

# Microstructure Development and Mechanical Properties of Ni Matrix/Carbide Composites

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**Abstract.** Nickel alloy matrix/dispersed carbide (VC, NbC, WC) composites were prepared by either flame-spray, liquid phase sintering, or solid state sintering. A commercial Ni-B-Si alloy was mixed with 15% vol. of carbide particles and used to prepare composite coatings by flame-spray, bulk composite materials by solid state sintering (below 1045°C) or liquid phase sintering (above 1050°C). Phase characterization was performed by X-ray diffraction, optical microscopy, scanning electron microscopy and X-ray fluorescence in energy and wavelength dispersive spectroscopy modes. Similar microstructural features were produced by thermal spray and liquid phase sintering: a Ni-rich matrix and a boron-rich intergranular phase. Sintered samples showed higher wear resistance than the coatings obtained by flame spraying. In both cases the wear mechanism is dominated by the plastic flow of the Ni-rich ductile matrix and the fracture of a boron-rich intergranular phase, the latter serving as a retainer. Carbide removal was observed for solid state sintered samples.

**Keywords:** carbides, composites, metal matrix composites, niobium carbide, vanadium carbide, wear

## Introduction

Applications requiring high-wear resistance often make use of composite materials consisting of fine hard ceramic particles dispersed in a transition metal matrix (Ni, Co, Cr), which serves as a tough binder. Ceramic materials include WC, TiC, B<sub>4</sub>C, TiB<sub>2</sub>, VC, TaC, NbC, and Al<sub>2</sub>O<sub>3</sub>, i.e. [1]. The mechanical stability of these systems, which in turn determine tool performance, depends on the characteristics of the metal/carbide interface and the nature of the intergranular phases.

Vanadium carbide is a less common hardening agent despite its high hardness and wear resistance [2]. It shows good tribological performance when dispersed in an iron alloy matrix or when deposited as a continuous coating [3, 4]. The use of NbC has been limited to Ni matrices. The wetting behavior at the Ni/NbC interface is relatively poor compared to WC or TiC when employed as reinforcements [5]. However, it has been observed that NbC can impart excellent wear characteristics to some Ni-Cr-B-Si alloys, when present as dispersed particles in proportions between 20 to 50 vol.% [6].

In order to systematically develop composite materials, a combination of experimental and theoretical studies has been undertaken. This work describes the methods used to develop Ni alloy/MC (M = V or Nb) composite materials for applications in the oil

industry. Their behavior is compared with a conventional composite material system like Ni alloy/WC. These traditional composites based on NiBSi alloys (with eventual addition of Cr, Mo and/or Fe) are commonly used in the form of thick coatings deposited either by thermal spraying or welding. These coatings are quite successfully controlling abrasion and erosion in the oil industry. Some typical applications are pistons for subsoil pumps coated by fused thermal spraying, welded hard-bands on drilling tubes and linings for the restoration of steel components in contact with slurry in refinery equipment. The expected final use for the composite systems developed in this work are as coatings for steel substrates and sintered preforms for fabrication of inserts in wear-resistant pieces.

### Materials and methods

The precursors used in this study were commercial powders, as follows:

- Vanadium carbide, 99% purity, 9  $\mu\text{m}$  mean particle size,  $\text{V}_8\text{C}_7$  as major phase (Good Fellow);
- Niobium carbide, 99% purity, 5.5  $\mu\text{m}$  mean agglomerates size, formed by irregularly shaped particles, of size less than 1  $\mu\text{m}$  (Cerac Corporated);
- Tungsten carbide, 99.5% purity, 45  $\mu\text{m}$  mean agglomerates size and particle size of about 1  $\mu\text{m}$  (Cerac Corporated);
- Nickel alloy, spherical particles of a NiBSi based alloy (wt% composition: 2.0 Si, 1.5 B, 0.2 Fe, 0.01 Mn, 0.03 Cr, balance Ni), 45  $\mu\text{m}$  mean size, consisting of Ni as the major phase and  $\text{Ni}_3\text{B}$  as a minor phase (Chromtec alloy from Eutectic + Castolin).

Carbide powders were milled in a SPEX-800 ball milling, with WC milling charge. During milling NbC and WC agglomerates were fractured to about 1  $\mu\text{m}$  mean particle size, while VC particles size remained unchanged. A mixture of 15% vol. of carbide and 85% metal matrix powders was prepared in an electric mortar, by blending for 30 min. in toluene as a lubricant.

