Microstructure Characterization of Nickel Matrix Composite Reinforced with Tungsten Carbide Particles and Produced by Laser Cladding

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1. Introduction

In recent decades, metal matrix composites (MMC) have been increasingly used for many industrial hardfacing applications, as these materials may possess distinct resistance against abrasive and adhesive wear even under severe operating conditions. The high wear resistance of MMC is mainly due to the fact that hard reinforcement particles remain intact under loading and, thus, counteract plastic surface deformation of the surrounding softer matrix.[1] This becomes particularly important if the mechanical properties of the matrix degrade at elevated temperature. Consequently, increasing the overall hardness of surfaces being in sliding contact tends to decrease the wear rate (i.e., the volume of material removed per unit sliding distance), e.g., as expressed by Archard’s equation.[2]

Many thermal spraying and welding processes for producing wear-resistant MMC claddings exist.[3,4] Researchers studied the process characteristics of high velocity oxy-fuel spraying (HVOF)[5–9] and its derivates,[10] atmospheric plasma spraying (APS) with[11] or without[12] laser support,
electric arc spraying (EAS)\textsuperscript{11–15} plasma-transferred arc surfacing/welding (PTAW)\textsuperscript{16–24} or gas metal arc welding (GMAW).\textsuperscript{25–31} Moreover, they investigated the microstructures and the wear resistances of MMC claddings, which consisted of different types of hard carbides embedded in comparatively soft iron-, cobalt-, or nickel-based matrices, and which were produced using the aforementioned processes.

In particular laser metal deposition (LMD), also known as laser cladding, has been established as efficient and flexible process for manufacturing wear-resistant MMC layers\textsuperscript{32,33} LMD utilizes the energy of a laser beam for superficial melting of the metal substrate and for fusing powders of carbides and metal alloys, which are either predeposited on the surface of the substrate (two-step process) or injected into the melt pool or laser spot, respectively (one-step process).\textsuperscript{34–37} Blends of nickel alloy powder and tungsten carbide powder composed of spherical or crushed particles are typically used for producing MMC claddings, which are suitable for abrasive wear applications at elevated temperatures and corrosive environments.\textsuperscript{38} Alternatively, a nickel alloy wire can be fed simultaneously with the carbide powder into the melt pool\textsuperscript{39,40}.

During LMD processing, the nickel-based wire or powder, respectively, melts and forms the matrix, in which the thermally more stable tungsten carbide particles are embedded. Partial dissolution of primary carbides and formation of secondary carbides can be observed at the interface between the matrix and the particles, which may affect the properties of the MMC cladding. In particular, the laser process parameters were identified to influence the dissolution tendency of the carbide particles and the microstructure of the cladding.\textsuperscript{39–52} Increasing the specific energy input by reducing the powder feed rate or the scanning speed of the laser beam,\textsuperscript{41,42} or by increasing the interaction time between the laser beam and the powder,\textsuperscript{43} was found to facilitate the dissolution of primary tungsten carbide particles in the metal matrix. At optimum laser power, carbide particles were homogeneously distributed within the matrix and needle-like secondary phases formed at the interfaces, which improved bonding between the particles and the matrix.\textsuperscript{44–46} Depending on the particular properties of the powder being processed, similar effect was also observed at maximum laser power but medium scanning speed,\textsuperscript{47} or at moderate laser power and high scanning speed.\textsuperscript{48}.

Excessive laser power, too low scanning speed, and too low powder feed rate cause severe dissolution of small spherical carbide particles, promote inhomogeneous distribution and clustering of particles, and facilitate formation of pores particularly at the zones between the overlapping cladding tracks.\textsuperscript{49} Moreover, high concentration of residual stresses makes the zones between the tracks susceptible to crack propagation,\textsuperscript{50} and lack of hard particles was observed to decrease the local wear resistance between the tracks.\textsuperscript{51} Therefore, the specific energy input is the key factor that has notably higher impact on the dissolution of primary carbides and on the formation of secondary phases than, e.g., the laser type used in the process.\textsuperscript{52}

Besides the laser process parameters, the initial temperature of the substrate has considerable influence on the microstructure of the cladding. Preheating the substrate to 300 °C was proposed to promote dissolution of tungsten carbide particles and to increase the overall hardness of the cladding, which is due to the formation of secondary carbides within the nickel-based matrix.\textsuperscript{53} In addition, preheating the substrate to 150–450 °C can reduce the cracking tendency of claddings containing high weight fraction of carbides.\textsuperscript{54,55} Increasing the average preheating temperature also allows for increasing the scanning speed of the laser beam and the powder feed rate, which improves the overall efficiency of the cladding process and reduces dissolution of tungsten carbides and formation of cracks.\textsuperscript{56–59} Moreover, a carbide-free buffer layer\textsuperscript{49,51} or a graded carbide-depleted buffer layer\textsuperscript{60} between the hardfacing layer and the substrate can prevent cracking.

