

Structure of Mo/Mo silicide composites infiltrated with molten Ni and subsequently compacted by HIP

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Received 15 August 2013, received in revised form 24 October 2013, accepted 24 October 2013

Abstract

Reactions during infiltration of Mo/Mo silicide wires with Ni and subsequent compaction with HIP were qualitatively assessed in this work. Intense reactions of Ni with Mo/Mo silicide composites were recorded. The extent of these reactions is determined by the amount of available Ni. If excessive Ni is available, Mo and Mo silicides are dissolved with detrimental effect on the composite structure. If less Ni is applied and the intimate contact of Ni with Mo/Mo silicides is shortened substantially, less intense reaction takes place providing the structure with MoSi₂ laths crystallized in Ni₂Si matrix and ternary MoNiSi appearing as intermediate phase between Mo₅Si₃ and Ni₂Si matrix. HIP moves the system further to equilibrium. Additional diffusion leads to the growth of ternary MoNiSi phase on the cost of Ni₂Si binary and Mo silicide phases. HIP improved the structural integrity of the Mo/Mo silicide/Ni composite, however, the oxidation resistance of newly formed phases should be further examined.

Key words: Mo silicides, infiltration, hot isostatic pressing, structural analysis

1. Introduction

Materials for high temperature applications typically require both outstanding mechanical properties and excellent oxidation resistance. Although some refractory metals including Mo exhibit high temperature strength and ductility, they demonstrate poor oxidation resistance as well. On the other hand, e.g., MoSi₂ is well known for excellent oxidation and corrosion resistance due to the formation of self-healing, glassy silica (SiO₂) layer for decades. The oxidation of metals and alloys at high temperatures has much in common with electrochemical corrosion. An oxide film should form in both cases, which should meet specific requirements: a continuous oxide layer over the surface, slow oxide growth through diffusion, and strong adhesion between the film and the base. Hence, only three oxides meet these requirements: Cr₂O₃, Al₂O₃ and SiO₂. However, at temperatures above 1470 K, only SiO₂ can effectively protect material against corrosion [1, 2].

Mo/Mo silicide composites based on metallic Mo core and protective surface Mo silicide layer have the potential to provide both improved toughness and high oxidation resistance. These composites can be prepared e.g. by silicon infiltration of Mo performs as already presented in [3]. This process is a kind of reactive infiltration where Si (l) – Mo (s) react to form Mo silicides. These reactions are accompanied by volume changes inducing internal stresses followed by formation of pores and cracks.

These should be eliminated e.g. by post infiltration compaction. However, it appeared that this was due to extreme high temperature strength of MoSi₂ quite difficult [4]. Even hot pressing at temperature as high as 1800 °C/60 min/30 MPa in vacuum was not sufficient to accomplish the compaction [5].

The compaction can be facilitated via some bonding agent reacting with the solid and hardly deformable Mo silicide interfaces.

The effect of Nb on compaction of Mo/Mo silicide composites was investigated in [3, 5]. It appeared that

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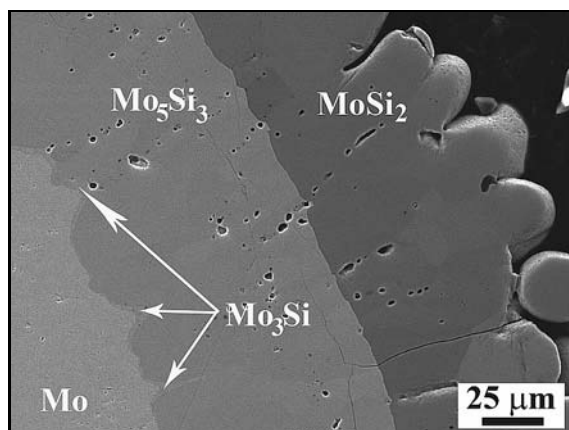


Fig. 1. SE micrograph revealing the initial structure in the cross section of thermally treated (1600°C/30 min/vacuum) Mo/Mo silicide composite wire.