The first process used in this study was flame-spraying of the NiBSi alloy and the NiBSi/MC mixture with an oxyacetylene flame torch. The coatings were deposited on SAE 1045 steel substrates. After deposition, the coatings were submitted to local fusion at about 1050–1100°C using the flame torch.

The second process consisted of treating bulk samples of the NiBSi alloy and NiBSi/carbides mixture under conditions of liquid phase or solid state sintering. The powder was uniaxially pressed at 113 MPa where green density of the pellets reached a constant value. The samples were heat-treated in an argon atmosphere between 900 and 1100°C. Sintered samples were metallographically prepared by diamond polishing and chemical etching in accordance with the ASTM E407 standard in a 50:50 vol. nitric acid/acetic acid solution. The microstructural morphology was observed by SEM with EDS and WDS detectors to determine the element distributions.

Vickers microhardness measurements were obtained with a Shimadzu tester, model 4046 with a 0.49 N load applied during 15 s (ASTM E384). The reported values are average

results of five measurements. Density tests were carried out according to the ASTM-D2320 method and six measurements were taken for each sample.

Friction and wear tests were carried out on samples metallographically polished and ultrasonically cleaned in acetone. These tests were performed on the Falex LFW-1 equipment in a block-on-ring configuration, using standard SAE 4620 steel rings (diameter of 49.2 mm) with a sliding speed 200 rpm, a normal load of 22.4 N and test durations of 70 min. Previous work [7] showed that the steady state was reached during this time. The friction force was continuously recorded during tests in order to determine the average friction coefficient in the steady state region. The wear volume was calculated from the measured values of the width of the wear scar, assuming a cylindrical shape [8].

## Results and discussion

Several temperatures and sintering times were tested in order to determine the conditions for solid and liquid state sintering. The SEM analysis revealed that the liquid phase in the NiBSi alloy was produced between 1045 and 1050°C. Figure 1 shows the microstructure of the NiBSi alloy treated under an argon atmosphere and conditions of (a) solid state sintering at 1000°C during 30 min. and (b) liquid phase sintering at 1100°C during 5 min. Optimal parameters for liquid phase sintering of the nickel alloy were found to be 1055°C and 5 min. These conditions correspond to the maximum density (see Table 1) without deformation. At higher temperatures or higher sintering times, considerable grain growth and macroscopic deformation of the samples was observed. The liquid phase sintered samples showed a Ni-B rich intergranular amorphous phase, as was indicated by WDS [9, 10] and XRD analysis [10]. This intergranular phase, which was hard and brittle (see Table 1), was not formed below 1045°C; instead a hard intragranular precipitate phase, as in the precursor alloy powders was observed (figure 1(a)).

Figure 1(c) shows the microstructure of flame-sprayed NiBSi samples. They showed coalescence of NiBSi grains and an intergranular phase like the liquid phase sintered NiBSi

Table 1. Average microhardness and relative density of the NiBSi alloy and NiBSi/MC composites sintered at various conditions.

Material	Sintering conditions		Microhardness (HV 50)			Relative density (%)
	Temperature (°C)	Time (min.)	Ni grains	Intergranular phase	MC grains	
NiBSi alloy	950	30	—	—	—	87.9
	1045	5	318	—	—	90.1
	1055	5	265	1030	—	92.4
NiBSi/15% vol. VC	950	30	431	—	2634	81.7
	1040	5	—	—	—	89.9
	1050	5	—	—	—	92.4
	1050	120	341	1234	2527	93.3
NiBSi/15% vol. NbC	1050	5	293	1134	1794	94.8
NiBSi/15% vol. WC	1050	5	—	—	—	92.9