Abrasive wear tends to decrease with increasing weight fraction of hard carbides, i.e., with increasing overall hardness of the cladding. However, depending on the type of particles, this effect may diminish beyond 30 wt%\textsuperscript{61} or may even turn into its opposite beyond 40 wt%.\textsuperscript{62} Optimum and maximum weight fractions of 25 and 50 wt%, respectively, were proposed for crack-free claddings with low porosity and homogeneous distribution of spherical tungsten carbides.\textsuperscript{47} Weight fractions up to 50 wt% were also recommended for thermomechanical rolling applications at high temperatures of 650 °C.\textsuperscript{51} Some researchers even obtained defect-free claddings with weight fractions of 60 wt%\textsuperscript{54} in studies using crushed carbides, the optimum weight fraction was 30 wt%,\textsuperscript{63} and superior wear resistance at both room temperature and high temperature of 700 °C was achieved at maximum weight fraction of 60 wt%.\textsuperscript{64} Increasing the weight fraction of carbides generally improves the wear resistance of MMC claddings; however, the tensile properties decrease significantly.\textsuperscript{65} Although the weight fraction of carbides and the size of the embedded particles were identified to influence most wear modes in MMC claddings,\textsuperscript{66–68} the distance between the carbide particles (“inter-particle distance”) was proposed to have stronger effect on the wear rate than the fraction or the equivalent diameter of the particles.\textsuperscript{69}

The dissolution tendency and the hardness of tungsten carbide particles and, thus, the wear resistance of MMC claddings are considerably influenced by the chemical composition of the particles. For instance, crushed particles consisting mainly of coarse-grained WC have lower dissolution tendency but also lower hardness than fused spherical particles consisting of fine-grained WC and W\textsubscript{2}C.\textsuperscript{70,71} In GMAW experiments, a possible dissolution mechanism of thermally unstable fused WC/W\textsubscript{2}C particles inside of a nickel-based matrix was observed: when primary W\textsubscript{2}C dissolves selectively at the surfaces of the particles,\textsuperscript{27} W and C are enriched in the surrounding nickel-based melt and the remaining particles act as nucleation sites for secondary WC forming from W and C.\textsuperscript{31} This mechanism, however, does neither account for possible phase transformation nor for fast diffusion of carbon within the solid at elevated temperature.

Dissolution of tungsten carbides within nickel-based matrices was also studied at defined temperature–time profiles in vacuum sintering using crushed WC particles\textsuperscript{72} and in liquid-phase sintering using spherical WC/W\textsubscript{2}C particles.\textsuperscript{73,74} Two different layers of carbides, each of both possessing lower hardness than the primary carbide particles, were identified at the matrix/particle interfaces. Formation of the inner layer (next to the primary particle) due to carbide dissolution was diffusion-controlled, whereas formation of the outer layer (next to the matrix)
due to boundary reactions between the nickel-based matrix and the WC/W₂C particles was reaction-controlled.\textsuperscript{[73]} With increasing process temperature or process time, the dissolution tendency of primary carbides and the formation of secondary phases increased. Once the hardness gradient at the interface became steeper, bonding between the carbide particles and the matrix decreased. Hence, smooth hardness or stiffness gradients may improve the wear resistance of MMC.\textsuperscript{[74]} In principle, this was confirmed by numerical simulations considering stiffness and thickness variations at the interface.\textsuperscript{[75]}

Crack- and pore-free layers and limited dissolution of reinforcing particles are only achieved with optimum LMD process parameters. Even though partial dissolution of primary carbides and formation of secondary phases seem to improve bonding of the particles inside the matrix, excessive dissolution must be prevented as hardness and, thus, wear resistance of the cladding would decrease. As the feasible process window is usually quite narrow, detailed investigation of the microstructure obtained with a particular combination of processing parameters and particle type is required for producing defect-free cladding layers. Therefore, the present work characterizes in detail the microstructure of a particular laser-clad MMC, which consists of a pore- and crack-free nickel matrix and of 30–50 wt\% of spherical tungsten carbide particles. This cladding was already optimized and tested at lab scale for potential application in steel hot rolling mills.\textsuperscript{[76]} As the hardness is considered as the key parameter influencing the wear resistance of MMC, special focus was placed on investigating the relationship between the hardness of the reinforcing particles and their microstructure, which depends significantly on the parameters of the particular LMD process and on the composition/type of the carbide particles.