hot pressing of Mo/Mo silicide wires with Nb interlayers at 1800°C/60 min/30 MPa in vacuum 30 Pa yielded compact composites with little pores and cracks. Interfacial reactions resulted in the decomposition of MoSi₂ followed by forming of Nb₅Si₃ silicide. The extent of reaction was ruled by the amount of Nb available for reaction. Low amounts of Nb resulted in only partial decomposition of MoSi₂ to Mo₅Si₃ followed by forming of thin (Nb, Mo)₅Si₃ ternary silicide.

Ni with its high temperature properties can be regarded as next candidate to the family of bonding agents. Moreover, the processing with Ni can be performed at significantly lower temperatures what might suppress the undesirable transformation of MoSi₂. The structure of Mo/Mo silicide composites infiltrated with molten nickel and subsequently compacted by HIP is assessed in this work.

2. Experimental material

Mo/Mo silicide composites were prepared by liquid silicon infiltration of Mo wire preforms followed by post infiltration heat treatment. Mo wires with the diameter of 1 ± 0.015 mm and 99.97 % purity (annealed, medium hard, purchased from Plansee Reute) were cut to the length of 25 mm, densely packed in graphite crucible and infiltrated with Si at the temperature of 1450°C. Monocrystalline Si with high purity (99.99999%) was used for infiltration. As-infiltrated composite was formed by Mo wires with silicide (MoSi₂, Mo₅Si₃) layers on their surface. The inter-wire locations were filled with remaining Si.

The infiltrated composite samples were subsequently annealed at 1600°C for 30 min in vacuum

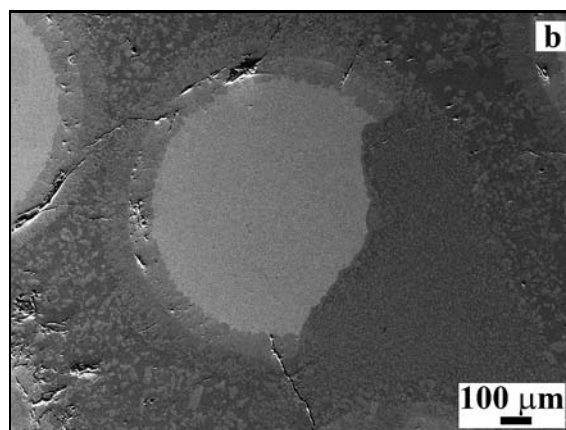
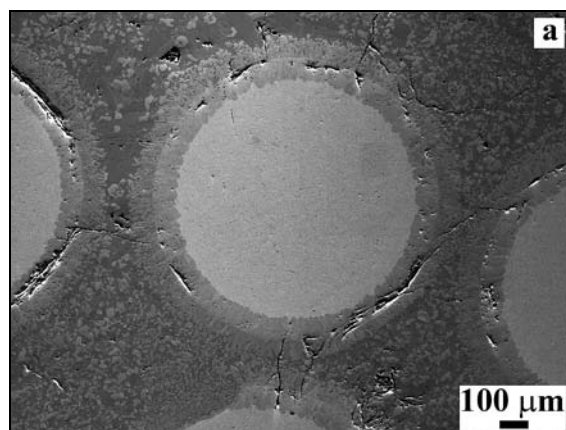


Fig. 2a,b. SE micrographs revealing the structure in the cross section of Mo/Mo silicide composite with less densely packed wires as-infiltrated with Ni.

30 Pa in order to transform all residual Si into silicides. This transformation was accompanied by disintegration of composite into separate Mo/Mo silicide wires. These wires were finally subjected to pressure-less infiltration with molten Ni at the temperature of 1500°C.

