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How to Determine Possible Interactions of Silicide and Aluminide in Preparation of Composites

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Silicide – aluminide composites could be considered as potential tool materials, because of high wear resistance and thermal stability. Recently, the alloys based on iron aluminide and silicide were tested, but they found to be very brittle due to the occurrence of brittle Fe-Al-Si ternary phases. On the other hand, in TiAl-Ti_5Si_3 composite, no ternary phase was formed during sintering, even though it can be expected based on thermodynamics. Therefore, this paper aims on finding the way how to test potential interaction between silicide and aluminide phase during preparation of these composites on the example of the FeSi – NiAl composite. The approach, proposed in this work, deals with the pre-sintered iron silicide, which was surrounded by aluminide powder in the sintering die and spark plasma sintered again. After that this model sample was annealed under various conditions and the FeSi – NiAl interface was observed. The experiments proved that no chemical reaction between FeSi and NiAl phase occurs during sintering and thermal exposure at 1000 °C. The visible interfacial layer is just a result of mutual diffusion.

Keywords: Aluminide, Silicide, Sintering, Reaction

1 Introduction

Due to high economic importance combined with high supply risk, EU defines the list of critical raw materials (CRM) since 2014 [1]. Some metals are listed there, including also tungsten and cobalt, which are of high importance for nowadays tooling industry and hence also for all manufacturing sectors [2,3]. There is a high pressure on increase of recyclability of these elements and also on their substitution, where it is relevant [4]. And even though titanium and nickel also appeared on the list recently, the substitution of cobalt and tungsten is still of major importance. One of the approaches, how this substitution can be realized, is the substitution of both matrix and the reinforcement, leading to novel composites. These solutions have been already tested worldwide, leading to the properties relatively similar to the WC-Co composites. Among them, the Ni-TiC composite or boron carbide should be mentioned [5,6]. In our research, we focused on materials containing silicide and aluminide. At first, these materials were prepared by reactive sintering, where both silicide and aluminide formed in situ from elemental powders during sintering. This was achieved in Ti-Al-Si system, where TiAl and Ti_5Si_3 phases were obtained, without any ternary phase. There was observed some partial mutual substitution of aluminium and silicon in both phases, but the system was still composed of two above-mentioned phases [7]. On the other hand, in Fe-Al-Si system, two different silicides (FeSi and Fe_3Si), aluminide phase (FeAl) and also brittle ternary phases ($Fe_3Al_2Si_3$, Al_2FeSi and others) were identified in the product [8]. The same phases occurred also when the material was manufactured by mechanical alloying and spark plasma sintering. And hence, the materials were highly brittle, even more than e.g. corundum ceramics. In order to overcome these problems, preparation of individual phases, their mixing and sintering was tested. This work aims to show the methods, which are applicable to reveal the potential interaction between the silicide and aluminide during preparation of the composites on the example of FeSi-NiAl.

2 Materials and Methods

The NiAl-FeSi composite with the weight ratio of aluminide to silicide 1:1 was prepared by separate synthesis of nickel aluminide and iron silicide by mechanical alloying. The blends of the chemical composition corresponding to NiAl and FeSi were prepared from elemental pure powders, which were mixed in appropriate amounts forming 20 g powder batches for mechanical alloying. The following powders were used to prepare the blend for MA: Fe (purity 99.9 %, particle size <44 μm, Strem Chemicals), Al (purity 99.7 %, particle size <44 μm, Strem Chemicals), Si (purity 99.5 %, particle size <44 μm, Alfa Aesar) and Ni (purity 99.99 %, particle size <150 μm, Strem Chemicals). Mechanical alloying of the blends was carried out in a planetary ball mill Retsch PM100, where the milling jar and also milling balls were made of AISI 420 stainless steel. Argon was used as the protective atmosphere during mechanical alloying. The mechanical alloying conditions were following: duration of 4 for NiAl and 10 h for FeSi, change of rotation direction each 15 min, rotational velocity of 400 rpm, batch of 20 g and the ball-to-powder weight ratio of approx. 15:1. The process conditions were optimized in the recent work [9].