2. Experimental Methodology

2.1. Cladding Process

A Trumpf DMD 505 LMD machine was used for cladding the surface of EN 1.2343 (X37CrMoV5-1) steel. The machine was equipped with a pulsed CO₂ laser and with a coaxial nozzle for powder feeding. The cladding consisted of two layers: 1) a soft and ductile nickel-based interlayer deposited directly onto the steel substrate; and 2) a hard MMC top layer of tungsten carbide particles embedded in the nickel-based matrix. The steel substrate was prepared by conventional milling. For producing the top layer, a powder blend of fused (cast) spherical mono- and ditungsten carbides (WC + W₂C), which is also referred as “CTC-S” or “WSC-S” powder, was injected into the melt pool of the interlayer reheated by the laser beam. This procedure prevents particle separation, which occurs when typical powder blends consisting of

| Powder | Designation | W | Ni | C | Cr | Fe | Si | B |
|--------|-------------|---|----|---|----|----|----|---|
| Ni alloy | NT–Ni–25 | bal. | 0.03 | – | 0.10 | 2.74 | 1.80 |
| WC + W₂C | NT–WSC–S | bal. | 0.02 | 3.40 | 0.03 | 0.14 | – | – |

2.2. Investigation Procedures

A PANalytical Empyrean diffractometer with Cu-Kα X-ray source, vertical goniometer, secondary monochromator, and PIXcel\textsuperscript{3D} area detector was used for X-ray diffraction (XRD) analysis of the as-received tungsten carbide powder. The X-ray source was operated with the acceleration voltage of 40 kV and with the beam current of 40 mA. The diffractogram was determined in 3427 intervals for angles between 10° and 100° within the two-theta (2θ) range. The total measurement time was about 4 h. Since the powder was randomly distributed in the sample holder, any texture influence on the results can be excluded. The diffractogram was indexed using collection codes (CC) of the Inorganic Crystal Structure Database (ICSD)\textsuperscript{[77]} and Powder Diffraction Files (PDF) of the PDF-2 database of the International Centre for Diffraction Data (ICDD).\textsuperscript{[78]} For simplicity, the volume fractions of the indexed phases were calculated using the PowderCell software by considering relative intensities according to the reference intensity ratio method.

After the cladding process, three samples with identical properties were prepared for comprehensive analysis of the MMC microstructure. The rod-shaped samples shown in Figure 1 with dimensions of about 10 mm × 1 mm × 1 mm were produced by wire cutting. The orientation of the samples was parallel to the cladding direction. Different analysis methods including XRD, X-ray micro-computed tomography (μCT), transmission electron microscopy (TEM) with selected area electron diffraction (SAED), as well as scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS), electron backscatter
diffraction (EBSD), and nanoindentation were employed for detailed characterization of both the as-received tungsten carbide powder and the MMC cladding.

The sample for μCT investigations (#1 shown in Figure 1) was used in wire-cut condition without any polishing. A high-resolution Xradia VersaXRM-500 μCT system was employed for capturing and visualizing the three-dimensional distribution of carbide particles inside the nickel-based matrix. The voxel size was 0.66 μm, and the region of interest had 1263 × 1984 × 1228 voxels. A median filter of five pixels was applied to the as-measured data for removing random noise. The Fiji software was used for postprocessing of the μCT data. Two wire-cut samples (#2 and #3 shown in Figure 1) and a small quantity of tungsten carbide powder were warm embedded for EDS, EBSD and TEM analyses. The samples were ground using sandpaper of grit sizes 320/800/1200/2000 and polished using diamond suspensions of 3 and 1 μm. Colloidal silica suspension (OP-S) was used for final polishing.

A TESCAN MIRA3 scanning electron microscope with an EDAX AMETEK Octane Super detector of 60 mm² and with an EDAX AMETEK Hikari Plus EBSD camera was used for EDS and EBSD measurements, respectively. Secondary electron (SE) and backscattered electron (BSE) images as well as EDS maps were acquired using the acceleration voltage of 20 kV and the working distance of 10–15 mm. EBSD and EDS measurements were performed simultaneously using the acceleration voltage of 30 kV, the working distance of 20–30 mm, and the spot size of 70–80 nm. The APEX software package was used for controlling the data acquisition, and the software OIM DataAnalysis 8.6 was used for EBSD data processing. Phases that yielded the highest confidence index (CI) were selected for reindexation. The data were then cleaned using the grain dilation filter with the grain tolerance angle of 15° and minimum grain size of 5 μm. The filter was applied to data points with CI < 0.01. The measured Kikuchi patterns were re-indexed using CHI Scan.

The sample lamella used for SAED measurements was prepared by the in situ lift-out method using a Thermo Fisher Scientific Scios 2 SEM equipped with a focused ion beam (FIB). The area of the sample lamella was 30 μm × 5 μm, and the thickness of the lamella was about 100 nm. A FEI TENCAI F20 TEM with the operating voltage of 200 kV and the spot size of three was then used for detailed SAED measurements. The SAED patterns were captured by a Gatan Rio16 30 fps full-HD camera, and they were analyzed using the JEMS software.

