Chapter 3: Synthesis of Materials and Experimental Procedure

This chapter describes the experimental procedures and the techniques used to synthesize and characterize the Ni_3Al intermetallic compound, reinforcement like Cu-modified or doped *h*BN (Cu-*h*BN) nanosheet and Ni_3Al-based self-lubricating composites. It also includes the details of the procedure and parameters adopted to examine friction and wear behaviour of Ni_3Al-based self-lubricating composites apart from the techniques like SEM, XRD and Raman spectroscopy implemented to characterize the worn surfaces of the tribo-pair after friction and wear testing.

3.1 Material Synthesis

3.1.1 Synthesis of Ni_3Al intermetallic compound

A mixture of commercially available powders was used to synthesise the Ni_3Al intermetallic compound by mechanical alloying. These powders included Ni (size: -325 mesh, purity: 99.8%), Al (size: 7–15 μm, purity: 99.5%), and Cr (size: -325 mesh, purity: 99%), which were procured from Alfa Aesar. Additionally, Mo (size: 1–5 μm, purity: 99%) and Zr (size: 5 μm, purity: 99%) powders were obtained from Sigma Aldrich, while B (size: 200 mesh, purity: 99%) was purchased from CDH in India.

To initiate the mechanical alloying process, the individual powders of Ni, Al, Cr, Zr, Mo, and B were mixed in specific weight percentages. The composition of these powders was as follows: 79.514 wt.% Ni, 8.12 wt.% Al, 5.209 wt.% Cr, 7.019 wt.% Mo, 0.129 wt.% Zr, and 0.0048 wt.% B. The mixing of the powders was carried out for a duration of 10 hours using a high-energy planetary ball mill (Make: VBCC Ceramics, Chennai, India). Tungsten carbide (WC) balls and a WC vial were employed as the milling media. The blending

process occurred at a speed of 200 rpm. Furthermore, a ball-to-powder ratio of 10:1, determined by weight, was maintained during the mechanical alloying process.

3.1.2 Preparation of Cu-modified *h*BN nanosheets (Cu-*h*BN)

The Cu-*h*BN was prepared by ultrasound-assisted exfoliation of *h*BN powder and chemical processing of Cu salt with a reducing agent. In the first step (Fig. 3.1), 5 *g* of *h*BN powder was exfoliated in 150 *mL* of water using an ultrasonic probe (Model: VCX 500; probe tip diameter: 13 mm; frequency: 20 *kHz*; Sonic & Materials, Inc. USA) for 1 hour. The resultant dispersion was centrifuged at 6500 rpm, which led to two distinct phases: the supernatant milky phase having highly dispersible *h*BN nanosheets (*h*-BNNSs) was separated from the precipitate (pellets at the bottom of each centrifuge tube) and dried in the forced convection oven to obtain the powder form. In the second step (Fig. 3.1), 17 *g* of the cupric chloride dihydrate ($CuCl_2.2H_2O$) was dissolved in 200 *mL* of water, which was followed by dispersion of *h*-BNNSs in an aqueous solution of cupric chloride. The aqueous solutions of ascorbic acid (1.41 *g* in 15 *mL*) and sodium borohydride (5 *g* in 500 *mL*) were separately added dropwise into the above-mentioned dispersion of *h*-BNNSs under continuous stirring, and the resultant reaction mixture was stirred for 24 hours. The developed product, i.e., Cu-modified *h*BN nanosheets (Cu-*h*BN), was separated by centrifugation, followed by multiple washes with distilled water to remove unreacted contents of cupric chloride and reducing agents, and finally dried in a forced convection oven.