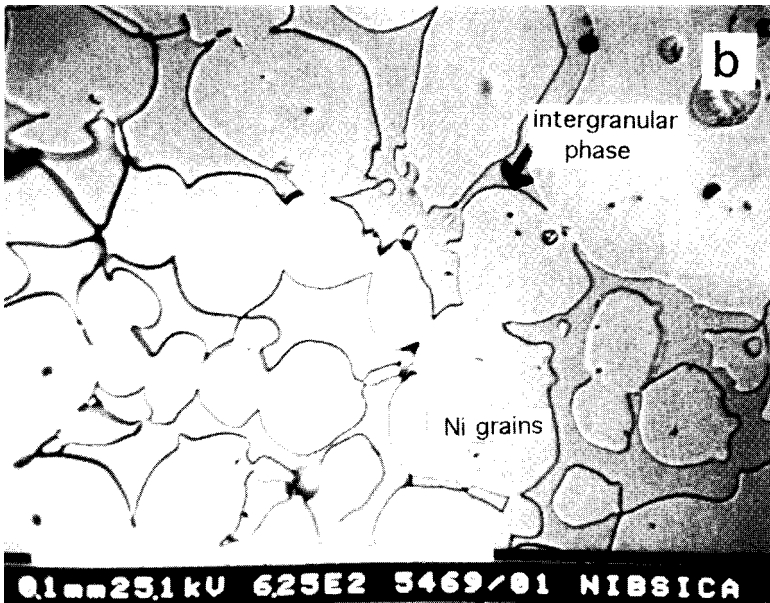
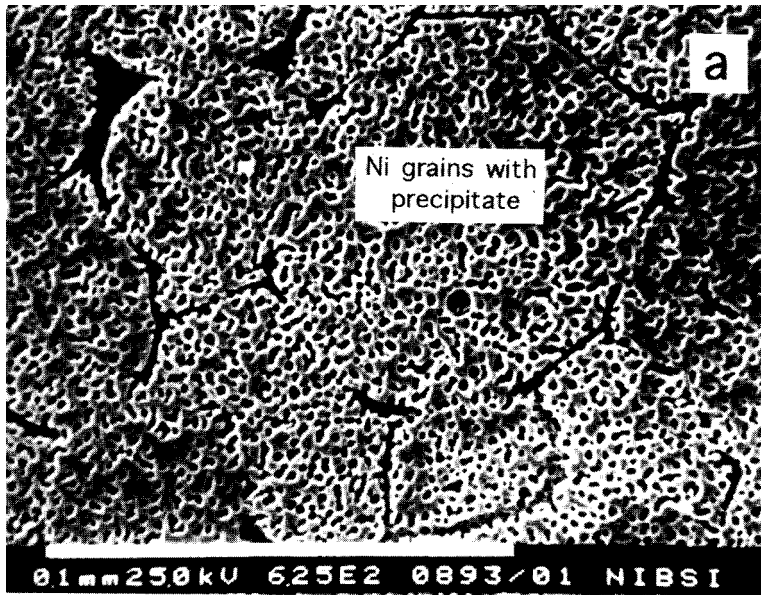


Figure 1. SEM micrographs of the NiBSi alloy powder: (a) sintered at 1000°C for 30 min. (solid state sintering), (b) sintered at 1100°C for 5 min. (liquid phase sintering), (c) deposited by flame-spray process.

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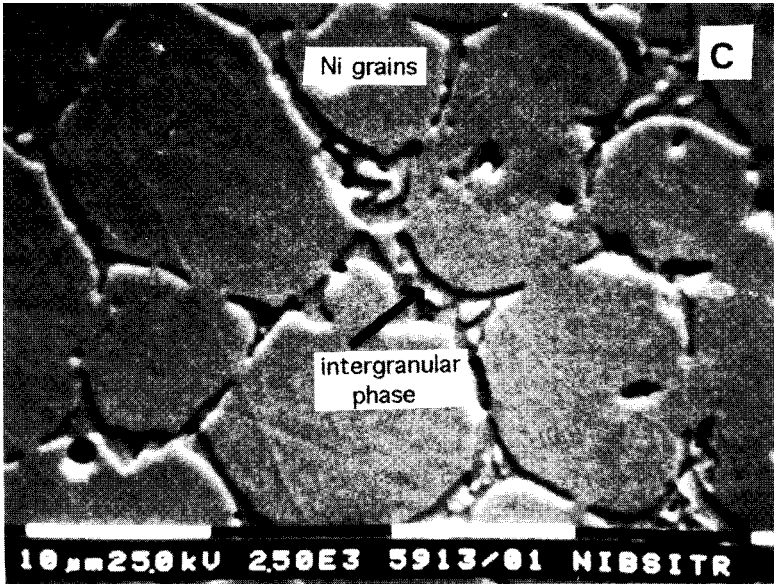


Figure 1. (Continued.)

alloy. It was also observed by SEM that in the NiBSi/VC composite, the carbide particles were somewhat less uniformly distributed and with smaller dimensions in comparison with the sintered samples. This is probably due to the high oxidation susceptibility of this carbide at temperatures above 400°C [11].

Figure 2 shows the microstructure of NiBSi/VC samples, heat treated under conditions of (a) solid state sintering and (b) liquid phase sintering. Composite samples produced by solid state sintering showed the same microstructure observed in the nickel alloy, with the carbide particle located between the nickel grains (compare figures 1(a) and 2(a)). The original grit carbide particles appear as rounded particle, suggesting that the vanadium carbide dissolves in the metal matrix. In figure 2(b), three different zones were observed by SEM. The matrix was formed by Ni-rich grains. The second zone is an intergranular network, formed by solution and reprecipitation of the original intragranular precipitates. As detected from the WDS analysis, the B concentration in this network was substantially higher than in the Ni-rich grains. The VC carbide particles were embedded in the intergranular Ni-B-rich network.