Nanoindentation mapping using a FemtoTools FT-NMT04-XYZ in situ nanoindenter with three-sided Berkovich tip was performed on a FEI Quanta 250 field emission gun scanning electron microscope (FEG-SEM), which was operated with the acceleration voltage of 10 kV and with the beam spot size of three in high vacuum mode. The nominal distance between the indentations in both x- and y-directions was 2 μm. This value was chosen as small as possible to resolve spatial hardness differences. Therefore, mutual influence between adjacent indentations due to plastic material deformation was consciously accepted. The MATLAB software was used for processing and visualizing the hardness map.

3. Results and Discussion

3.1. Tungsten Carbide Powder

The SE image of the as-received tungsten carbide powder shown in Figure 2a confirms the particle size distribution provided by the powder manufacturer. Even though about 98 wt% of the powder consists of spherical particles with diameters of < 45 μm, it is evident that a few particles are actually nonspherical or have diameters of < 10 μm. Figure 2b,c shows high-resolution SE images of typical spherical carbide particles with serrated surfaces.

Figure 3 illustrates results of EBSD measurements performed on the as-received tungsten carbide powder. Figure 3a shows two basic types of particles, namely 1) coarse-grained particles consisting of a few large grains or even of a single grain; and 2) fine-grained particles consisting of numerous small grains that are stochastically oriented. The phase map of Figure 3b identifies coarse-grained particles consisting of W2C with hexagonal crystal structure. Identifying the crystal structure of fine-grained particles was challenging using EBSD with limited spatial resolution; however, these particles presumably consist of both W2C and WC with hexagonal crystal structure. Figure 3c reveals that fine-grained particles were generally badly indexed (blue regions, CI ≈ 0), whereas coarse-grained particles were well indexed (red regions, CI ≈ 1), although the crystal structure of their surfaces was unidentifiable (blue surface layers, CI ≈ 0).
consisting of fine grains most likely have serrated surfaces, as exemplarily shown in Figure 2c.

Figure 4 shows the measured XRD diffractogram of the as-received tungsten carbide powder, which was indexed using CC of the ICSD and PDF of the ICDD PDF-2 database. According to this indexation two phases with trigonal, two phases with hexagonal, one phase with face-centered cubic (fcc), and one phase with body-centered cubic (bcc) crystal structures were identified. The trigonal phases are ditungsten carbides $W_2C_{1-x}$ and $W_2C$ (space groups #162 and #164), and the hexagonal phases are ditungsten carbide $W_2C$ (space group #194) and monotungsten carbide WC (space group #187). The fcc phase is monotungsten carbide WC$_{1-x}$ (space group #225), and the bcc phase is elemental tungsten (space group #229). XRD did not allow for distinguishing between phases with similar space groups (i.e., #162, #164 and #194), because those phases have very similar characteristic diffractograms. As listed in Table 2, in particular, the lattice parameters of space groups #164 and #194 are virtually identical. Detailed analysis of different polymorphic modifications of the $W_2C$ and WC phases is provided elsewhere.[79–81] As specific designations of phases and phase

![Figure 3](image-url) Results of EBSD measurements on as-received tungsten carbide powder; a) inverse pole figure map, b) phase map, and c) confidence index map.

![Figure 4](image-url) XRD diffractogram of as-received tungsten carbide powder.

| Space group | General phase designation | Cell parameters ($a$, $b$, and $c$ were round to 3rd decimal, $d$ as 4th digit may differ in CC and PDF) | ICSD CC | ICDD PDF | Phase fraction [vol%] |
|-------------|---------------------------|---------------------------------------------------------------|---------|-----------|----------------------|
| #162 P31m   | $W_2C$$_{1-x}$            | $a = b = 0.518$ nm, $c = 0.472$ nm                            | 40956   | 35-0776   | 64.7                 |
| #164 P3m1   | $W_2C$                    | $a = b = 0.300$ nm, $c = 0.473$ nm                            |         |           |                      |
|             |                           | $a = \beta = 90.0^\circ$, $\gamma = 120.0^\circ$            |         |           |                      |
| #194 P6$_3$/mmc | $W_2C$          | $a = b = 0.299$ nm, $c = 0.473$ nm                            | 196711  | 72-0097   |                      |
| #187 P6m2   | WC                        | $a = b = 0.291$ nm, $c = 0.284$ nm                            | 196712  | 20-1316   | 23.5                 |
|             |                           | $a = \beta = \gamma = 90.0^\circ$                           |         |           |                      |
| #225 Fm3m   | $W$                      | $a = b = c = 0.424$ nm                                        | 424342  | 04-0806   | 5.9                  |
|             |                           | $a = \beta = \gamma = 90.0^\circ$                           |         |           |                      |
| #229 Im3m   |                           | $a = b = c = 0.316$ nm                                        | 76151   |           | 5.9                  |
modifications may differ and cell parameters provided in literature are often slightly different, the space groups and their corresponding numbers are more suitable for identifying phases and their modifications.