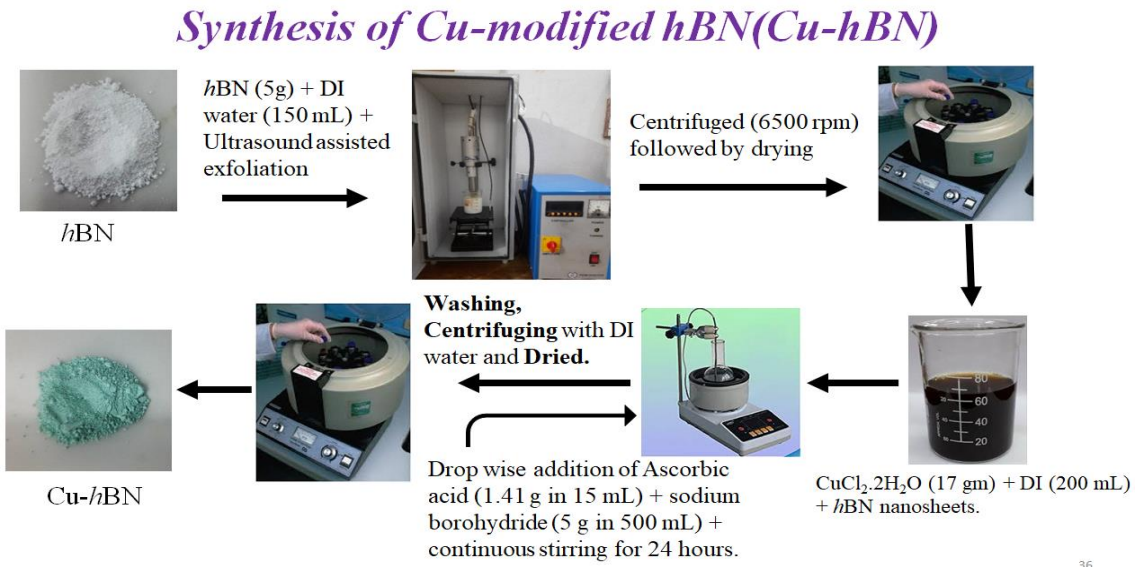

Fig. 3.1: Process flow for synthesis of Cu-modified hBN (Cu-hBN) nanosheets.

3.2 Vacuum hot press sintering of composites

3.2.1 Ni_3Al-based composites containing Ag, WS_2, and Ag-WS_2

The milled powder of Ni_3Al was mixed with 10 wt.% Ag (Nano Shel, Size: 40-50 μm, Purity: 99 %), 10 wt.% WS_2 (Sigma Aldrich, Size: 2 μm, Purity: 99 %), and 5 wt.% Ag-5 wt.% WS_2, each for a 3-hour duration at a speed of 200 rpm to synthesise composites. The powder mixture was packed into a BN-coated graphite mould with an inner diameter of 30 mm and put in a vacuum hot press sintering furnace (VBCC Ceramics, Chennai, India). The milled powders were cold pressed at 500 *kg* before being evacuated to a vacuum of 10^{-4} *mbar* in the furnace. After maintaining a vacuum of 10^{-4} *mbar*, the furnace was heated at a rate of 10 °C/min, kept steady for 5 minutes at 600 °C and heated again to 900 °C at which a compaction pressure of 35 MPa was applied until 1150 °C. The holding time was 15 minutes at 900 °C and 20 minutes at 1150 °C, then cooling to room temperature. The composition, designation, and sintering parameters of all composite specimens are given in Table 3.1. A schematic diagram of a typical vacuum hot press sintering furnace is shown in Fig. 3.2.

Table 3.1: Composition and vacuum hot press sintering parameters of Ni_3Al-based composites.

Sample Designation	Ni_3Al (wt.%)	Ag (wt.%)	WS_2 (wt.%)	VHP Sintering parameters	
				Compaction pressure (MPa)	Max. Temperature (°C)
Ni_3Al **(NI)**	100	0	0	35	1150
Ni_3Al-Ag **(NI-10A)**	90	10	0	35	1150
Ni_3Al-WS_2 **(NI-10W)**	90	0	10	35	1150
Ni_3Al-Ag-WS_2 **(NI-10AW)**	90	5	5	35	1150

3.2.2 Ni_3Al-based composites containing Ag, Cu-*h*BN, and Ag-Cu-*h*BN

The above-mentioned process was also used to prepare the Ni_3Al-based self-lubricating composites containing 10wt.% Ag, 10wt.% Cu-modified *h*BN nanosheets (Cu-*h*BN), and 5wt.% Ag-5wt.% Cu-modified *h*BN nanosheets (Cu-*h*BN). The composition, designation, and sintering parameters of all composite specimens are given in **Table 3.2**.

Table 3.2: Composition and vacuum hot press sintering parameters of Ni_3Al-based composites.