Crucibles enabling less densely as well closely packed arrangements of Mo/Mo silicide wires were employed and two different infiltration modes were applied. In order to achieve a good nickel penetration, less densely packed Mo/Mo silicide wires were embedded into Ni powder bath. This was subsequently heated and molten Ni fulfilled all empty inter-wire spacings. More closely packed wire arrangements were infiltrated with Ni that had been melted outside the crucible, i.e., without intimate contact with Mo/Mo silicide wires.

Finally, as-infiltrated samples were encapsulated in Ta tubes and compacted by hot isostatic pressing at 1200°C/100 MPa/2 h. As-infiltrated and HIP-ed samples were subjected to metallographic examination.

As-compacted composites were cut and prepared

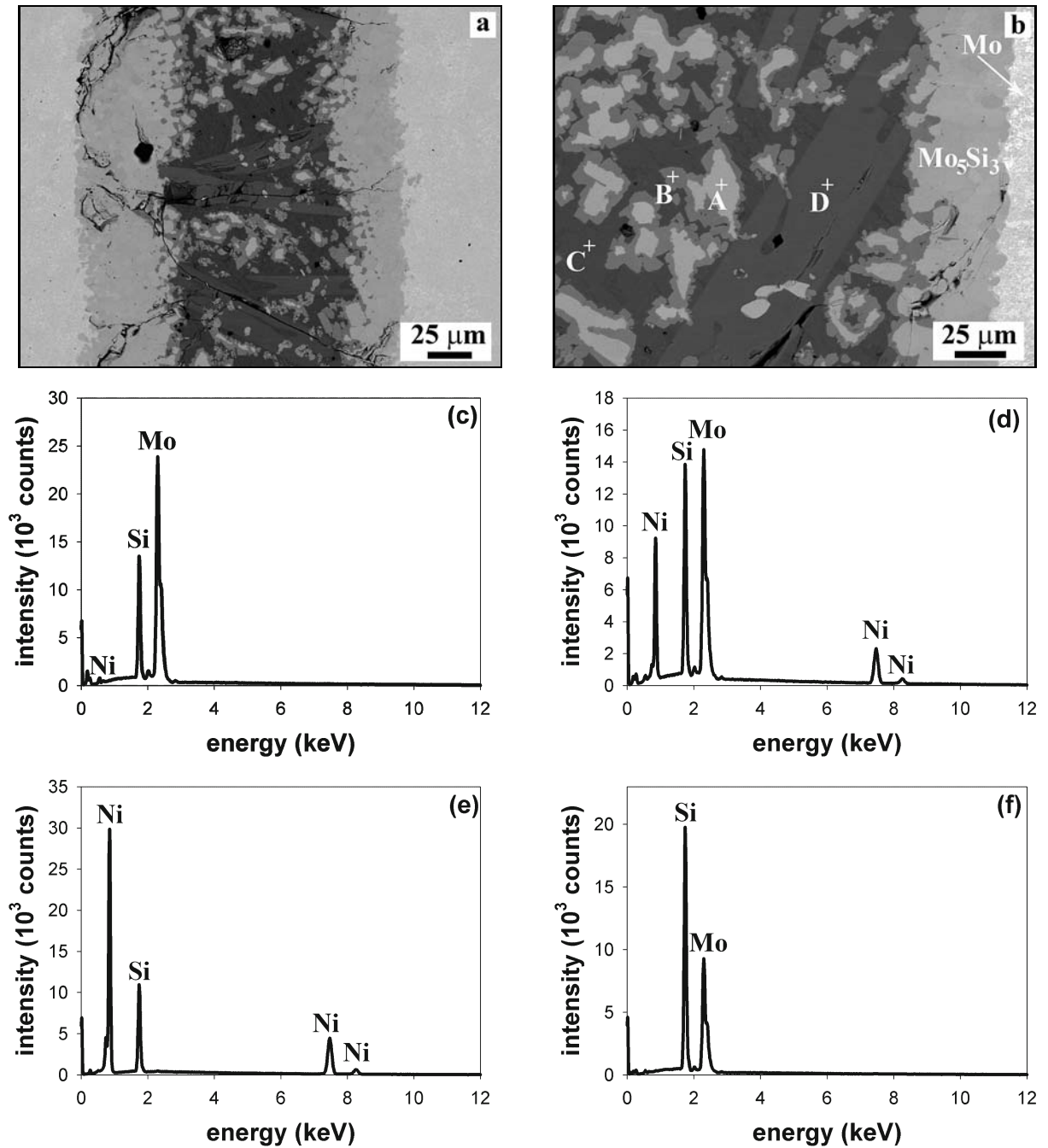


Fig. 3. SE micrographs revealing the microstructure of the interfacial region of Mo/Mo silicide composite infiltrated with Ni (a, b) and EDX spectra corresponding to 60.2 at.% Mo; 2.8 at.% Ni; 37.0 at.% Si (Mo_5Si_3) in A (c); 33.6 at.% Mo; 33.6 at.% Ni; 32.8 at.% Si (MoNiSi) in B (d); 66.7 at.% Ni; 33.3 at.% Si (Ni_2Si) in C (e) and 33.8 at.% Mo; 66.2 at.% Si (MoSi_2) in D (f).

for structural observations by a standard metallographic procedure. Electron microscopy observations were performed using field emission scanning electron microscope JEOL 7600F. Structural studies were performed using secondary electron (SE) microscopy observations. Energy-dispersive spectroscopy (EDS) was employed for chemical analysis using Oxford EDX system (INCA Energy).

3. Results