In order to determine the interaction between FeSi and NiAl, the samples composed of FeSi solid piece embedded in NiAl were prepared and subsequently annealed. FeSi powder was sintered, embedded to NiAl and sintered again. Firstly, the FeSi phase was sintered to the form of a cylindrical sample of 20 mm in diameter, then the sample was cut to quarters. This FeSi was placed to the sintering die and surrounded by the NiAl powder for the second sintering. Both sintering routes were done by spark plasma sintering (SPS, FCT Systeme HP-D10, Rauenstein, Germany) at the temperature 1000 °C with a pressure of 48 MPa for 10 min. The heating rate of 300 °C/min was used in this process, while the samples were cooled by the rate of 50 °C/min after the sintering process was completed. The sintered samples were characterized by the route described below and then annealed at 1000 °C for 1-4 h.

Microstructure and local changes in chemical composition of the interface between FeSi and NiAl after second sintering was observed using TESCAN VEGA 3 LMU scanning electron microscope equipped by an energy-dispersive spectrometer X-max 20 mm^2 (EDS, Oxford Instruments, High Wycombe, United Kingdom) after etching of prepared samples by modified Kroll's reagent (10 ml HNO_3, 5 ml HF, 85 ml H_2O).

From the changes in chemical composition, the diffusion paths of individual elements and their apparent diffusion coefficients were determined. For the calculation of apparent diffusion coefficients D, following equation (1) was applied:

$$D = \frac{x^2}{2 \cdot t} \tag{1}$$

Where:
x [m]…The diffusion path,
t [s]…The annealing duration.

The applied model expects the one-dimensional diffusion (inward/outward) in the direction perpendicular to the FeSi-NiAl interface.

In order to identify potential changes in phase composition, the composite FeSi-NiAl was prepared by blending of these phases in weight ratio of 1 :1, sintered by the means of spark plasma sintering using the same procedure and studied by X-ray diffraction (XRD) by PANalytical X'Pert Pro diffractometer with Co anode and evaluated using the HighScore Software Package with PDF-2 database.

3 Results and Discussion

After second sintering, there is a transition zone between FeSi and NiAl visible by SEM in backscattered electrons (BSE) mode, see Figure 1. At the left side of the image, the FeSi phase can be seen, while the NiAl phase is located at the right. It shows lower porosity of the aluminide than of silicide, which can be connected with higher plasticity of aluminide at the sintering temperature, which improves the compressibility of the powder during the spark plasma sintering process. It is also visible that the silicide phase is not fully homogeneous, containing probably also other silicide than FeSi.

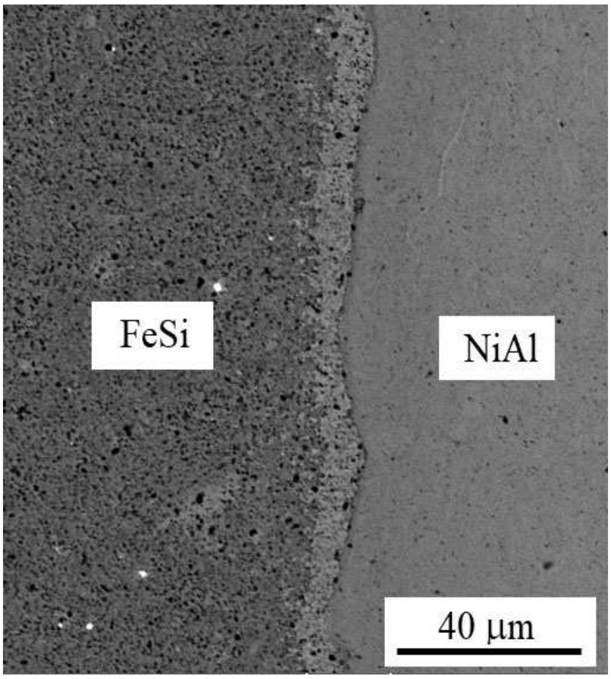

Fig. 1 *Microstructure of FeSi-NiAl sintered at 1000 °C*

The interface region was analysed by EDS and the elemental map revealed just a slight decrease of the silicon concentration in the transition zone, accompanied by the increase of aluminium (Figure 2). Therefore, it can be highly expected that this region is the iron silicide, where silicon was partially substituted by aluminium

