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The Evaluation of the Non-Toxic Ferrous Matrix Based WC Reinforced Composites: A Review

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Abstract

Metal matrix composites are mainly used as a cutting tool insert material. These types of materials are essential to maintain desired mechanical and microstructure properties at elevated temperatures due to friction and wear. Nano sized Tungsten Carbide reinforced composites are mostly used for these conditions. The production of sintered nano sized Tungsten Carbide reinforced composites are done by using powder metallurgy. The different mass ratios of elements including mostly Cobalt and the others could be added as binder phase. The binder phase provides to metal matrix composite superior features including high elasticity, good solubility, similar thermal conduction coefficient and, effective liquid phase sintering mechanism. Cobalt is one of the base elements of high-performance superalloys and rechargeable battery technology. Also, 40% of global need supplied by a single country makes itself higher-priced. It is also known that Cobalt is a high skin allergen and carcinogenic. Together with these obstacles, the investigations of low-cost, non-toxic, or reduced-toxicity materials are always needed. In this study, the related current literature has been investigated in detail. The studies focus on an alternative matrix that providing mentioned conditions explained with pros and cons.

Keywords: Non-Toxic Materials; Powder Metallurgy; Sintered Carbides; The Carbon Window

1. Introduction

MMC structures are newly formed materials by mixing different elements or alloys with a mass or volume scale. The primary purpose of making MMC materials is to bring and unite the best properties of components in the microstructure [1, 2]. MMC materials have two components. These are matrix and reinforcement phases.

The matrix phase covers the reinforcement phase and ensures homogeneous dispersion within the microstructure. On the other hand, reinforcement materials reveal their unique properties to develop the newly formed composite material. As a result of this combination variety, the newly formed materials have unique mechanical and microstructural properties which not found on both sides. MMC can be produced by many production methods include casting and powder metallurgy (PM) technique [2].

The cutting inserts are composed of multiple compounds and elements as MMC structures. The inserts are usually produced mainly from carbide and nitrides as reinforcing materials (TiC, WC, TiN, CrN, etc.). Such compounds that are ionic or covalently bonded have ultra-high melting temperatures and hardness. Lean carbide or nitride are brittle and difficult to manufacture in complex shapes [3]. For this reason, the binder must be added. The PM technique is used mainly in the production of cutting tool inserts. In this method, parts are made of metal powders. The Traditional PM process is followed; the powders are pre-molded to the desired shape, pressed compactly, and sintered to create a chemical bond. Sintering is usually done at a temperature nearly above the melting temperature of the binder. One of the essential factors in the sintering process is the wetting capability of the binder phase. The binder material is expected to fill the gaps in the microstructure well, wet the main reinforcing phase, and dissolve in it [2].

Different researchers have carried out experimental and theoretical studies on W-Fe-C systems. The focus of the studies was on the C ratio, austenite (Fe-γ) ratio, and Fe-containing carbide structures. Uhrenius, Forsén [4], studied the carbide, ferrite, and austenite ratios in the structure at 1000°C. They reported that the C ratios in

W-Mo-Fe-C, W-Fe-C, and Mo-Fe-C systems varied between 0.012 and 0.097. In the ternary W-Fe-C system, they observed ferrite (Fe-α), M_6C, Fe_3C, and austenite.

Kirchner, Harvig [5], investigated carbide and austenite formation kinetics in the W-Fe-Cr-C system. The studies were carried out at three temperatures, 900°C, 1000°C, and 1100°C. They reported that as the ratio of W and Cr in the structure increased, $M_{23}C_6$ type carbide lost its stability compared to M_6C type carbides. They also reported that $M_{23}C_6$ type carbides for W-Fe-C systems are metastable at these temperature ranges. This occasion has been confirmed by other studies as well [6, 7]. In another study, Upadhyaya [8] investigated the formation kinetics of Fe-containing MC, M_6C, and $M_{12}C$ carbides in metal matrix composites. He found that carbide formations containing lean Fe were metastable and brittle in his study. This occasion indicates that Fe alone cannot show sufficient binder performance. Ni also exhibits good corrosion resistance due to its similarity to Co in terms of microstructural properties. Researchers consider it an alternative binder due to the proximity of melting points to Co [8]. The fact that the lattice structure is face-centered cubic also ensures that it has a ductile character. However, the main reason why Ni or any element cannot be used directly alternative to Co in a pure state is that it has high stacking fault energy [9]. The high stack faulting energy reduces the strength of the material. This situation causes lower hardenability in the materials to be formed. Ni can wet and dissolve WC well. But it is insufficient to perform on its own.

