J. Refract. Met. Hard Mater.* **2017**, *67*, 105–114. [CrossRef]

61. Dong, W.; Zhu, S.; Wang, Y.; Bai, T. Influence of VC and Cr_3C_2 as grain growth inhibitors on WC–Al_2O_3 composites prepared by hot press sintering. *Int. J. Refract. Met. Hard Mater.* **2014**, *45*, 223–229. [CrossRef]
62. Su, Q.; Zhu, S.; Bai, Y.; Ding, H.; Di, P. Preparation and elevated temperature wear behavior of Ni doped WC-Al_2O_3 composite. *Int. J. Refract. Met. Hard Mater.* **2019**, *81*, 167–172. [CrossRef]
63. Hui, J.; Han, B.; Weiwei, D.; Zhu, S. High-temperature oxidation behaviour of vacuum hot-pressed WC-15 wt% Al_2O_3 composites. *Ceram. Int.* **2022**, *48*, 12184–12192. [CrossRef]
64. Loh, N.; Sia, K. An overview of hot isostatic pressing. *J. Mater. Process. Technol.* **1992**, *30*, 45–65. [CrossRef]
65. Wang, H.; Fang, Z.Z.; Sun, P. A critical review of mechanical properties of powder metallurgy titanium. *Int. J. Powder Metall.* **2010**, *46*, 45–57.
66. Adivi, H.G.; Ebrahimzadeh, I.; Hadi, M.; Tayebi, M. The effect of alumina nanoparticles addition on high-temperature wear behavior of intermetallic iron aluminide produced by the spark plasma sintering process. *Surf. Rev. Lett.* **2020**, *27*, 2050004. [CrossRef]
67. Aristizabal, M.; Rodriguez, N.; Ibarreta, F.; Martinez, R.; Sanchez, J. Liquid phase sintering and oxidation resistance of WC–Ni–Co–Cr cemented carbides. *Int. J. Refract. Met. Hard Mater.* **2010**, *28*, 516–522. [CrossRef]
68. Shoufa, L. Oxidation behavior of WC–Co cemented carbide in elevated temperature. *Mater. Res. Express* **2018**, *5*, 095801. [CrossRef]
69. Bhaumik, S.; Balasubramaniam, R.; Upadhyaya, G.; Vaidya, M. Oxidation behaviour of hard and binder phase modified WC-10Co cemented carbides. *J. Mater. Sci. Lett.* **1992**, *11*, 1457–1459. [CrossRef]
70. Aristizabal, M.; Ardila, L.; Veiga, F.; Arizmendi, M.; Fernandez, J.; Sánchez, J. Comparison of the friction and wear behaviour of WC–Ni–Co–Cr and WC–Co hardmetals in contact with steel at high temperatures. *Wear* **2012**, *280*, 15–21. [CrossRef]
71. Lin, N.; He, Y.; Zou, J. Enhanced mechanical properties and oxidation resistance of tungsten carbide-cobalt cemented carbides with aluminum nitride additions. *Ceram. Int.* **2017**, *43*, 6603–6606. [CrossRef]
72. Tarraste, M.; KÜBARSEPP, J.; JUHANI, K.; Arvo, M.; Viljus, M. Effect of Carbon Stabilizing Elements on WC Cemented Carbides with Chromium Steel Binder. *Mater. Sci.* **2019**, *25*, 202–206. [CrossRef]
73. Zhang, J.; Saeed, M.H.; Li, S. Recent progress in development of high-performance tungsten carbide-based composites: Synthesis, characterization, and potential applications. In *Advances in Ceramic Matrix Composites*; Woodhead Publishing: Sawston, UK, 2018; pp. 307–329.