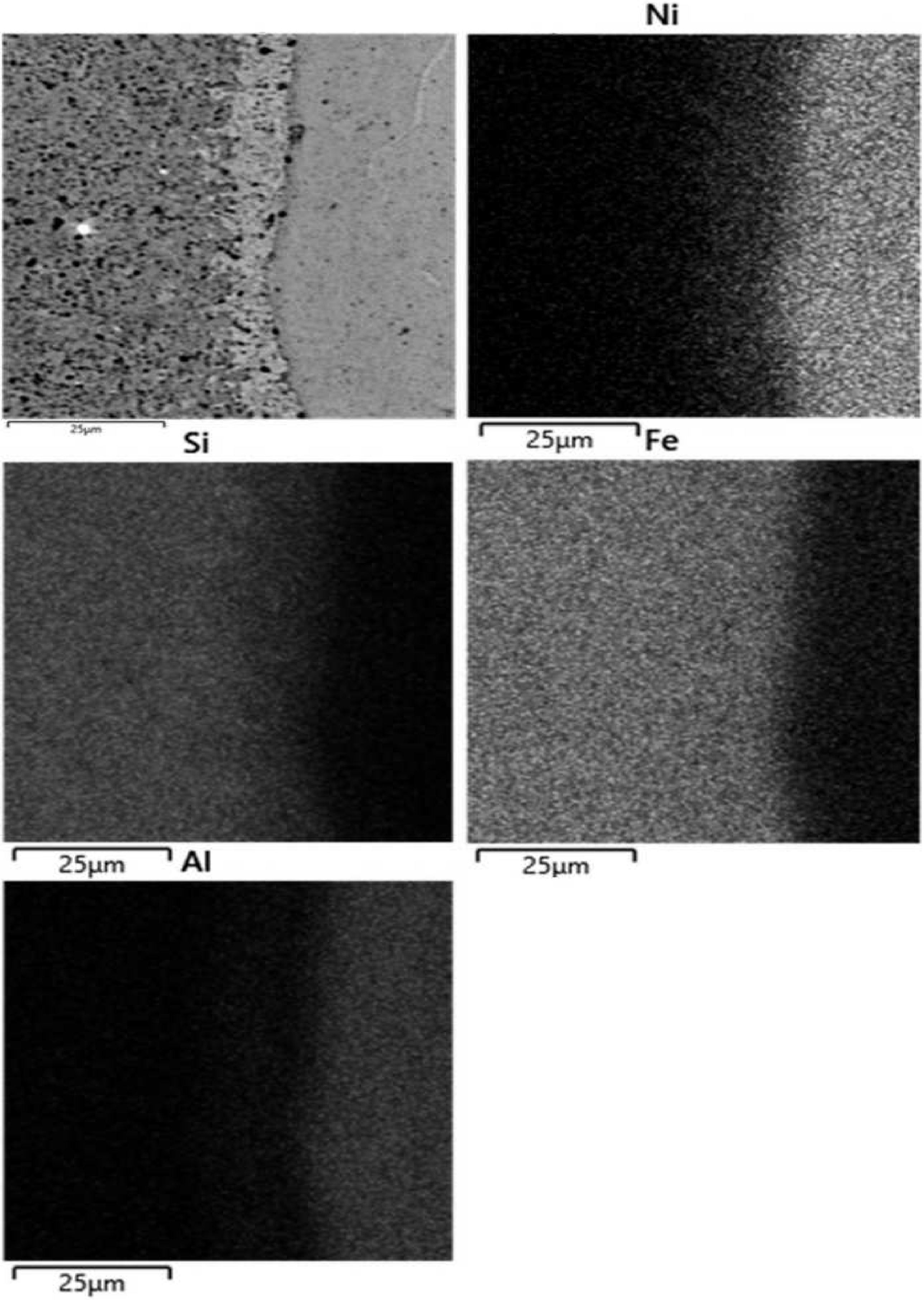

Fig. 2 *EDS map of the distribution of elements in the interface region between FeSi and NiAl phases*

After annealing at 1000 °C for 1 and 4 h, the width of this region increased, see Figure 3.