The initial structure of the thermally treated Mo/Mo silicide composite wire is presented in Fig. 1. The infiltration with Si and subsequent thermal treatment resulted in the formation of all three Mo silicides. Close to the Mo wire core a thin layer of Mo_3Si can be found, followed by Mo_5Si_3 . The surface layer is formed by columnar crystals of MoSi_2 phase.

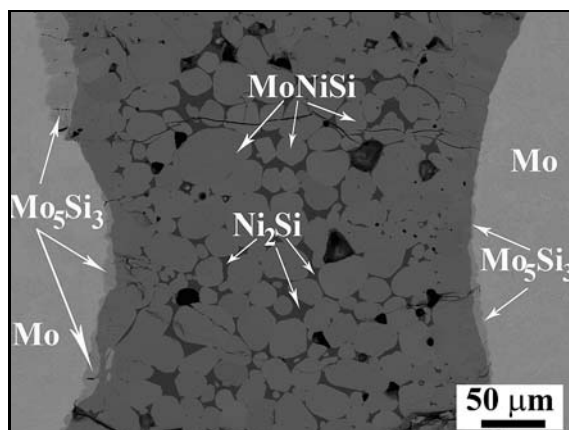


Fig. 4. SE micrograph revealing the microstructure of the inter-wire region of Mo/Mo silicide composite infiltrated with Ni and compacted by HIP.

3.1. Structure of Mo/Mo silicide samples infiltrated with Ni

Infiltration with Ni yielded compact samples, however, with numerous cracks as shown in Fig. 2a. Apparently Ni reacted quite intensely with Mo/Mo silicide wires during infiltration. Depending on the amount of available Ni the extent of the reaction differed substantially.

In the case of less densely packed wire arrangements Mo silicides and even metallic Mo are dissolved in Ni bath as presented in Fig. 2.

Less intense reaction was observed in samples with more closely packed wires where lesser amount of Ni was used for infiltration. Typical structures of interfacial regions in longitudinal sections are presented in Fig. 3.

There is a dark grey matrix between the wires with grey irregular grains and elongated lath-like objects. The EDX analysis confirmed that the Mo core was covered with continuous layer of Mo_5Si_3 . The former surface layer of MoSi_2 did not appear any more. Grey irregular crystals correspond to Mo_5Si_3 (Fig. 3c) with some Ni. These crystals are decorated with darker phase corresponding to stoichiometric MoNiSi (Fig. 3d). The dark matrix is formed by Ni_2Si intermetallic phase (Fig. 3e). The dark grey laths correspond to MoSi_2 (Fig. 3f). There is no intermediate phase between MoSi_2 and Ni_2Si .