74. Li, S.; Li, J.; Li, Y.; Liu, F.; Ao, W. Dense pure binderless WC bulk material prepared by spark plasma sintering. *Mater. Sci. Technol.* **2015**, *31*, 1749–1756. [CrossRef]
75. Romaniv, O.; Vasyliv, B. Some features of formation of the structural strength of ceramic materials. *Mater. Sci.* **1998**, *34*, 149–161. [CrossRef]
76. Teppernegg, T.; Klünsner, T.; Kremsner, C.; Tritremmel, C.; Czettl, C.; Puchegger, S.; Marsoner, S.; Pippan, R.; Ebner, R. High temperature mechanical properties of WC–Co hard metals. *Int. J. Refract. Met. Hard Mater.* **2016**, *56*, 139–144. [CrossRef]
77. Mari, D.; Gonseth, D. A new look at carbide tool life. *Wear* **1993**, *165*, 9–17. [CrossRef]
78. Luo, P.; Liang, Y.; He, G.; Yang, Y.; Tian, X. Effects of multi-layer graphene on the fracture toughness and wear resistance of WC-11Co cemented carbide. *J. Asian Ceram. Soc.* **2022**, *10*, 453–464. [CrossRef]
79. Emanuelli, L.; Pellizzari, M.; Molinari, A.; Castellani, F.; Zinutti, E. Thermal fatigue behaviour of WC-20Co and WC-30 (CoNiCrFe) cemented carbide. *Int. J. Refract. Met. Hard Mater.* **2016**, *60*, 118–124. [CrossRef]
80. Hadi, M.; Rafiaei, S.M.; Fernandes, F. The effect of Mo_2C additions on the oxidation resistance of (Ti,W) CN cermets as base material for the production of cutting tools. *Ceram. Int.* **2023**, *49*, 21538–21545. [CrossRef]
81. Karimi, H.; Zare, A.; Hadi, M.; Sadeghi, M.; Ghasemi, A. The Effect of Mn Addition on Oxidation Resistance of Ti-48Al Synthesized by Mechanical Alloying. *J. Metall. Mater. Eng.* **2016**, *27*, 93–106.
82. Zare, A.; Hadi, M.; Ghasemi, A.; Karimi, H.; Sadeghi, M. Investigating the Effect of Microstructure on Oxidation Behavior of Ti47Al48Mn5 Alloy Synthesized by Mechanical Alloying. *J. Adv. Mater. Eng.* **2022**, *34*, 31–48. [CrossRef]
83. Samani, M.N.; Shokuhfar, A.; Kamali, A.R.; Hadi, M. Production of a nanocrystalline Ni_3Al-based alloy using mechanical alloying. *J. Alloys Compd.* **2010**, *500*, 30–33. [CrossRef]
84. Hadi, M.; Kamali, A.R. Investigation on hot workability and mechanical properties of modified IC-221M alloy. *J. Alloys Compd.* **2009**, *485*, 204–208. [CrossRef]
85. Ogwu, A.; Davies, T. Proposed selection rules for suitable binders in cemented hard metals with possible applications for improving ductility in intermetallics. *J. Mater. Sci.* **1992**, *27*, 5382–5388. [CrossRef]
86. Sikka, V.; Mavity, J.; Anderson, K. Processing of nickel aluminides and their industrial applications. In *High Temperature Aluminides and Intermetallics*; Elsevier: Amsterdam, The Netherlands, 1992; pp. 712–721.
87. Miracle, D.B.; Senkov, O.N. A critical review of high entropy alloys and related concepts. *Acta Mater.* **2017**, *122*, 448–511. [CrossRef]
88. Tsai, M.-H.; Yeh, J.-W. High-entropy alloys: A critical review. *Mater. Res. Lett.* **2014**, *2*, 107–123. [CrossRef]
89. Dewangan, S.K.; Mangish, A.; Kumar, S.; Sharma, A.; Ahn, B.; Kumar, V. A review on high-temperature applicability: A milestone for high entropy alloys. *Eng. Sci. Technol. Int. J.* **2022**, *35*, 101211. [CrossRef]
90. George, E.P.; Raabe, D.; Ritchie, R.O. High-entropy alloys. *Nat. Rev. Mater.* **2019**, *4*, 515–534. [CrossRef]
91. Khallaf, A.H.; Bhlol, M.; Dawood, O.; Ghayad, I.; Elkady, O.A. Effect of tungsten carbide (WC) on electrochemical corrosion behavior, hardness, and microstructure of CrFeCoNi high entropy alloy. *J. Eng. Appl. Sci.* **2022**, *69*, 43. [CrossRef]

92. Khallaf, A.H.; Bhlol, M.; Dawood, O.; Elkady, O.A. Effect of WC addition on the mechanical properties and microstructure of CrFeCoNi high entropy alloy by powder metallurgy technique. *Int. J. Mech. Eng.* **2022**, *7*, 1127–1134.