Hard carbides such as WC are the most commonly used cutting tool reinforcement phase in MMC materials. Due to high hardness and chemical stability at elevated temperatures, WC advances rapidly among them. Co is an essential element that makes WC a cutting tool material. Due to having a similar thermal conductivity coefficient and excellent wettability in WC, Co provides superior toughness, elasticity, and liquid phase sintering occurrence [10]. However, Co is one of the base elements of high-performance superalloys, and rechargeable battery technology increases its production cost [11]. It is also a severe skin allergen and cancer trigger [12]. Due to these reasons, the search for non-hazardous alternative binder materials continues.

In this study, the microstructural and mechanical properties of nonhazardous and economical elements and compounds, which can be an alternative to the toxic Co element in sintered WC materials, were investigated as literature data. Within the scope of the article, applied alternative binding matrix materials in the literature was investigated. Identified candidate material were divided into groups and are presented to the readers with their pros and cons.

2. Materials and Methods

2.1. WC Reinforced Metal Matrix Composites

MMC materials are one of the most successful produced engineering materials. Sintered carbides, mainly composed of WC bonded with Co or the other elements and alloys, are also MMC materials. In the English technical literature, sintered carbides are known as “Cemented Carbides.” The term "cement" is given because the binder acts like a "cement" among hard carbide grains. For sintered carbide materials, the binding capacity of the binder is an essential factor. Fig. 1 represents the main components of sintered carbides consisting of WC and binder matrix. WC phase is exhibited as grey layers, while the binder exhibits black layers. The role of the binder is of great importance for these materials. Fig. 2 shows the mechanical properties of carbide structure based on research. One can be implied that WC has superior mechanical properties among the carbides.

The first produced Co content sintered WC carbides goes back to the 1920s in history. It has been used in wire production and defense industry applications [13]. Over time, it has begun to be used as a cutting tool in the manufacturing industry by replacing high-speed steel due to its high mechanical properties. When today's manufacturing industry cutting tool materials are examined, it is noteworthy that MMC materials still form a vital part of the tool materials industry [14, 15]. For many years, the Co element has been under surveying about the substitution with nontoxic and economical candidates. Among the reasons for change is the price fluctuation of Co and especially for hazardous effects [16]. Co powder is known to be carcinogenic and skin allergen [17]. It is known that approximately 90% of the WC tools used in the industry are Co-based due to their high hardness and wear resistance [18].

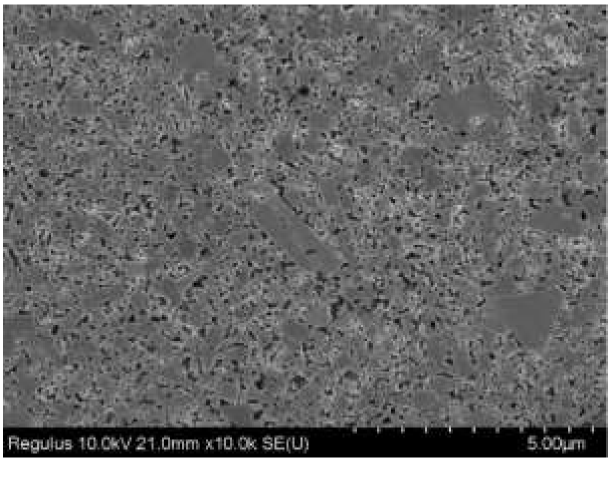

Figure 1. Typical nano-sized WC reinforced MMC containing 10% binder (wt)

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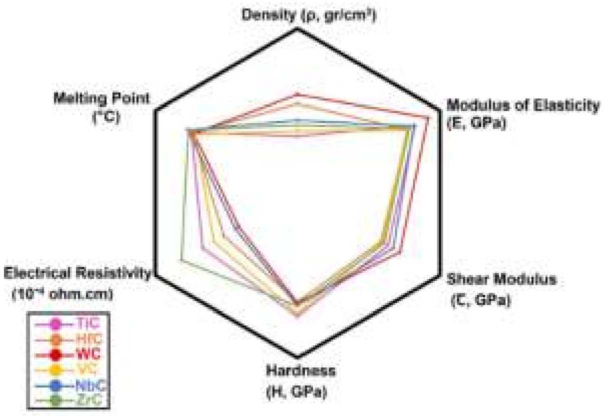

Figure 2. Mechanical performance of carbides. The figure was created by authors based on the data of Bauccio [19]

WC-based sintered carbides are the most important among the cutting tool materials. So, superior material performance, price fluctuation, and hazardous effects of Co element enhance the efforts to seek alternative binders even more.