3.2. Structure of Mo/Mo silicide composite infiltrated with Ni and compacted by HIP

HIP at $1200^\circ\text{C}/100\text{ MPa}/2\text{ h}$ obviously advanced the diffusion processes in the infiltrated composite leading the system closer to equilibrium. As can be seen in Fig. 4 the reaction of Ni with the Mo silicides proceeded leading to the decomposition of Mo_5Si_3 .

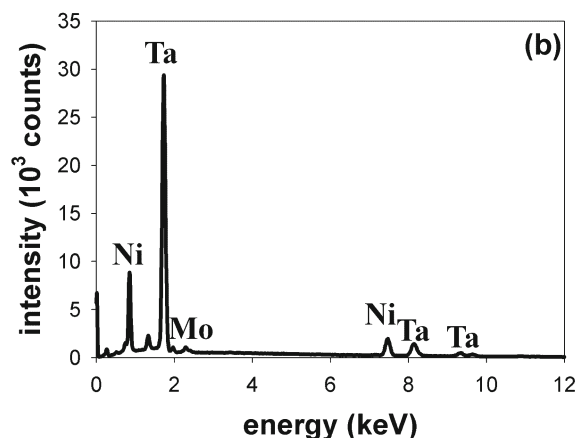
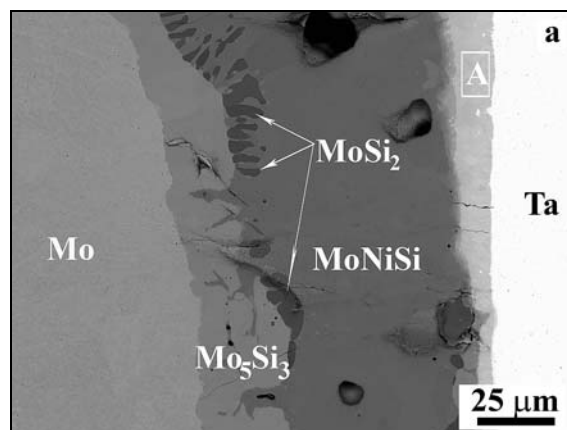


Fig. 5. SE micrograph revealing the microstructure of the interfacial region between Ta tube and Mo/Mo silicide composite infiltrated with Ni and compacted by HIP (a) and EDX spectra corresponding to 54.4 at.% Ta; 42.6 at.% Ni; 3.0 at.% Mo in A (b).

Only some isolated rests of former continuous Mo_5Si_3 can be found as indicated with white arrows. The irregular crystals of Mo_5Si_3 seen in Ni_2Si matrix in Fig. 4 disappeared completely. These processes have run on the cost of Ni_2Si phase that was largely consumed providing Ni component for the sake of ternary MoNiSi phase. The inter-wire region is now occupied predominantly by more or less globular grains of MoNiSi phase embedded in minor Ni_2Si matrix.

The activity of Ni was suppressed in favour of Ni-Ta reaction in the region neighbouring the Ta tube wall. This reaction has formed the interfacial layer with composition corresponding to the mixed zone of $\text{Ta}_2\text{Ni} - \text{Ta}_{6.5}\text{Ni}_{6.5}$ phases with some small amount of Mo as shown in Fig. 5. The Ni_2Si phase is no more present in this location. Besides the Mo_5Si_3 layer even some rests of MoSi_2 appearing as dark grey islands can be found.