93. Xu, B.; Zhou, Y.; Liu, Y.; Hu, S.; Zhang, G. Effect of different contents of WC on microstructure and properties of CrMnFeCoNi high-entropy alloy-deposited layers prepared by PTA. *J. Mater. Res.* **2022**, *37*, 719–727. [CrossRef]
94. Wu, T.; Chen, Y.; Lin, B.; Yu, L.; Gui, W.; Li, J.; Wu, Y.; Zeng, D. Effects of WC on the microstructure, wear and corrosion resistance of laser-deposited CoCrFeNi high entropy alloy coatings. *Coatings* **2022**, *12*, 985. [CrossRef]
95. Zhu, G.; Liu, Y.; Ye, J. Early high-temperature oxidation behavior of Ti (C, N)-based cermets with multi-component AlCoCrFeNi high-entropy alloy binder. *Int. J. Refract. Met. Hard Mater.* **2014**, *44*, 35–41. [CrossRef]
96. Fang, Y.; Chen, N.; Du, G.; Zhang, M.; Zhao, X.; Cheng, H.; Wu, J. High-temperature oxidation resistance, mechanical and wear resistance properties of Ti (C, N)-based cermets with $Al_{0.3}$CoCrFeNi high-entropy alloy as a metal binder. *J. Alloys Compd.* **2020**, *815*, 152486. [CrossRef]
97. Wu, X.; Shen, J.; Jiang, F.; Wu, H.; Li, L. Study on the oxidation of WC-Co cemented carbide under different conditions. *Int. J. Refract. Met. Hard Mater.* **2021**, *94*, 105381. [CrossRef]
98. Penrice, T. Alternative binders for hard metals. *J. Mater. Shap. Technol.* **1987**, *5*, 35–39. [CrossRef]
99. Pereira, P.; Vilhena, L.; Sacramento, J.; Senos, A.; Malheiros, L.; Ramalho, A. Tribological behaviour of different formulations of WC composites. *Wear* **2022**, *506*, 204415. [CrossRef]
100. Liu, R.; Wu, X.J.; Kapoor, S.; Yao, M.X.; Collier, R. Effects of Temperature on the Hardness and Wear Resistance of High-Tungsten Stellite Alloys. *Metall. Mater. Trans. A* **2015**, *46*, 587–599. [CrossRef]
101. Hadi, M.; Bayat, O.; Meratian, M.; Shafyei, A.; Ebrahimzadeh, I. Oxidation properties of a beta-stabilized TiAl alloy modified by rare earth elements. *Oxid. Met.* **2018**, *90*, 421–434. [CrossRef]
102. Zhang, M.; Jiang, Y.; Lin, N.; Kang, X.; Yan, Y.; Huang, J.; Liu, Y.; Qiu, S.; He, Y. Investigation of the oxidation behavior and high oxidation-resistant mechanism of Ti (C, N)-based cermets. *Corros. Sci.* **2020**, *177*, 108959. [CrossRef]
103. Mostajeran, A.; Shoja-Razavi, R.; Hadi, M.; Erfanmanesh, M.; Barekat, M.; Firouzabadi, M.S. Evaluation of the mechanical properties of WC-FeAl composite coating fabricated by laser cladding method. *Int. J. Refract. Met. Hard Mater.* **2020**, *88*, 105199. [CrossRef]
104. Mostajeran, A.; Shoja-Razavi, R.; Hadi, M.; Erfanmanesh, M.; Karimi, H. Wear behavior of laser cladded WC-FeAl coating on 321 stainless steel substrate. *J. Laser Appl.* **2020**, *32*, 042015. [CrossRef]