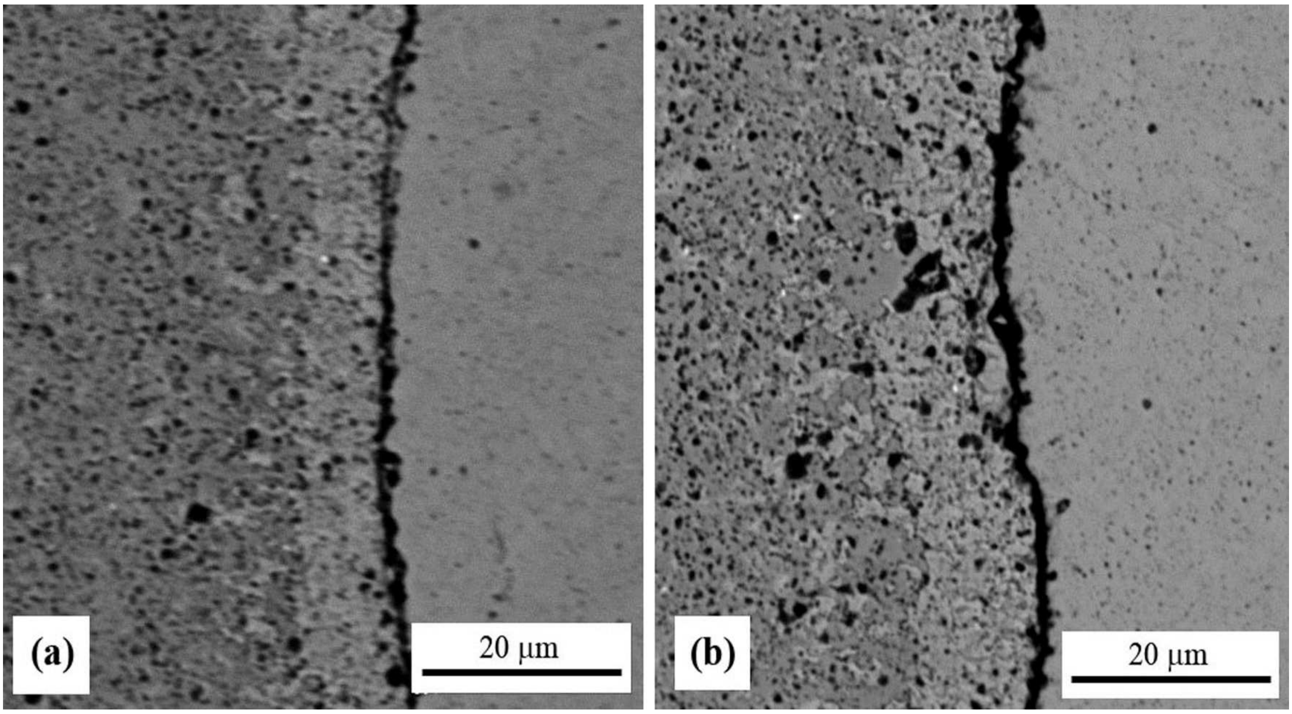

Fig. 3 *Microstructure of FeSi-NiAl sintered at 1000 °C for 1 h (a) and 4 h (b)*

In order to quantify the changes around the interface, the point EDS analysis was carried out across the interface in the as-sintered and annealed samples. For the illustration, the location of the points is shown in Figure 4. By this analysis, the profiles of individual elements were obtained, see the sample profile of iron in Figure 5. The profile shows that iron enriched the nickel aluminide to relatively large distance. The largest diffusion path was obtained for nickel, which probably easily penetrates to iron silicide (Table 1). It can be also seen that silicon diffuses faster to aluminide than aluminium to silicide. It can be also connected with solubility of these elements in both phases.