The WC phase provides the necessary strength and wears resistance to the MMC for the sintered carbides, while the Co contributes to the toughness and ductility. Different elements and compounds can also be added to the structure to prevent abnormal grain growth and increase the microstructure's mechanical properties. For example, VC can also be added to the microstructure as a WC grain inhibitor even though it enhances the mechanical properties of the material, increasing processing costs [20].

Sintered WC – Co is typically used in drilling or cutting tools and manufacturing wear-resistant materials due to its superior hardness and wear resistance. The main usage areas are turning, milling operations, glass cutting tools, and plastic deformation applications such as forging-drawing dies and mining operations tools [15].

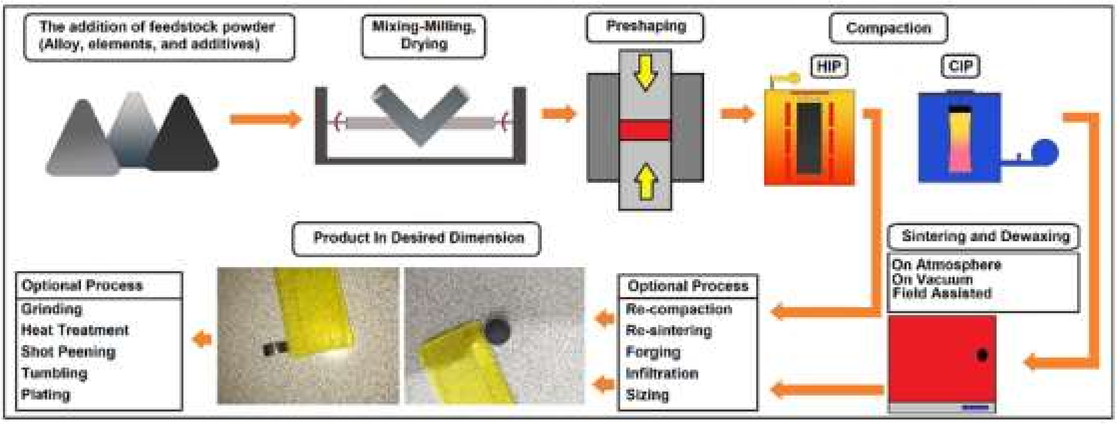

Figure 3. The basic production schema of MMC

Fig. 3 shows the basic production techniques of sintered carbide for powder metallurgy. The powders are mixed and pressed, then sintered at temperatures around 1300ºC -1500ºC, where the binder transforms the liquid phase. Due to the differences in thermal expansion coefficients, carbide grains are forced to compaction, while the binder phase forces the microstructure to the tension, and both phases equalize each other. Thus, homogeneous stress-free structures are obtained [21].

2.2. The importance of WC as a Reinforcement Material

Within the scope of the current research, WC preserves its rigidity, hardness, and chemical stability at elevated temperatures. Three intermediate compounds are presented for WC formations. These are W_2C, WC_{1-x}, and WC. The W_2C compound can exist in three different crystal structures. These are α-W_2C in the orthorhombic crystal structure, β-W_2C in an irregular hexagonal structure, and γ-W_2C in a hexagonal structure. The most stable structure at room temperature is α-WC in a hexagonal structure. This structure has no solid resolution up to 2538˚C.

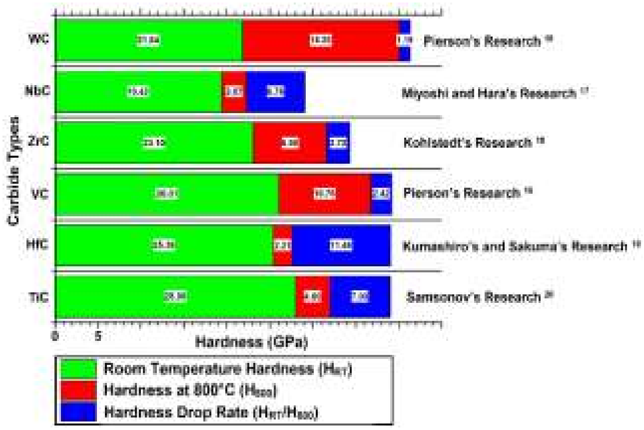

Figure 3. The hardness derivation of the metal carbides

W_2C overreacts with the C binder, causing brittleness, while the amount of C reduces toughness and stiffness. In another alloy, WC + C, the amount of carbon reduces hardness but does not affect toughness and sintering conditions [22].