Figure 3 shows the microstructure of NiBSi/WC composites obtained by solid state sintering; similar microstructure was observed for NiBSi/NbC composites. Compared with the microstructure of the NiBSi/VC system, these composites show a more homogeneous distribution of the carbide particles, due to the smaller particle size of the carbide precursors. Qualitative diffusion experiments carried out in previous work [10] in the NiBSi/NbC system showed that during heating, B migrates towards the NbC particles, while silicon is apparently uniformly distributed among the different phases.

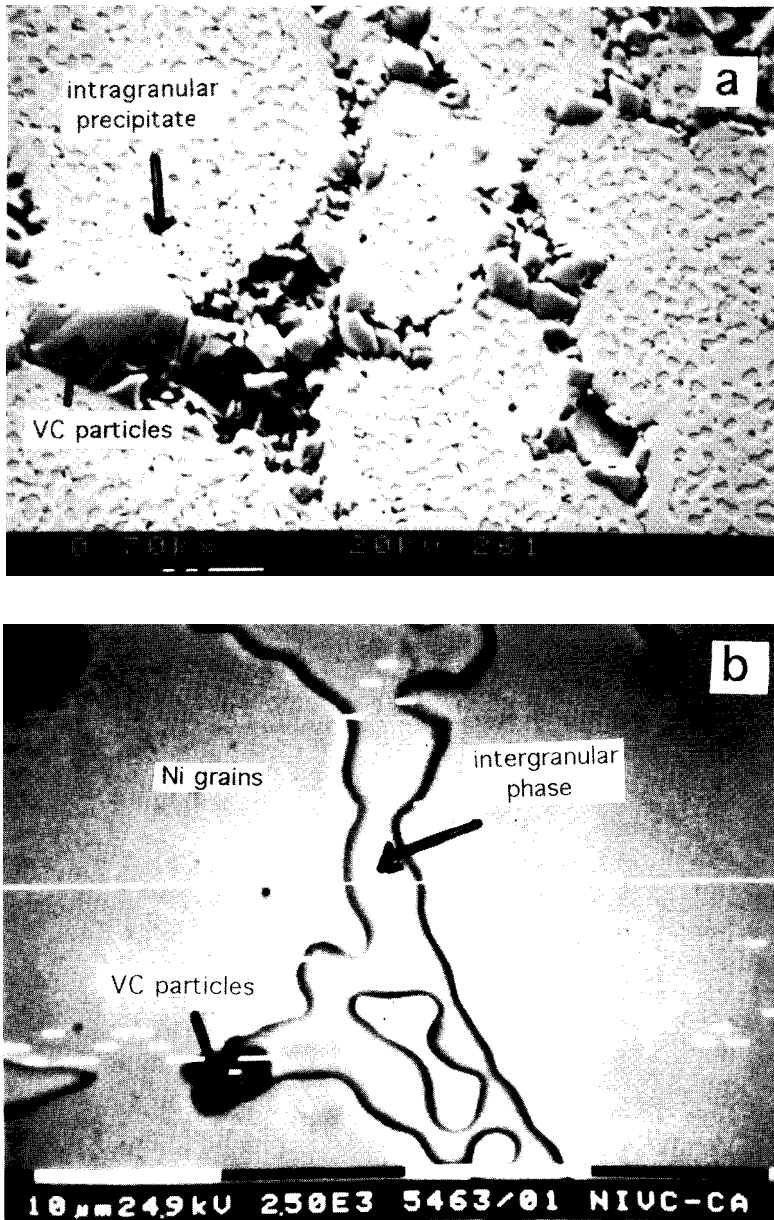


Figure 2. A representative microstructure of NiBSi/15% vol. VC sintered at: (a) 950°C for 30 min. (solid state sintering), and (b) 1100°C for 5 min. (liquid phase sintering). The boron profile obtained by WDS line scan shows maximum concentration in the intergranular phase.