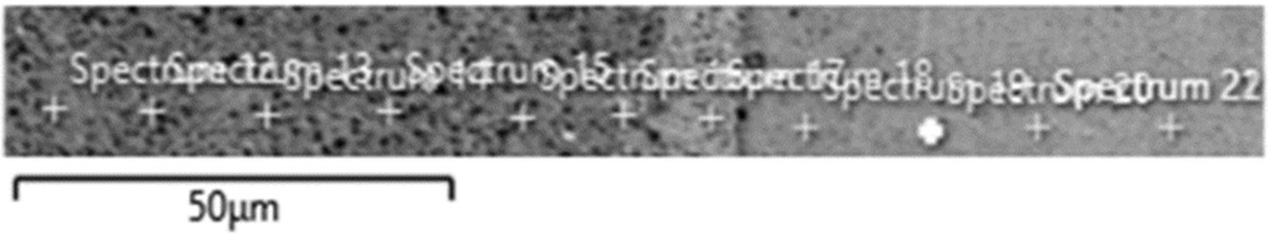

Fig. 4 *Location of the points in EDS analysis of the interface region between FeSi and NiAl phases*

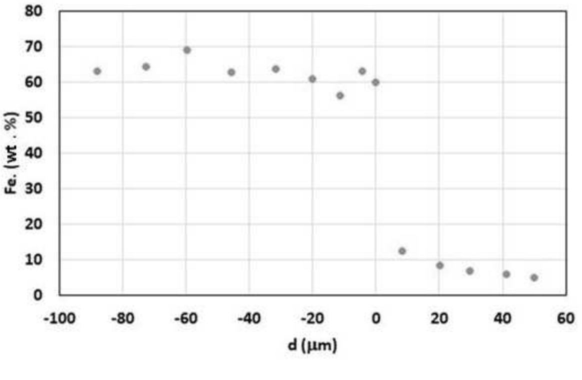

Fig. 5 *EDS concentration profile of iron across the interface between FeSi and NiAl (in the points presented in Figure 3)*

Tab. 1 *Diffusion paths of the elements in the samples sintered and annealed at 1000 °C*

Annealing duration (h)	**Diffusion path (µm)**			
	Ni	**Al**	**Fe**	**Si**
0 (as-sintered)	25	14	35	50
1	46	20	30	41
4	77	36	53	53

Tab. 2 *Apparent diffusion coefficients ($m^2 s^{-1} \times 10^{-12}$) in aluminide and silicide phase calculated on the basis of the data in Table 1*

Annealing duration (h)	Total time at the temperature, including sintering (min)	Ni	Al	Fe	Si
0	15	0.35	0.11	0.68	1.39
1	75	0.24	0.04	0.10	0.19
4	255	0.19	0.04	0.09	0.09