105. Holmström, E.; Lizarraga, R.; Linder, D.; Salmasi, A.; Wang, W.; Kaplan, B.; Mao, H.; Larsson, H.; Vitos, L. High entropy alloys: Substituting for cobalt in cutting edge technology. *Appl. Mater. Today* **2018**, *12*, 322–329. [CrossRef]
106. Qian, C.; Liu, Y.; Cheng, H.; Li, K.; Liu, B. Effect of the carbon content on the morphology evolution of the η phase in cemented carbides with the CoNiFeCr high entropy alloy binder. *Int. J. Refract. Met. Hard Mater.* **2022**, *102*, 105731. [CrossRef]
107. Qian, C.; Liu, Y.; Cheng, H.; Li, K.; Liu, B.; Zhang, X. The effect of carbon content on the microstructure and mechanical properties of cemented carbides with a CoNiFeCr high entropy alloy binder. *Materials* **2022**, *15*, 5780. [CrossRef]
108. Li, X.; Wei, D.; Vitos, L.; Lizarraga, R. Micro-mechanical properties of new alternative binders for cemented carbides: CoCrFeNiWx high-entropy alloys. *J. Alloys Compd.* **2020**, *820*, 153141. [CrossRef]
109. Fa, C.; Jungui, Z.; Shijia, L.; Keke, G.; Pinqiang, D.; Chao, L.; Xiaofeng, Z. The microstrcture and high-temperature oxidation resistance of tungsten carbide with high entropy alloys as binder. *J. Ceram. Soc. Jpn.* **2022**, *130*, 477–486. [CrossRef]
110. Qin, Y.; Yuan, J.; Zhuang, Y.; Ma, B.; Luo, L.; Wu, Y. Study on Effect of High-Entropy Alloy Binder on Microstructure and Properties of WC Cemented Carbide Doped with Rare Earth Oxide. *Coatings* **2023**, *13*, 273. [CrossRef]
111. Solodkyi, I.; Teslia, S.; Bezdorozhev, O.; Trosnikova, I.; Yurkova, O.; Bogomol, I.; Loboda, P. Hardmetals prepared from WC-W2C eutectic particles and AlCrFeCoNiV high entropy alloy as a binder. *Vacuum* **2022**, *195*, 110630. [CrossRef]
112. Velo, I.L.; Gotor, F.; Alcalá, M.; Real, C.; Córdoba, J. Fabrication and characterization of WC-HEA cemented carbide based on the CoCrFeNiMn high entropy alloy. *J. Alloys Compd.* **2018**, *746*, 1–8. [CrossRef]
113. Luo, W.; Liu, Y.; Luo, Y.; Wu, M. Fabrication and characterization of WC-AlCoCrCuFeNi high-entropy alloy composites by spark plasma sintering. *J. Alloys Compd.* **2018**, *754*, 163–170. [CrossRef]
114. Mueller-Grunz, A.; Alveen, P.; Rassbach, S.; Useldinger, R.; Moseley, S. The manufacture and characterization of WC-(Al) CoCrCuFeNi cemented carbides with nominally high entropy alloy binders. *Int. J. Refract. Met. Hard Mater.* **2019**, *84*, 105032. [CrossRef]
115. Luo, W.; Liu, Y.; Dong, B.; Wu, Z.; Zhou, L. Corrosion resistance of WC-based cemented carbides with 10 wt% AlxCrCoCuFeNi high-entropy alloy binders. *Intermetallics* **2022**, *151*, 107738. [CrossRef]