Fig. 4 exhibits the hardness behavior of the different carbides upon the increasing temperature. It is observed that WC maintains its strength at 800°C compared to other carbide types. It is seen that WC has the lowest hardness drop ratio at elevated temperatures. These conditions make WC relatively more featured than other carbides [22].

3. Results and Discussion

3.1. Binder Materials

Today, many metals, compounds, and alloys are on trial as matrix materials for WC reinforced MMC. The most significant feature expected from the matrix material should improve inter-reinforcing bonding and overall structural strength. In this context, the general properties of the most common metals and alloys used as matrix material are summarized below.

Many studies have been conducted on carbide materials with sintered WC-Co content, including different binders. It is observed that current studies have been limited to experimental studies on the coating of the sintered carbides. This study focused on determining the properties required to select the best binder combination to replace Co by using literature. In the scope of the study, the microstructural, mechanical, and tribological properties of the materials were considered in the selection of binders. The literature research on the current topic has been expressed under seven main sections, including Co, Ni, Fe, Fe-Mn, Fe-Al, FeAl-B, and Fe-Ni binder content. Related literature topics were researched, and the studies were summarized according to the determining criterion.

3.2. Co-Based Binder Systems

The composition of the sintered WC-Co determines the microstructure and mechanical properties significantly. WC-Co binary phase combinations contain graphite and carbide phases called eta (η, which can be seen in Fig. 5 as black zones) that are not desired to form in the microstructure. These phases cause a significant deterioration of both the mechanical properties and the tribological properties of the composite. This pernicious situation is prevented by C control at the stoichiometric level in WC. Therefore, the carbon content must be kept within a narrow limit to obtain the desired compound with optimum properties.

Besides, some Co-containing carbides have negative effects on the mechanical properties of the microstructure. Co-containing carbides are formed in compositions in the range of W_2C_4 (MC_2 type) and $Co_{3.2}W_{2.8}C$ (M_6C type) and are nucleated and grown during the sintering process.

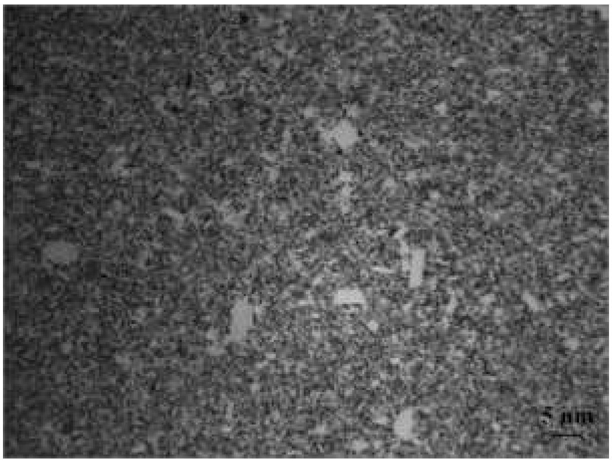

Figure 5. Typical microstructure of sintered carbides contain eta (η) type carbides and graphite

Co-containing M_6C carbides interact less with the binder, loosening the microstructure and reducing WC's contribution to the strength of the MMC material. This causes the general microstructure to become brittle. Two types of phases, M_6C and $M_{12}C$, are formed during sintering. Of the two types of phases, M_6C occurs in compositions in the range of W_2C_4 to $Co_{3.2}W_{2.8}C$, while $M_{12}C$ occurs in the form of Co_6W_6C. The M6C is in equilibrium with the liquid phase during the sintering process. The M_6C interacts less with the binder phase to loosen up the bondings of the microstructure. It also reduces the contribution of WC to the strength of the composite material and causes the overall bulk material to become brittle. Conversely, in the $M_{12}C$ type, it occurs in the form of small grains scattered all over the matrix when cooling after solidification. Due to the increased grain limit, it provides high strength and less brittleness [28-30].

3.3. Ni-Based Binder Systems

Co is the most commonly used traditional binder metal for WC reinforced composite materials. Ni is thought to be the most likely candidate to replace Co to the research. However, Ni's high ductility and low tribological properties prevented its commercial applicability [30-32]. Bonny, De Baets [33], examined the abrasive wear resistance of WC reinforced composite material with four different Ni phase contents at different wear load and sliding speeds. As a result of their experiments, they found that the hardness and wear resistance increased as the amount of the binder phase decreased. The highest wear resistance was observed in the group containing 10% Ni with Cr_3Cr_2 addition compared to the lean Co phase. Even if the Ni ratio increased in all samples, the wear resistance did not perform higher than the reference group.

