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# Fabrication and corrosion resistance of HVOF-sprayed $Ni_2Si$ intermetallic compound

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ABSTRACT

In this study, $Ni_2Si$ powders were deposited onto 420 stainless steel substrate using high velocity oxy-fuel (HVOF) process. The coatings were characterized by X-ray diffractometery, optical and scanning electron microscopy and microhardness measurements. Tafel polarization tests and electrochemical impedance spectroscopy (EIS) measurements were employed to study corrosion performance of the coatings in 70% $H_2SO_4$ media at room temperature. Here, a dense sintered $Ni_2Si$ was used as reference material. The results showed the phase composition of HVOF coating is similar to that of feedstock powders. The corrosion rate of HVOF $Ni_2Si$ coatings was much lower than that of 420 stainless steel substrate but slightly higher than that of bulk $Ni_2Si$. Further investigation showed that both thermally sprayed and sintered (reference) $Ni_2Si$ alloys exhibited similar anodic polarization behavior including a narrow active section followed by a wide passive region.



## 1. Introduction

Nickel silicide intermetallic compounds exhibit interesting electrochemical, mechanical and electrical properties such as high temperature corrosion resistance and sulfuric acid resistance [1–13]. In this regard, $Ni_2Si$ compound has been of considerable interest in electronic industry due to low electrical resistivity. In addition to electronic properties, $Ni_2Si$ compound also enjoys high hardness as well as good corrosion and wear resistance [1,7–9].

The development of bulk $Ni_2Si$ compound as a corrosion and wear resistant material may encounter restrictions due to low ductility and high production costs of this compound [1]. Consequently, interest in $Ni_2Si$ coating technologies is on the rise. $Ni_2Si$ based coatings have been fabricated by slurry pack cementation (siliconizing) of electrodeposited nickel layers on copper substrate [14]. This coating has shown low friction coefficient and high hardness. On the other hand, sputtering process has been also used to fabricate $Ni_2Si$ thin films. In this regard, corrosion and wear resistant coatings with high hardness have been obtained [1,7,8].

Previous methods used to fabricate $Ni_2Si$ coatings exhibit some disadvantages. For example, siliconizing of nickel coating is a time consuming process (it involves two steps; electrodeposition and subsequent pack cementation process) [14]. Since this process is performed at high temperatures (higher than 900 °C), so, metallurgical microstructure and mechanical properties of the substrate can be changed. In addition, distortion can occur in some cases. In addition, sputtered $Ni_2Si$ coatings have low thickness (<1 μm). They may not be suitable for harsh corrosive environments [1,7,8].

Thermal spray processes can be used to fabricate $Ni_2Si$ coatings. In these processes, the powder or wire feedstock is heated to form molten or semi-molten particles which are accelerated and then strike onto a substrate to form coating layers. Thermal spray processes can be applied in site. Due to low temperature (<200 °C) of processes, the distortion and metallurgical changes can be minimized. These processes can be performed on various substrates to fabricate 50–1000 μm thick coatings. Among thermal spray processes, high velocity oxy-fuel (HVOF) process is suitable for fabrication of corrosion resistant coatings due to lower porosity of resultant coatings. HVOF involves ignition of a gas or liquid fuel (e.g. hydrogen or kerosene) in a chamber under high pressures. Here, the particles become heated and accelerated by a jet flame made from high pressured mixture of oxygen and a fuel. Molten and softened particles strike the substrate at a high velocity (300–1200 m/s). Therefore, thick (>50 μm) and dense coatings with good adhesion and, commonly, with low oxidation can be obtained using HVOF [15,16]. Therefore, development and fabrication of HVOF $Ni_2Si$ coatings may be interesting.

The aim of this study was to characterize $Ni_2Si$ coatings fabricated by HVOF spraying. The corrosion resistance of the coatings in 70% $H_2SO_4$ solution has been evaluated.

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**Table 1**
HVOF process parameters.

| Spray parameters | Unit |
|---|---|
| Stand off distance | 35 cm |
| Oxygen flow rate | 830 l/min |
| Kerosene flow rate | 260 ml/min |
| Nozzle length | 20 cm |
| Powder feed rate | 60 g/min |
| Carrier gas ($N_2$) flow rate | 3 l/min |

## 2. Experimental procedures

$Ni_2Si$ intermetallic powders with a particle size range of 20–63 μm were used as feedstock. The powders were produced using a mechanochemical approach as described in previous paper [9] followed by crushing and sieving. 420 stainless steel (Fe – 0.179 C – 14 Cr – 0.429 Ni – 0.490 Si – 0.610 Mn – 0.003 P – 0.0363 S – 0.013 Mo wt.%) disks with the diameter of 4 mm and thickness of 20 mm were used as substrate. Before spray procedure, SiC grits were used to blast the substrates to obtain surfaces with a roughness ($R_a$) of 10 μm. Then, acetone was used to clean the samples. A Met Jet III HVOF system (Metallization Ltd., Dudley, UK) using kerosene as a liquid fuel was utilized to deposit Ni–Si coatings. The process parameters are listed in Table 1. A sintered $Ni_2Si$ specimen was used as a reference material. The reference material was fabricated by mechanical alloying of Ni–Si powders [9], compaction in a 1 cm die at 750 MPa and subsequent reaction sintering at 1050 °C for 1 h in a vacuum furnace (VAS, Germany). The operating pressure of furnace was lower than 0.01 mbar.