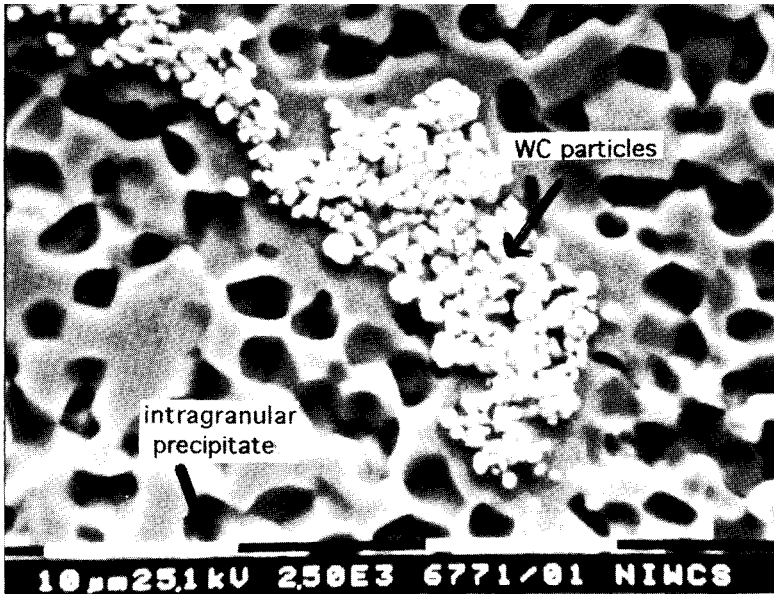


Figure 3. SEM micrograph of NiBSi/15% vol. VC WC composite obtained by solid state sintering.

Table 1 shows the average microhardness and density measurements of the NiBSi alloy and NiBSi/MC composites. The higher microhardness of the Ni-alloy grains was obtained for solid state sintering conditions (431 HV). For liquid phase sintered samples the microhardness decreases, since the intragranular precipitates were segregated; the intergranular network observed in this case showed a microhardness of about 1100 HV. Standard deviations between 5 and 9% were found for these measurements. The relative density increased with the sintering temperature and reached maximum values of about 93% at 1050°C. However this density is quite low for industrial application and other fabrication processes such as hot isostatic pressing are being explored.

Table 2 shows the results of the measured friction coefficient and wear loss. Low variation was observed in the mean friction coefficient in the steady-state stage. Wear differences between sintered samples are also low; however some influence of the sintering temperature and the carbide concentration was found. The type of carbide also determines the wear volume: NiBSi/WC and NiBSi/VC composites showed similar values, although, a higher wear rate was observed for NiBSi/NbC. Flame-sprayed samples showed significant wear loss compared with sintered samples. This behavior could be explained by the fact that the B-rich network is more densely distributed in thermally coated samples, increasing the probability of exposing a larger fraction of this brittle phase to high stresses. As observed by SEM in previous work [7], upon catastrophic failure of the brittle intergranular network, the ductile Ni phase is free to flow under pressure, increasing the wear rate. The presence of VC particles increased wear rate in the case of flame sprayed samples. For solid state sintering, lower wear volume and carbide removal was observed.

Table 2. Influence of sintering conditions on wear behavior.

Material	Fabrication procedure	Sintering temperature (°C)	Average friction coefficient	Wear volume (mm <sup>3</sup> )
NiBSi Alloy	Thermal spray	—	0.68	0.22
	Liquid phase sinter.	1100	0.76	0.12
NiBSi/15% vol. VC	Thermal spray	—	0.66	0.35
	Solid state sinter.	1040	0.94	0.09
	Liquid phase sinter.	1050	0.85	0.11
	Liquid phase	1100	0.70	0.14
NiBSi/30% vol. VC	Liquid phase sinter.	1050	0.87	0.08
NiBSi/15% vol. NbC	Liquid phase sinter.	1050	0.80	0.16
NiBSi/15% vol. WC	Liquid Phase Sinter.	1050	0.91	0.08

Note: The sintering time was 5 min. for all samples.

## Conclusions

Flame spraying and liquid phase sintering were used to produce NiBSi/MC composites. These materials were characterized by the presence of a Ni-rich matrix with a brittle B-rich intergranular network. The wear and friction behavior is rather similar for all materials since it appears to be controlled by the fracture of the B-rich net and the plastic flow of the ductile Ni-rich matrix.

For solid-state sintering, intergranular precipitates, similar to the precursor powders and microstructures, free of the intergranular deleterious phase were obtained. This microstructure seems to decrease the wear behavior. However solid state sintered composites showed lower density, so the fabrication process must be improved in order to obtain denser material with low concentration of the intergranular phase.

The stability of the NiBSi/VC and NiBSi/NbC composite materials was shown to depend on the stability of the amorphous intergranular net, more than on the adhesion of the carbides to the metal matrix, as was the case for NiBSi/WC [8].

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