Ni's high ductility also provides higher mechanical properties. Tarragó, Ferrari [9], produced WC-reinforced MMC materials with Ni matrix. They compared the mechanical properties of the produced materials with the WC-Co material. They found that composites with Ni matrix exhibit similar fatigue strength. The crack propagation tests reported that Ni-containing material showed more stable crack propagation.

Besides the production cost of Co, it adds composite higher mechanical properties, making it a superior and more preferred binder than Ni. Also, the resolutions of Co and Ni in WC are pretty different from each other. Co can solve more WC at higher temperatures than Ni [31]. At low temperatures, it was found that the situation reversed [4]. However, this situation cannot provide the necessary contribution in cases where liquid phase formation is desired. In the case of compositions containing excessive C at high temperatures, the solubility of Ni and Co was found to be almost the same [34]. This indicates that Ni will increase its effectiveness when used with different elements. Also, the Ni element forms $Ni_xW_yC_z$ type carbides in the Ni-W-C system like Co. Different studies have determined that this type of carbide formed is more ductile than Co-containing carbides [31, 35].

Ni exhibits good corrosion resistance due to its similarity to Co in terms of microstructural properties. Due to the similar melting points to Co, researchers thought it to be an alternative binder [8]. Penrice [36], made a theoretical study on alternative binder matrix materials to Co. He studied Ni, Re, Ru, Mo, and Cr elements. He observed that although Re and Ru have similar effects as Co. Due to their unit cost and rare earth elements status, these elements aren't attractive as potential candidates. He also stated that Cr and Mo additives provide higher strength but have low corrosion resistance compared to Co. The author also reported that Ni is an austenitic binder due to its face-centered cubic structure and that it can also turn into a body-centered cubic structure in alloys if it can be used with other elements such as Fe, C, Cr, Mo. He reported that Ni's austenitic structure was also suitable for heat treatment.

Some studies are using one or more Co, Mo, Cr, V, and Mn elements to increase the hardness and strength of Ni alloys. The results of numerically computational phase methods (CALPHAD) determined that the phase would be stable in binders with different contents. Also, it has been observed that Ni performs better hardness and toughness properties in comparison to Co ingredients [37-39]. Guo, Xiong [8], produced Ni-WC-TiC-Mo_2C composite materials in different proportions and grain sizes. They applied bending and hardness tests to the produced MMC. It has been determined that the bending strength decreases with the decrease of the Ni ratio. Also, the strength of the reinforcing phase increases with decreasing grain size. It is known that Mo_2C is a well-known grain growth inhibitor. It was observed that with the increase of Mo_2C additive, the WC grain structure shrank, and the hardness and bending strength increased.

The fact that the crystallographic structure of the Ni element is a face-centered cubic provides a ductile behavior. But the main reason Ni or any element cannot be used directly instead of Co is stacking fault energy. [9]. High stacking error energy reduces the strength of the material. This situation caused the lower hardenability of the MMC materials. The inadequate performance of the alternative binders forces the industry to use Co-Ni-containing compositions. The development of non-toxic material is a need.

3.4. Fe-Based Binder Systems

Different researchers carried out experimental and theoretical studies on W-Fe-C systems. The orientation of most of the studies was on the C ratio, austenite (Fe-γ) ratio, and Fe-containing carbide compound in the microstructure. Uhrenius, Forsén [4], researched to determine the carbide, ferrite, and austenite ratios in the microstructure at 1000°C. They reported that C ratios in W-Mo-Fe-C, W-Fe-C, and Mo-Fe-C systems ranged from 0.012 to 0.97. The balance between ferrite (Fe-α), M6C, Fe3C, and austenite was observed in the triple W-Fe-C system. Kirchner, Harvig [5], investigated carbide and austenite formation kinetics in the W-Fe-Cr-C system. The studies were carried out at three temperatures: 900°C, 1000°C, and 1100°C. They reported that as the ratio of W and Cr in the structure increases, $M_{23}C_6$ type carbide loses its stability compared to M_6C type carbides. They also reported that $M_{23}C_6$ type carbides for W-F-C systems were metastable at these temperature ranges. This situation was confirmed by different studies. [6, 7]. Hou, Linder [16], and C. B. Pollock [40] investigated the variations of the stoichiometric composition of Fe matrix composites. Both papers reported homogeneous formation gaps for $M_{12}C$ and a smaller composition gap for M_6C than other binder types. In terms of formation kinetics, it was determined by these studies that it provides a more homogeneous microstructure. To evaluate mechanical properties, Moskowitz, J. [41] produced WC-Fe composites. They investigated the amount of brittle η phase (Fe_3W_3C) formed in materials produced in different ratio. They examined the mechanical (bending test) and tribological (abrasive wear) properties of the produced MMC. In the tests carried out, they determined that relatively close results were obtained for Co alloys.