The phase composition of samples was investigated by X-ray diffractometry (XRD, Philips X'Pert-MPD) using Cu Kα radiation (λ = l.54056 Å) generated at 40 kV and 30 mA. Cross-section of the coatings was investigated using an optical and a scanning electron microscope (SEM, Philips XL30) operated at 20 kV with an energy dispersive spectroscopy (EDS) for microanalysis. The porosity content was measured using Image Tool 3.00 software. The microhardness values were measured with a microhardness tester (Buehler Micromet II) at a load of 50 g. Vickers indentation marks were performed on ten different locations on each sample.

All specimens were mechanically polished down to 1200 grit SiC paper before corrosion experiments. Then, they were washed in distilled water and ethanol followed by drying in warm air. After 1 h immersion, Tafel polarization tests were performed in a three electrode set-up consisting of platinum wire as a counter electrode and standard calomel electrode (SCE) as a reference. The tests were performed in 70% $H_2SO_4$ solution at a scan rate of 1 mV/s using an AMETEK potentiostat (model PARSTAT 2273). The polarization scan ranged from −250 (vs. open circuit potential) to 2000 mV (vs. SCE). Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHz–10 mHz and the voltage amplitude of 10 mV peak-to-peak regarding to open circuit potential. The number of points per decade in the EIS test was 5. The EIS spectra were analyzed using Zview software. The corrosion experiments were carried out on three different locations on each specimen. The area of the sample surface exposed to the corrosive solution in the three-electrode cell was 0.5 $cm^2$.

## 3. Results and discussion

### 3.1. Characterization of $Ni_2Si$ materials

Fig. 1 shows the secondary electron micrograph of feedstock powders. The powders appear angular and polygonal in shape as a result of crushing [15,16]. The particle size range of powders is 20–63 μm with the average size of 45 μm. For characterization of feedstock powders, an overall EDS measurement was performed.

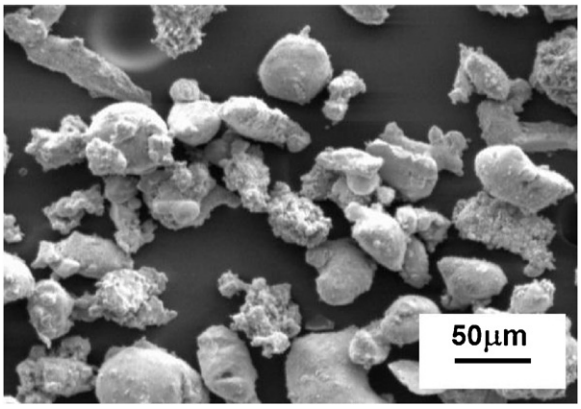


**Fig. 1.** SE micrograph showing morphology of $Ni_2Si$ feedstock powders.

The chemical composition of powders was found to be Ni – 35 Si (at.%). X-ray diffractograms of various $Ni_2Si$ samples are observed in Fig. 2. Due to numerous diffraction lines, the diffractograms are presented in two Bragg angle ($2\theta$) ranges (20–60° and 60–100°) to identify and distinguish them easily. Only peaks of δ-$Ni_2Si$ with orthorhombic structure were detected in HVOF, sintered and powder specimens (the miller indices of δ-$Ni_2Si$ diffraction lines are shown in Fig. 2). A large number of peaks are observed in each diffractogram. It is well-known that crystal structures with lower symmetry like orthorhombic can exhibit a large number of diffraction peaks during XRD experiments [17]. In contrast, in cubic crystals like $\beta_1$-$Ni_3Si$ [4], the number of diffraction lines decreases due to high symmetry of crystal structure.

It can be seen in Fig. 2 that the phase composition of $Ni_2Si$ powders has not been changed during HVOF spraying. δ-$Ni_2Si$ phase exhibits congruent melting as seen in Ni–Si phase diagram [15,16]. It means that this phase is thermodynamically stable till its melting point (1300 °C) [10–13]. In addition, high heating and cooling rates (>$10^5$ K/s) and also short in-flight times (<0.001 s) experienced by particles during HVOF process lead to compositional homogeneity which hinders diffusional phase transformations. These two factors favor the phase stability of δ-$Ni_2Si$ feedstock powders during HVOF spraying. Although HVOF, sintered and powder specimens exhibited similar phase composition, however, some differences can be observed in their diffraction lines. In the case of $Ni_2Si$ powder

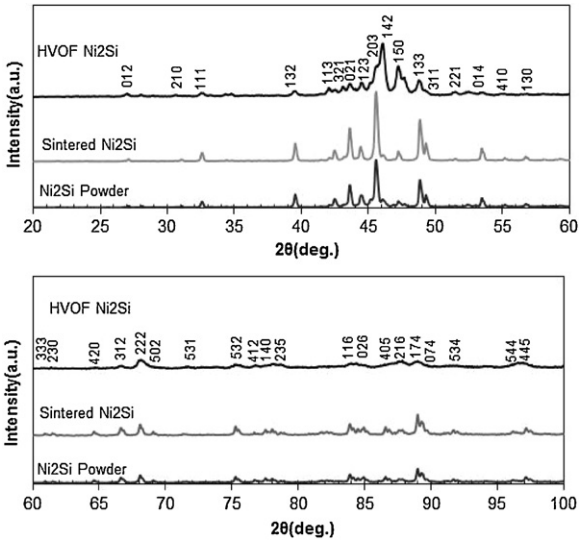


**Fig. 2.** XRD patterns of various $Ni_2Si$ specimens; powder, coating and reference material; the identified peaks are belonging to δ-$Ni_2Si$.