Sample Designation	Ni_3Al (wt.%)	Ag (wt.%)	Cu-*h*BN (wt.%)	VHP Sintering parameters	
				Compaction pressure (MPa)	Max. Temperature (°C)
Ni_3Al **(NI)**	100	0	0	35	1150
Ni_3Al-Ag **(NI-10Ag)**	90	10	0	35	1150
Ni_3Al-Cu-*h*BN **(NI-10BN)**	90	0	10	35	1150
Ni_3Al-Ag-Cu-*h*BN **(NI-10AgBN)**	90	5	5	35	1150

3.2.3 Ni_3Al-based composites containing WS_2, Cu-*h*BN, and WS_2-Cu-*h*BN

The aforesaid methodology was also employed for the fabrication of self-lubricating composites based on Ni_3Al, which comprised of 10wt.% WS_2, 10wt.% Cu-doped *h*BN nanosheets (Cu-*h*BN), and 5wt.% WS_2-5wt.% Cu-doped *h*BN nanosheets (Cu-*h*BN). The composition and designation of all composite specimens are given in Table 3.3.

Table 3.3: Composition and vacuum hot press sintering parameters of Ni_3Al-based composites.

Sample Designation	Ni_3Al (wt.%)	WS_2 (wt.%)	Cu-*h*BN (wt.%)	VHP Sintering parameters	
				Compaction pressure (MPa)	Max. Temperature (°C)
Ni_3Al **(NA)**	100	0	0	35	1150
Ni_3Al-WS_2 **(NAW)**	90	10	0	35	1150
Ni_3Al-Cu-*h*BN **(NAB)**	90	0	10	35	1150
Ni_3Al-WS_2-Cu-*h*BN **(NAWB)**	90	5	5	35	1150

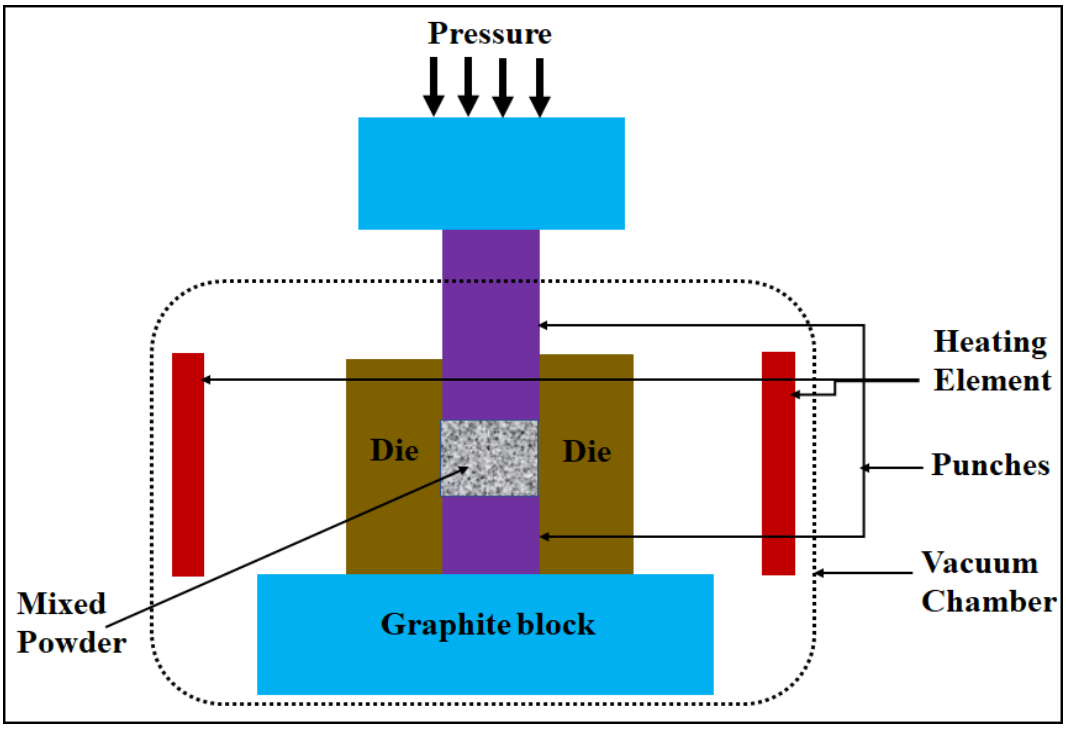

Fig. 3.2: Schematic diagram of a typical vacuum hot press sintering furnace.