The XRD results that are summarized in Table 2 are basically in good agreement with the EBSD results. Calculating phase fractions based on the XRD results revealed that almost 90 vol% of the powder consist of tungsten carbides having either trigonal or hexagonal crystal structure. Almost two-third of the powder consist of ditungsten carbides \((W_2C, W_2C_{1-x})\) and almost one-third of the powder consist of monotungsten carbides \((WC, WC_{1-x})\), which is in accordance with the specification of the powder manufacturer.\(^{[76]}\) The actual two-phase composition including mono- as well as ditungsten carbides is typical for fused (cast) spherical tungsten carbide particles.\(^{[71]}\) Thus, particles consisting of very fine grains – which do not allow for reliable analysis of the crystal structure by using conventional EBSD – contain not only ditungsten carbides but also monotungsten carbides.

3.2. MMC Cladding

3.2.1. Distribution of Carbidic Particles

The typical microstructure of the as-deposited MMC cladding is shown in Figure 5a. The particle diameters are \(< 50 \mu m\). Large particles are dense and have comparatively smooth surfaces, medium-size particles have serrated surfaces, but most of the small particles are completely fragmented. Partial or complete fragmentation results from carbide dissolution during LMD processing. Figure 5b shows the distribution of carbide particles inside the metal matrix (total volume of \(500 \times 500 \times 1500\) voxels with overall dimensions of about \(0.33 \text{ mm} \times 0.33 \text{ mm} \times 1 \text{ mm}\)) measured using \(\mu\)CT. The three-dimensional visualization confirms that the MMC cladding contains numerous spherical carbides of different size that are more or less homogeneously distributed; however, closer examination also reveals regions which contain slightly less particles. Due to the limited spatial resolution of the \(\mu\)CT system, neither distinguishing between the carbide particles and their surface layers nor resolving exactly the morphology of these thin layers was possible. Moreover, the small difference in the densities of WC and \(W_2C\) did not allow for distinguishing between both phases.

The histogram of the \(\mu\)CT data with gray values in the range of 0–255 is shown in Figure 6. It includes two distinct peaks: the lower peak corresponds to the carbide particles, whereas the higher peak corresponds to the nickel-based matrix. Since the smooth transition from the high peak to the low peak does not allow for distinguishing clearly between matrix and particles, the gray value of 164 at the local minimum was chosen as threshold. The volume fraction of particles in the MMC, \(f_{\text{vol, par}} \approx 18\) vol%, was calculated as number of voxels above the threshold divided by the total number of voxels. The actual weight fraction of carbides in the MMC, \(f_{\text{wt, par}}\), was estimated based on the average density of the carbides and the nickel-based matrix.
densities of tungsten carbide particles and nickel-based matrix, \( \rho_{\text{par}} \approx 16.6 \, \text{g cm}^{-3} \) and \( \rho_{\text{mat}} \approx 8.9 \, \text{g cm}^{-3} \)

\[
f_{\text{wt\ par}} = \frac{f_{\text{vol\ par}}}{\rho_{\text{par}} f_{\text{vol\ par}} + \rho_{\text{mat}} (1 - f_{\text{vol\ par}})}
\]  

(1)

According to Equation (1), the actual weight fraction of carbides was \( f_{\text{wt\ par}} \approx 30 \, \text{wt} \%, \) which is on the lower boundary of the nominal range of 30–50 wt\%. This can be attributed 1) to the locally restricted inhomogeneous distribution of carbide particles within the investigated volume, as some regions contained less particles; 2) to almost complete dissolution of small particles, which can contribute only very little to the reinforcement of the matrix; and 3) to the approximation of the volume fraction by using the “sharp” threshold.

Figure 7 shows detailed high-resolution micrographs of typical spherical tungsten carbide particles and their surface layers embedded in the nickel-based matrix. Since the typical thickness of these layers is about 5 \( \mu \)m, small particles with original diameters of < 10 \( \mu \)m appear totally fragmented. As exemplarily shown in Figure 7a, they transformed into a network of comparatively fine grains. In contrast, fragmentation of large particles occurred only on their surfaces, as exemplarily illustrated in Figure 7b. Grains at the inner interface (i.e., next to the original particle) are very fine, whereas grains at the outer interface (i.e., next to the nickel-based matrix) are comparatively coarse and blocky. The different grain sizes and morphologies indicate that two types of grains or phases, respectively, are present in the surface layers.