Upadhyaya [21], investigated the formation kinetics of Fe-containing $M_{12}C$ carbides in MMC. He found that Fe content $M_{12}C$ carbide formation was not observed. This indicates that Fe alone does not have sufficient binding performance. Schubert, Fugger [42], examined the WC-Fe structures. They found that the WC phase prevents grain growth due to the high affinity of Fe compared to Co. They also found that this condition provides high hardness after sintering. However, they found that high C affinity triggered the formation of M_6C phases known to be hard and brittle. They reported that using only the Fe element as a binder material shows low corrosion resistance and that single Fe use is insufficient for WC reinforced composite materials.

3.5. Fe-Mn Based Binder Systems

Another system considered as an alternative to the Co element is Fe-Mn alloys. It can be considered an advantage that the Mn element is an austenite trigger. It is also known that Mn increases the strength of the steel. Besides, having a body-centered cubic lattice structure makes Mn easy to form like Ni. However, the low melting temperature makes drawbacks for use as a matrix phase. Schubert, Fugger [42], produced a WC-(FeMn) content MMC. Because of the low melting temperature of the Mn element, they could not use high sintering temperatures to reach the melting of Fe. They observed that after the sintering process, which was performed at 1380°C for 1 hour, 16% of Mn remained in the microstructure. Mn mass losses were observed. The evaporated Mn particles caused high porosity in the microstructure. Therefore, Fe-Mn cannot be used effectively for cutting insert material.

3.6. Fe-Al Based Binder Systems

Fe-Al is a good alternative to Co due to its excellent physical and mechanical properties. It has been researched by many researchers for making composites containing Fe-Al and WC. It was found that the Fe-Al content composites have performed equivalent wear resistance, hardness, and oxidation resistance as WC-Co [43-45]. In general, the corrosion resistance of Fe-Al is known to perform better than that of the Co metal [46]. This situation indicates that Fe-AL content composites have the potential for use in corrosive environments. Apart from that, Fe-Al has some disadvantages. In terms of thermodynamic calculations, it has been calculated that the ability to solve WC is lower compared to Co (2% at 1450°C). While the spark plasma sintering (SPS) technique provides performance equivalent to Co, the conventional PM has been found to exhibit lower tribological and mechanical properties [46]. This situation concerns economic costs.

3.7. FeAl-B Based Binder Systems

The potential use of Boron (B_2) content FeAl structures in high-temperature applications has been investigated by many researchers for the last 20 years [43, 47-49]. Adding (FeAl)B2 alloys performs better oxidation, corrosion, wear-resistance, and strength. The enhancing microstructural mechanism for this situation is work hardening [43]. Ahmadian, Wexler [50], produced the hot-pressed WC-FeAl-B composite to observe the B_2 effect. Their study observed that a small amount of B_2 additives (500ppm) could increase the toughness and prevent WC grain growth. They also found that B_2 additive composites perform higher abrasive wear resistance. This situation makes B_2 content intermetallics potential candidates for WC reinforced MMC.

3.8. Fe-Ni Based Binder Systems

Fe-Ni compositions are currently being studied by many researchers to replace the conventional Co binding phase or to reduce the Co ratio due to a pretty low production cost. When the results are evaluated in microstructural and mechanical properties, chemical composition, and process conditions are well determined, these alloy systems could achieve comparable or even superior properties to Co-containing binders. [29]. Also, by carefully controlling the Fe-Ni composition ratio, carbon content, and thermodynamic processes, the desired degree of stability of the binding phase could be achieved. Thanks to the stable phase presence provided, it is predicted that with the transformation toughening seen in the Fe-Ni binder, higher toughness will be obtained without loss of hardness compared to the classical WC-Co composition [51].