3.3 Characterization of powders and Ni_3Al-based composites

3.3.1 Field emission scanning electron microscopy of powders and composites

The morphology of the elemental powders, ball-milled powders, and Ni_3Al-based composites have been examined under a field emission scanning electron microscope (Model: Nova Nano SEM 450, Make: FEI Company of USA).

3.3.2 Thermogravimetric Analysis of ball-milled powders

Thermogravimetric analysis (TGA-50, Shimadzu, Asia Pacific Pte Ltd.) was used to analyse the thermal behaviour of ball-milled powders of Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-5wt.% Ag-5wt.% WS_2 up to 800 °C at a heating rate of 10 °C/min with N_2 gas flowing into the furnace at 100 ml/min.

3.3.3 Transmission electron microscopy of Cu-*h*BN powders

The microstructural features of *h*BN nanosheets (*h*-BNNSs) and Cu-modified or doped *h*BN nanosheets (Cu-*h*BN) were probed by capturing the micrographs at different magnifications using a transmission electron microscope (Model: JEM 2100, Make: JEOL). In this context, the ethanolic dispersion of each sample was drop-cast on the Lacey Carbon TEM grid for collecting the micrographs.

3.3.4 XRD and XPS of Cu-*h*BN powders

The XRD pattern of Cu-*h*-BN was collected using an X-ray diffractometer (Model: Rigaku Smart lab, Make: Rigaku Corporation) to examine the crystalline features of constituent materials/components in Cu-*h*BN. The chemical features of Cu-*h*BN, particularly the nature of copper oxides, were evaluated using an X-ray photoelectron spectroscope (Model: K-Alpha XPS, Make: Thermo Scientific).

3.3.5 X-ray diffraction analysis of powders and composites

The phase composition of elemental powders, ball-milled powders and Ni_3Al-based composites were determined by subjecting the powder to an X-ray diffractometer (XRD:

Rigaku, Smart lab, Germany) with Cu K_α monochromatic radiation in the 2θ range from 10°-100°.

3.3.6 Hardness and density measurement

The density of the sintered specimens was measured using the Archimedes principle. The average value of Vickers micro-hardness has been reported after taking a minimum of 10 indentations in each composite specimen by using a semi-automatic microhardness tester (Micro Mach Technologies, Pune, India) with an indentation load of 200 *g* and a dwell time of 10 *s*.

3.4 Dry sliding friction and wear testing

The friction and wear tests on the composite specimens, namely, Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-10wt.% Cu-*h*BN, Ni_3Al-5wt.% Ag-5wt.% WS_2, Ni_3Al-5wt.% Ag-5wt.% Cu-*h*BN, and Ni_3Al-5wt.% WS_2-5wt.% Cu-*h*BN were conducted using a ball-on-a-disk high-temperature uni-directional rotary tribometer (Model: TR-20LE-DHM-PHM-800; Make: DUCOM, Bangalore, India) against a stationary silicon-nitride ball (Si_3N_4, Dia.: 6 mm) following ASTM G99-95 standards. All the tests were conducted at RT, 200 °C, 400 °C, 600 °C, and 800 °C at a constant load of 10 N and fixed sliding velocity of 0.2 m/s. The selection of the test configuration, counterface material, and test conditions were based on previously published research work [25,34,129]**.** Si_3N_4 was chosen as the counterpart due to its high hardness and high-temperature anti-oxidation property, which reflects the wear resistance mechanism of Ni_3Al-based composites. The hardness of the counter-body Si_3N_4 ball was 16.2 GPa or 1652 HV, which is noted to be much higher than base Ni_3Al (355 HV or 3.481GPa), and its wear rate during the sliding process is one order of magnitude less than that of the Ni_3Al and composite specimens, allowing us to conveniently investigate the tribological properties of Ni_3Al-based composites containing Ag, WS_2, Cu-*h*BN, Ag-WS_2, Ag-Cu-*h*BN, and WS_2-Cu-*h*BN at elevated temperatures

without considering wear of counter Si_3N_4 ball. Each composite specimen was polished with emery sheets up to a grit size of 1200, followed by cloth polishing with alumina and wet polishing using 0.05 μm diamond paste before being subjected to a wear test. The surface roughness value of the specimens before the wear test was estimated to be 0.0505 μm. All the tests were conducted at 35 to 55 % relative humidity. All the tests were run for 30 minutes, corresponding to a sliding distance of 360 m.