Many particles in the as-received powder consist of fine grains of both mono- as well as ditungsten carbides. During LMD processing, the particles were heated by the laser beam, and they were in direct contact with the hot nickel-based melt. Hence, their surfaces were exposed to higher temperature than their inner regions. This is supposed to facilitate selective dissolution of primary W\(_2\)C grains on the particle surface and subsequent formation of coarse secondary carbides on the remaining network of fine primary WC grains.\(^{[31]}\)

3.2.2. Composition of Carbide Particles

The results of the EBSD analysis on the as-deposited MMC cladding are shown in Figure 8. In Figure 8a, colored particles

Figure 7. Micrographs showing a) typical spherical tungsten carbide particles and their surface layers and b) different grains within the surface layer. The red arrow marks the position of a small particle, which is totally fragmented.

Figure 8. Results of EBSD analysis on the as-deposited MMC cladding; a) inverse pole figure map, b) phase map, c) confidence index map.
consisting either of a single grain or of a few large grains as well as black particles consisting of numerous fine grains with corresponding grain boundaries are visible. The phase map of Figure 8b confirms that two basic types of particles, namely fine-grained and coarse-grained particles exist. The inner regions of the particles were mainly indexed as W₂C (space group #194, CC 77 567, green areas), whereas the surface layers of the particles were indexed as WC (space group #187, CC 246 151, red areas). Comparing Figure 8a,b with Figure 8a,b clearly reveals that particles of the as-received tungsten carbide powder do not have distinct continuous surface layers, even though the crystal structures of the inner regions are virtually identical in both as-received and as-deposited conditions. Therefore, the layers must have been formed during the LMD process.

As exemplarily shown in Figure 7b, the inner surface layer has formed due to selective dissolution of fine grains of W₂C at the matrix/particle interface, whereas the formation of the outer surface layer can be explained by nucleation and growth of comparatively coarse secondary grains. The grains of both surface layers were indexed as WC (space group #187), but it cannot be ruled out that they contain also nickel coming from the matrix. Hence, the phase designation should rather be more general NiₓWᵧC than WC. Among the three ternary carbides, M₄C, M₆C, and M₁₂C identified in the W–C–Ni system, only M₆C participates in liquid–solid equilibria. For instance, XRD measurements revealed that secondary NiₓWᵧC (i.e., M₆C) may form in the nickel-based matrix of claddings reinforced with spherical WC particles. However, this does not exclude possible formation of other ternary carbides, and further investigations are required for determining the actual composition of the surface layers.

As shown in Figure 8c, the crystal structure of most particles consisting of a few large grains was well indexed (CI ≈ 1), whereas the crystal structure of particles consisting of very fine grains was badly indexed (CI ≈ 0).

Figure 9 provides a detailed view on the microstructure of the as-deposited MMC cladding. Figure 9a,b shows element distribution maps of tungsten and nickel measured using EDS. High tungsten contents are only detected inside the particles (red areas), whereas high nickel contents are only detected inside the matrix (blue areas). The inner regions of the particles do not contain any nickel, but closer examination reveals that nickel is present in the surface layers. However, due to the limited resolution of the element distribution maps it is not clear, whether only areas between the fine carbide grains or the grains themselves contain nickel.

As shown in Figure 9e, not only the particles but also the matrix consists of two main phases, namely the primary nickel dendrites and the interdendritic regions. Figure 9f illustrates that only the dendrites are well indexed (CI ≈ 1), whereas reliable indexation of interdendritic regions was not successful (CI ≈ 0). Even though the particles and their surface layers consist of phases with different crystal structures, Figure 9d shows that the grain orientations are often quite similar or dependent on each other. Figure 9f confirms that the quality of indexation decreases significantly with the grain size, which explains the relatively bad indexation of particles consisting of fine grains.

Within the relevant range of composition, the equilibrium W–C phase diagram identifies hexagonal monocarbide with space group #187 as stable phase at room temperature, since the eutectoid transformation W₂C → WC + W occurs when the temperature decreases below about 1250 °C. Cubic monocarbide with space group #225 does not exist under equilibrium conditions at room temperature.

Figure 9. Results of EBSD analysis on tungsten carbide particles inside the nickel matrix; element distribution maps of a) tungsten and b) nickel, c) index-of-quality map, d) inverse pole figure map, e) phase map, f) confidence index map.
When the particles are heated and then cooled relatively slowly during the LMD process, thermally induced 1) phase transformation of metastable mono- and ditungsten carbides to stable monotungsten carbides; 2) selective dissolution of ditungsten carbides within the nickel-based melt; and 3) subsequent formation of secondary WC/Ni\textsubscript{x}W\textsubscript{y}C phases are supposed to occur. As growth of secondary phases may preferably start at remaining primary WC grains on the particle surfaces, the fundamental grain orientations are preserved. Hence, a crystallographic relationship between primary and secondary carbides is supposed to exist.