The apparent diffusion coefficients calculated by eq. (1) from the diffusion paths in Table 1 are summarized in Table 2. It can be seen that the values for annealed samples are almost constant with time and therefore it can be concluded that they are, with high probability, the correct values of diffusion coefficients of particular elements in silicide and aluminide. Even though there is a general lack of data about the diffusivity of the studied elements (Fe, Ni, Al, Si) in iron silicide and nickel aluminide, the determined values of apparent diffusion coefficients are in the same order as the self-diffusion coefficients of iron in Fe-Al and Fe-Si phases[10]. However, there is a deviation of the apparent diffusion coefficients calculated on the sample in the as-sintered state without annealing. The values are significantly higher in the case of iron and silicon. This phenomenon can be probably explained on the basis of the temperature distribution in spark plasma sintering. In this process, the heating is not uniform. The surfaces of the particles in contact are heated much more than their cores, which results in high temperature and even partial melting on the surface of the particles. The reasons for this are in the Joule heating effect, where there is higher electrical resistivity in contact points of the particles due to improper contact and also due to slight oxidation of the particles surfaces. In spark plasma sintering, the formation of discharge between individual particles, leading to plasma, is also discussed. The occurrence of plasma could lead to a dramatic increase of the temperature on the surfaces of sintered powder particles. Therefore, the high apparent diffusion coefficients calculated in the as-sintered state are probably connected with rapid diffusion at high temperature (and maybe also in different environment – melt) along the surfaces of the particles.

The above statements are correct in the case that there is no chemical reaction between silicide and aluminide. In order to prove that there is no significant chemical reaction between iron silicide and nickel aluminide, the composite was prepared by blending of iron silicide and nickel aluminide, as described in chapter 2, and XRD analysis was carried out. The results showed that the Fe_5Si_3 phase appeared during sintering (Figure 6). This phase, which is stable at the temperature above 825 °C [11], was probably stabilized by relatively quick changes of the temperature during sintering process and possibly also due to the mutual diffusion of the elements, which could stabilize it. The EDS analysis of the interface layer showed the content of silicon of 36 ± 1 at. %, together with 12 ± 2 at. % of aluminium. When we assume that aluminium substitutes silicon, then we'll get approx. 48 at. % of silicon equivalent (i.e. Si +Al contents), which well corresponds to the FeSi phase (50 at. % of Si). When only silicon is taken into the account and the substitution by aluminium is expected on the iron positions of the lattice (which is not highly probable), then the phase could be Fe_5Si_3 (37.5 at. % of Si). However, Fe_5Si_3 was detected already after sintering of pure FeSi sample and therefore, the Fe_5Si_3 phase is rather responsible for the heterogeneity of the iron silicide side of the sample in Figure 1. In that case we can state that there is no mutual reaction between the nickel aluminide and iron silicide, and the apparent diffusion coefficients can be taken as real diffusion coefficients.

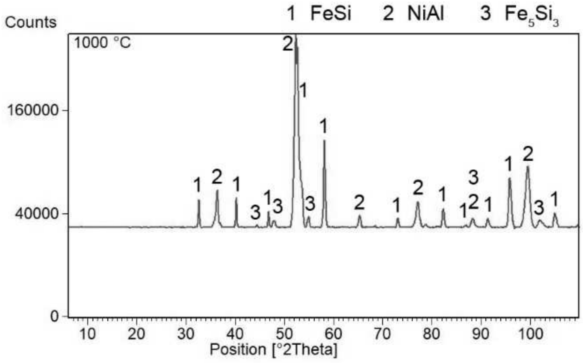

Fig. 6 *XRD pattern of the FeSi-NiAl composite sintered at 1000 °C*

4 Conclusion

This work was devoted to the description of potential interaction between iron silicide and nickel aluminide, which are considered as reinforcement and matrix of the novel composite, respectively. The mutual diffusion, leading to the formation of secondary solid solutions, is considered as useful, because of improved bonding of the phases. On the other hand, the reaction leading to brittle products, is very dangerous and has to be avoided. In this work we found that the spark plasma sintering and even further thermal exposure at 1000 °C for 1 and 4 h did not lead to the formation of any unwanted ternary phase. An interface layer, which was obtained on the interface between these phases, is a result of mutual diffusion of the elements between silicide and aluminide and it not any new compound. The apparent diffusion coefficients of Ni, Fe, Si and Al in aluminide and silicide phase were determined.

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