The wear mass losses of composites were measured by an electronic balance (A & D instruments, India) having an accuracy of 1×10^{-7} kg. Each test at a particular load, speed and temperature was repeated at least thrice and the average data for volume loss after each test was used for the analysis of specific wear rate. The specific wear rate (W, mm^3/Nm) was calculated using the formula

$$W = V/SL \tag{3.1}$$

where V stands for the volume loss in mm^3, S for the sliding distance in m, and L for the applied load in N.

The torque on the sample is calibrated in terms of friction force as indicated on the machine, using a fixed distance of lever arm of the apparatus. The tribometer had a computerised data acquisition system and strain gauge force transducer for measuring frictional force. The frictional force was recorded continuously by a computer. The coefficient of friction has been determined from the friction force and the normal loads; only pre-calibrated dead loads have been used.

Figure 3.3 presents a schematic diagram of a high-temperature ball-on-disc tribometer set up for friction and wear tests. The tribometer was attached to an induction heater that heated the rotary disc from the bottom. After placing the composite specimen and the Si_3N_4 ball in their respective fixtures, the composite specimen was heated to the desired temperature using an induction heater before being loaded against the Si_3N_4 counterface. The requisite

load was applied to the arm after achieving the desired temperature, and the ball and composite specimen were brought into contact. The pyrometer was used to ensure that the appropriate temperature was maintained. The friction force during each run was recorded through a data acquisition system in a computer that had an interface with a tribometer. The data from the start to the end of the test has been used to estimate the coefficient of friction. Each test was done at least three times, and the average data has been reported. After each run, the tribometer and induction heater were switched off and left to cool to ambient temperature before the sample was weighed.

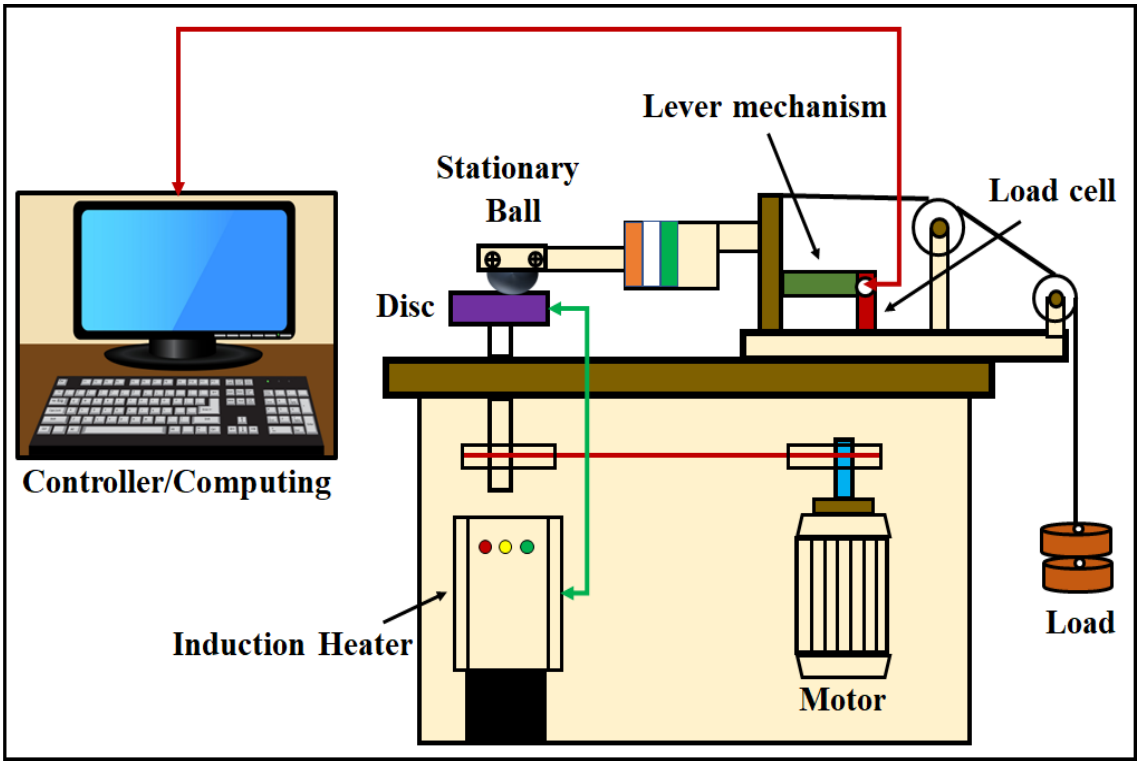

Fig. 3.3: Schematic diagram of high-temperature ball-on-disc tribometer set up for friction and wear tests.