Figure 10 illustrates Kikuchi patterns measured using EBSD at different regions of the microstructure. Based on the indexing of these patterns, the crystal structures of inner particle regions, surface layers, and matrix grains were identified as hexagonal W\textsubscript{2}C, hexagonal WC, and face-centered cubic (fcc) nickel, respectively. Hexagonal and trigonal crystal structures of W\textsubscript{2}C are preserved. Hence, a crystallographic relationship between primary and secondary carbides is supposed to exist.

Figure 10. Kikuchi patterns measured using EBSD and indexed as a),c),e) hexagonal W\textsubscript{2}C at the inner regions of the particles, as b),d) hexagonal WC at the surface layer of the particles, and as f) face-centered cubic nickel at the grains of the matrix.

Figure 11. Sample lamella used for TEM measurements with measurement spots a) and b) and indexation of corresponding SAED patterns.
were undistinguishable, as both have nearly identical Kikuchi patterns. In addition, the low symmetry of trigonal W2C does not allow for reliable indexation. In general, fine grains make the exact determination of Kikuchi patterns difficult, which explains the comparatively low value of CI associated with the indexation of the pattern shown in Figure 10a. Thus, these particles presumably contain also WC, and their crystal structure could be rather trigonal than hexagonal.

In order to validate the results of EBSD analysis, TEM analysis was performed on a representative tungsten carbide particle consisting of fine grains. Figure 11 shows the sample lamella prepared from this particle using FIB milling; the measurement spots a) and b) are marked with red dots. Indexation of the corresponding SAED patterns according to CC 159 903 and CC 30 008, respectively, identified trigonal ditungsten carbide W2C1–x (space group #162) at both spots. Identifying the phase, however, was not always as clear as at these two spots, as the SAED patterns measured at other spots matched both trigonal and hexagonal crystal structures.

Comparing the compositions of as-received and as-deposited carbide particles reveals that most of them were stable during LMD processing. However, thermally induced dissolution of primary W2C/W2C1–x occurred. Large particles dissolved partially on their surfaces, and small particles were fragmented or they even dissolved completely. Hence, small carbide particles with diameters of < 10 μm are virtually ineffective with respect to reinforcing the nickel-based matrix. Reducing the energy input of the LMD process, e.g., either by decreasing the laser power or by increasing the cladding speed, would probably reduce the dissolution tendency. Adapting the powder feed rate for maintaining the volume fraction of carbides in the MMC and increasing the preheating temperature of the substrate for reducing the cracking tendency would be necessary. Nevertheless, changing critical process parameters may reduce thermally induced carbide dissolution, but it carries the risk of defect formation, as only a narrow process window for achieving pore- and crack-free cladding microstructures exists.[51]

3.2.3. Hardness of Carbide Particles

The normalized hardness map illustrated in Figure 12a was measured on the small area of 40 μm × 40 μm as shown in Figure 12b. This area includes sections of three carbide particles with their surface layers as well as the nickel matrix between these particles. Figure 12c shows in detail the microstructure of a typical surface layer. In SEM-BSE images, regions containing comparatively light elements (i.e., Ni) appear darker than regions containing comparatively heavy elements (i.e., W). Hence, distinguishing between the almost tungsten-free nickel-based matrix (dark gray), the tungsten-rich inner region of the carbide particle (light gray), and the fragmented surface layer that contains less tungsten and presumably nickel (medium gray) is possible.

The minimum and maximum hardness values within the small area shown in Figure 12b are about 5 GPa at the nickel matrix and about 35 GPa at the center of the large tungsten carbide particle consisting of fine grains, respectively. Phase map and inverse pole figure map of the indentation area are shown in Figure 12d,e. These maps demonstrate that the two particles
consisting of fine WC/W2C grains have thick surface layers, while the particle consisting of a large single W2C grain has a comparatively thin surface layer. This strongly indicates that the size and the morphology of primary grains (coarse grains vs. fine grains) do not only influence the properties of the particles but also influence the formation mechanisms and the properties of the surface layers. For instance, as illustrated in Figure 12a, the two fine-grained particles possess approx. one-fourth higher hardness than the coarse-grained particle. This can be explained based on the Hall–Petch equation,

\[ H = H_0 + k_d d^{-1/2} \]

which states that strength and hardness of polycrystalline materials are inversely proportional to the square root of the grain size.