There are studies about the PM method and various sintering techniques under different Fe and Ni binding ratios. A literature survey was carried out regarding the mechanical and microstructural behaviors. The studies that are found are summarized below:

Cramer, Preston [31], examined the production and mechanical properties of WC- (Fe-Ni) composite materials containing Fe-Ni in situ forms. Ni powders were melted on Fe-WC material which was pre-shaped differently. As a result of the study, 97% theoretical density and 6.72 GPa hardness was observed on WC-(FeNi) pellet composite material. They reported that Fe-Ni could be an alternative to WC-Co materials after proper sharpening operations for machining. Hou, Linder [16], investigated the effect of C ratio in materials on Curie temperature and binding content of carbides formed in WC-(Fe-Ni) composite. They found that Ni was austenitic, and it changed the paramagnetic specialty based on the content of carbides. Increasing the C ratio from 5.72% to 5.83% increased the curie temperature from 200˚C to 572˚C. They determined by XRD methods that even the slightly varying C ratio, the dramatic variation of the Curie temperature was due to the formation of Ni-rich carbides. De Oro Calderon, Agna [52], produced MMC materials consisting of WC and AISI 360L. Experimental studies examined the microstructural and mechanical properties in terms of four different matrix phase ratios. They reported that the binder material does not retain its stainless steel property and shows an austenitic behavior even at increasing sintering temperatures. In addition, they found that $M_{23}C_6$ and M_7C_3 type carbide formation kinetics are high due to the Cr-rich stainless steel binder. Because of the high C range, undesired metastable η type carbides were observed in all control group samples.

Fernandes, Puga [53], formed a compound by applying high-energy grinding technique with different parameters to nano-sized WC-AISI 304 powder containing 12% stainless steel by mass. As a result of the dilatometry analysis, they observed that M_6C type carbides, which are known to have low mechanical and microstructural properties. Besides, it was determined that nano-sized powders perform better binding and activation energy in solid-state sintering than micron-sized powders. Tarraste, Kübarsepp [54], used AISI 430L ferritic stainless steel to produce WC-reinforced composite material. They examined microstructural properties for produced MMC at constant sintering temperature at five different binder chemical ratios and six different sintering temperatures. They found that the practical density increases as the sintering temperature decreases. The liquid phase formed between high sintering temperatures (1100˚C -1200˚C). They also found that the increased binder phase ratio enhances the fracture toughness. They stated that this situation was related to the binder phase ratio, increasing C value, and correspondingly decreasing η phase ratio in the microstructure.

It has been confirmed by many studies that, the ratio of the liquid phase in the structure is very critical. In the liquid phase sintering process, the matrix is melted and bonds to the reinforcement, followed by cooling and solidification. It is recommended that the matrix ratio should not be more than 25% for liquid phase sintering processes in the industry. [2].

Cacciamani [55], obtained a binary Fe-Ni diagram numerically and experimentally in his study. As a result, they showed that melting temperatures for the Fe-Ni mixture state containing 10-20% Ni are in the 1400°C band while Co can solve them WC amount in ranges are around 1900°C. This shows that the binders with Fe-Ni content can provide sintering at much lower temperatures. This occasion would decrease the thermal distortion of bulk composite material. Also, these temperatures are lower for Ni alloys that are predicted to exhibit similar mechanical properties. Fe-Ni alloys can provide lower temperatures for sintering. Liquid phase sintering temperatures are around 1400°C in Fe-Ni containing nearly 20% Ni. They exhibited that Ni alloys would provide the desired hardness and strength by adding the Fe element to the structure.

Fernandes, Senos [56], produced composite materials using the SPS technique with WC-AISI 304 stainless steel powder. They examined the effect of sintering at different temperatures on material density, brittle η phase formation, and liquid phase occurring formation temperature. They found that sintering at high temperatures reduced the density but increased the liquid phase ratio. They reported that the used alloy composition caused the formation of eutectic structures at 1100˚C.

Wittmann, Schubert [57], produced composite materials containing WC-Fe-Ni content. They reported that the formation of the brittle Fe_3W_3C phase can be prevented by lowering the carbon density. But more importantly, they reported that with the addition of Ni or a similar austenite phase formation trigger element, the alloy exhibits equivalent bending strength comparison to Co. Besides, with the optimum addition amount of Ni, it has been observed that the structure transformed into the austenitic state. They also reported that the heat treatments can improve the Fe-Ni matrix due to the austenitic structure.

Gonzalez, Echeberria [58], produced WC-Fe-Ni-C composite materials with a PM technique. They applied different heat treatments to the produced specimens. Microstructures and mechanical properties of heat-treated materials were investigated. It has been determined that the highest fracture toughness occurs in the bainitic transformed matrix, which is also equivalent to the traditional WC-Co reference group. They reported that it would be beneficial in terms of K_{1c} to transform the binder phase into a bainitic or martensitic microstructure by heat treatment. They also emphasized that this would improve dynamic toughness without any loss in hardness.