Table 3.4: Tribological testing parameters for Ni_3Al-based composites

Variables	Composition	Temperature	Load	Speed	Sliding distance
Composition and Temperature	NI	RT, 200 °C, 400 °C, 600 °C and 800 °C	10 N	0.2 m/s	360 m
	NI-10A				
	NI-10W				
	NI-10B				
Composition and Temperature	NI	RT, 200 °C, 400 °C, 600 °C and 800 °C	10 N	0.2 m/s	360 m
	NI-10Ag				
	NI-10BN				
	NI-10AgBN				
Composition and Temperature	NA	RT, 200 °C, 400 °C, 600 °C and 800 °C	10 N	0.2 m/s	360 m
	NAW				
	NAB				
	NAWB				

3.5 Characterization of worn surfaces

3.5.1 Field emission scanning electron microscopy of worn surfaces

In order to explore the prevailing mechanisms of wear, the sliding surfaces of the worn composites, namely, Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-10wt.% Cu-*h*BN, Ni_3Al-5wt.% Ag-5wt.% WS_2, Ni_3Al-5wt.% Ag-5wt.% Cu-*h*BN, and Ni_3Al-5wt.% WS_2-5wt.% Cu-*h*BN, as well as worn counterface Si_3N_4 balls under each test condition, were examined using a Field-emission scanning electron microscope (FESEM: Nova Nano SEM 450, FEI, USA and FESEM: Apreo S, ThermoFisher) combined with backscattered electron detector (BSED) and energy-dispersive X-ray spectrometers (EDS).

3.5.2 X-ray diffraction and Raman spectroscopy analysis of worn surfaces

The worn surfaces of Ni_3Al-based composite specimens have been subjected to X-ray diffraction analysis to examine the formation of new phases that might have resulted from the tribo-chemical reactions at the interface due to sliding. The X-ray Diffractometer (XRD:

Rigaku, Smart lab, Germany) with Cu K_α monochromatic radiation (λ=0.1541 nm and 40*k*V operating voltage) in the 2θ range from 20°-100° with two-dimensional D/MAX RAPID II-CMF detector of micro area diffraction unit has been used to reveal the presence of various compounds at the worn surface.

The worn surface of the composite and counterface ball were also subjected to high-resolution confocal Raman imaging (WITec alpha 300 RAS, Oxford Instruments, Germany) to reveal the formation of new compounds/phases due to tribo-chemical interactions. The worn scar of composite samples was loaded to the stage of the Raman spectrometer under the laser lens. A diode laser source with an excitation wavelength of 532 nm at a magnification of objective lens of 100X with a grating of 600 groves per mm was used. The accumulations were 10 with an integration time of 1 sec and a laser line width of 50-100 of a picometer. The spot size was 350 nm with 100X objective 0.9 NA. A visible monochromatic laser light source was focused on worn surfaces, and scattered light was collected and analysed using a spectrometer. The Raman spectra was typically recorded as intensity versus Raman shift frequency (cm^{-1}). The obtained Raman spectra were carefully analysed using reference data to identify the various phases/compounds formed, considering their corresponding peak intensities and Raman shift. The results obtained from the X-ray diffraction and Raman spectroscopy are presented and discussed in Chapters 4 and 5, respectively.

3.5.3 Examination of cross-section of worn surfaces

The cross-section and thickness of oxide layers for Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-10wt.% Cu-*h*BN, Ni_3Al-5wt.% Ag-5wt.% WS_2 and Ni_3Al-5wt.% Ag-5wt.% Cu-*h*BN at 800 °C were analysed using field emission scanning electron microscopy (ESEM) in conjunction with an energy dispersive detector (EDS), and the hardness of the glaze layer formed at 800 °C for Ni_3Al-5w.% Ag-5wt.% WS_2 was measured using a microhardness tester.