4. Summary and Conclusions

The microstructure of a MMC consisting of fused spherical tungsten carbide particles embedded in a nickel-based matrix was characterized. The MMC was produced by laser cladding. Based on the results of the detailed experimental investigations, the following conclusions were drawn: 1) Almost two-thirds of the as-received tungsten carbide powder consisted of ditungsten carbides with either hexagonal (W6C) or trigonal (W2C, W2C1-x) crystal structures, and almost one-third of the powder consisted of monotungsten carbides with mainly hexagonal (WC), but also cubic (WC1-x) crystal structures. Minor amount of elemental tungsten (W) was also detected. Clear distinction between hexagonal and trigonal crystal structures was not possible; 2) Most of the tungsten carbide particles were quite stable during LMD processing; however, selective thermally induced dissolution of the W2C/W2C1-x phases was observed. Large primary particles partially dissolved on their surfaces, whereas small particles were fragmented or they even completely dissolved. Secondary WC/Ni,WC phases formed predominantly on the surfaces of the remaining particles, i.e., at the matrix/particle interfaces. A crystallographic relationship between primary and secondary carbides was observed; 3) In both conditions of the particles, as-received and as-deposited, the grain size of the tungsten carbides varied from coarse to fine, even though their crystal structures were mostly identical.Nanoindentation mapping revealed that a) particles consisting of numerous fine grains were harder than particles consisting of a few coarse grains, which can be attributed to Hall–Petch strengthening and that b) particles consisting of fine WC/W2C grains were harder than their surface layers consisting of fine WC/Ni,WC grains; 4) As the surface layers of the as-deposited tungsten carbide particles were less hard than the center regions of the particles, the hardness gradually decreased from the center of the particles across their surface layers toward the nickel-based matrix. This hardness gradient and the serration of the particle surfaces due to carbide dissolution and formation are supposed to improve bonding between the matrix and the particles; 5) Some of the secondary carbides that formed after dissolution of primary carbides at the matrix/particle interfaces presumably contained nickel. Hence, not only tungsten and carbon diffused from partially dissolving primary carbides into the matrix but also nickel from the matrix was incorporated into the secondary carbides. Determining the compositions and the formation mechanisms of these carbides requires further investigations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hardfacing, laser cladding, laser metal deposition, LMD, metal matrix composites, MMC, nickel alloy, tungsten carbides, wear resistance

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[1] T. W. Clyne, P. J. Withers, An Introduction to Metal Matrix Composites, Cambridge University Press, Cambridge, UK 1993.
[2] J. F. Archard, J. Appl. Phys. 1953, 24, 981.
[3] L. Pawlowski, The Science and Engineering of Thermal Spray Coatings, 2nd ed., John Wiley & Sons, Chichester, UK 2008.
[4] P. F. Mendez, N. Barnes, K. Bell, S. D. Borle, S. S. Gajapathi, S. D. Guest, H. Izadi, A. K. Gol, G. Wood, J. Manuf. Processes 2014, 16, 4.
[5] D. A. Stewart, P. H. Shipway, D. G. McCartney, Acta Mater. 2000, 48, 1593.
[6] Q. Yang, T. Senda, A. Ohmori, Wear 2003, 254, 23.
[7] L.-M. Berger, S. Saaro, T. Naumann, M. Wiener, V. Weihnacht, S. Thiele, J. Suchánek, Surf. Coat. Technol. 2008, 202, 4417.
[8] W. Fang, T. Y. Cho, J. H. Yoon, K. O. Song, S. K. Hur, S. J. Youn, H. G. Chun, J. Mater. Process. Technol. 2009, 209, 3561.
[9] M. R. Ramesh, S. Prakash, S. K. Nath, P. K. Sapra, B. Venkataraman, Wear 2010, 269, 197.
[10] J. Pulsford, S. Kamnis, J. Murray, M. Bai, T. Hussain, J. Therm. Spray Technol. 2018, 27, 207.
[11] N. Serres, F. Hlawka, S. Costil, C. Langlade, F. Machi, Appl. Surf. Sci. 2011, 257, 5132.
[12] Q. Zhan, L. Yu, F. Ye, Q. Xue, H. Li, Surf. Coat. Technol. 2012, 206, 4068.
[13] P. Nirantarmpong, H. Koiprasert, Surf. Coat. Technol. 2011, 206, 440.
[14] P. Sheppard, H. Koiprasert, Wear 2014, 317, 194.
[15] W. Tillmann, L. Hagen, D. Kokalj, Surf. Coat. Technol. 2017, 331, 153.
[16] R. L. Deuis, J. M. Yellup, C. Subramanian, Compos. Sci. Technol. 1998, 58, 299.
[17] J. F. Flores, A. Neville, N. Kapur, A. Gnanavelu, Wear 2009, 267, 213.