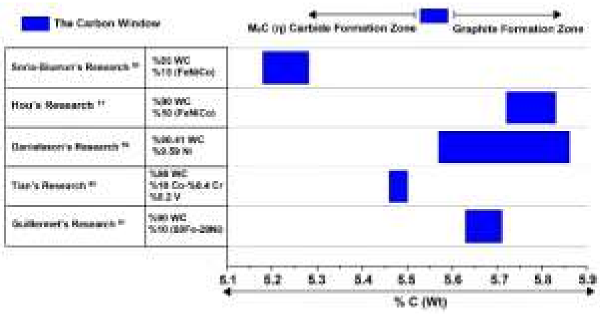

Figure 6. The carbon window of different compositions

Fig. 6 shows researchers' carbon content research of different WC- % 10 compositions. When the diagram is examined, it is seen that a large part of the composition consists of M_6C and Graphite structures. M_6C carbides and graphite structure are known to be brittle. The reason for the formation of these structures can be seen from the diagram, which depends on the C ratio by mass.

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Therefore, the C ratio in the microstructure of MMC is critical and needs to be adjusted correctly. The amount of C contained in the composition should be optimized to prevent the formation of Graphite and M_6C. The critical carbon content region must be determined correctly after choosing the Fe: Ni ratio to achieve satisfactory results. In the literature, this situation is referred to as a carbon window.

The lower and upper values of the carbon window vary according to the elements and their proportions in the matrix alloy. According to the studies to be carried out, the matrix ratio included in mass should be well computed [62]. Carbon windows should be calculated using either experimental or CALPHAD methods for matrix combinations for different ratios. This situation also occurs in Fe-Ni compositions. Fig. 6 shows the carbon window ranges for a different compositions. As shown in Fig. 6, the carbon range of the Co content alloys is narrower than Ferrous based alloys. Thus, it is known that the Ni element cannot be a matrix material alone due to high stack faulting energy and health issues [63]. Therefore, the Fe-Ni alloy mixture is more appropriate as a potential candidate.

There is also research evaluating the martensitic transformation of Fe-Ni and Co binders [64, 65]. Acet, Schneider [65] showed that the compositions containing up to 30% Ni are suitable for martensitic transformation. Therefore, it appears that the properties of the Fe-Ni content matrix in this range can be improved by cryogenic or conventional heat treatment [66].

Table 1 emphasizes the critical alteration in the use of different matrix for WC-reinforced MMC materials. It is seen that the lean alternative binder matrix materials as Fe and Ni cannot provide the requirements as lean Co performs.

Table 1. Significant changes due to the use of different binder matrix in composites

Matrix Type	Comparison to Co Binder Matrix	Author
Fe Matrix	• Grain growth inhibition • Lower oxidation resistance due to C affinity • Brittle η phase formation • Higher average hardness • Lower atmospheric corrosion resistance	[36, 41, 57]
Fe-Co-Ni	• Higher fracture toughness • Higher abrasive wear resistance • More free C in the microstructure	[67]
Fe_3Al-B	• Fine-grain structure • Equivalent fracture toughness and wear resistance	[68]
Fe-Mn	• Higher porosity • Evaporation of Mn element during the sintering process • Very low fracture toughness • Equivalent hardness • Lower wear resistance	[42]
Ni Matrix	• Higher corrosion resistance • Lower hardness and wear resistance	[8, 9, 36]
Ni_3Al, NiAl	• Higher corrosion resistance • Lower bending strength and wear resistance • Equivalent hardness	[43, 68-70]
Ni-Cr-Mo	• Equivalent toughness and hardness	[71]
Ni-Si	• Lower hardness • Higher bending strength	[72]
Ni-Cr	• Higher porosity ratio in the microstructure • Equivalent toughness • Higher sintering temperature requirement • Lower electrical conductivity	[30]

4. Conclusion

When the comparative literature was carefully examined, it was seen that the use of different matrix materials in WC reinforced composites had essential effects on mechanical and tribological properties. The using effects of the different elements and alloys as an alternative matrix are explained by different mechanisms, including sintering type and temperature, grain growth preventing, and forming a new compound. Under the influence of the mechanisms mentioned above, Fe-Ni, Fe-Ni-Co, and Fe3Al-B alloys could provide equivalent or higher mechanical and microstructural performance than plain Co elements. It is reasonable to use Fe-Ni-based materials suitable for heat treatment, such as cryogenic heat treatment, which is also cheap and reduced toxicity situation, would provide equivalent or higher contributions comparison to Co variants.

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Author's Contributions

Esad Kaya: Drafted and wrote the manuscript.
Mustafa Ulutan: Assisted and supervised the planning progress. He also revised interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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