4. Discussion

Ni is basic component in superalloys designed for

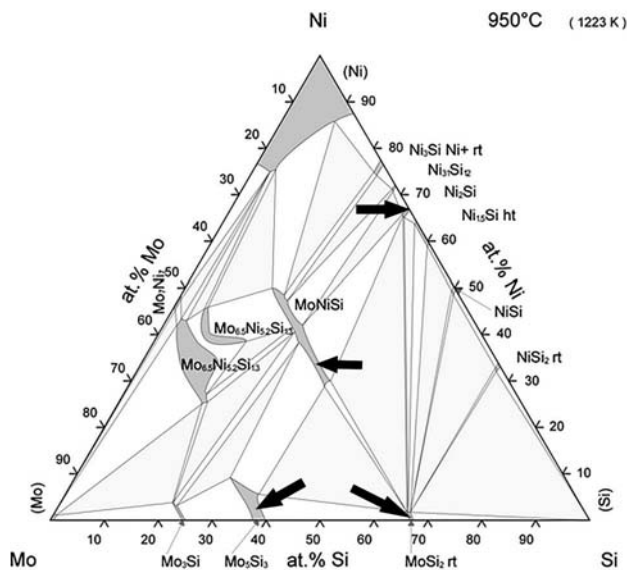


Fig. 6. Mo-Ni-Si phase diagram [6].

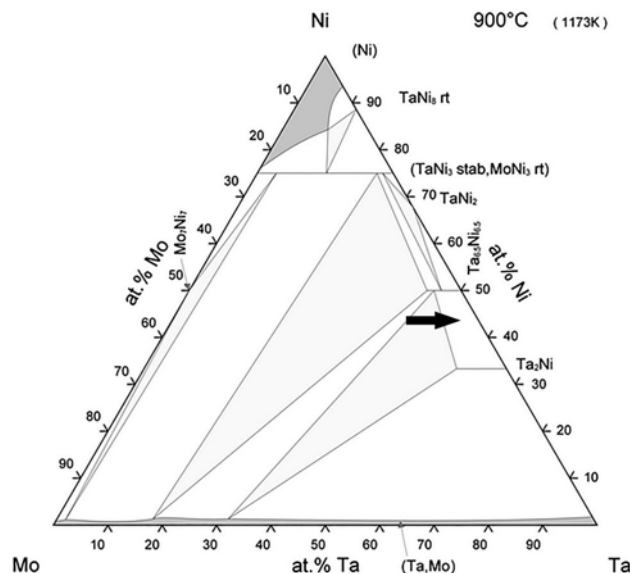


Fig. 7. Mo-Ni-Ta phase diagram [8].

high temperature exploitation. Moreover, it reacts with both Mo and Si forming binary and ternary compounds and can therefore be regarded as a promising candidate for bonding of Mo silicides.

4.1. Structure of Mo/Mo silicide samples infiltrated with Ni

The structural observations performed on Mo/Mo silicide wire composites infiltrated with Ni revealed the intense mutual reaction. The extent of this reaction is governed mostly by the amount of available Ni. The appearance of particular phases and morphologies is determined by the local chemistry. Phases with stoichiometric compositions as well as regions with phase mixtures can be recognized.

In the case of less densely packed wires relatively large amount of molten Ni came into contact with Mo/Mo silicide wires. Moreover, they were in intimate contact with Ni already during preheating. As shown in Fig. 2 the mutual reaction has led to dissolving of Mo silicides and even Mo what actually destroys the composite.

Therefore more closely packed wire arrangements were examined. In this case smaller empty spaces are in the inter-wire regions what results in less Ni needed for infiltration. Additionally, as Ni was melted outside the crucible, the time of contact was limited to some seconds. This has led to less intense reaction as shown in Fig. 3.

The typical phase compositions as presented in Fig. 3 are indicated with dark arrows in the phase diagram in Fig. 6. The spectrum shown in Fig. 3c with small amount of Ni corresponds to binary Mo_5Si_3 whereas spectrum in Fig. 3d corresponds to stoi-

chiometric MoNiSi compound. Similarly, spectrum in Fig. 3e corresponds to binary Ni_2Si and MoSi_2 in Fig. 3f.

Although Ni reacts with Mo silicides, numerous cracks are formed most probably due to the lack of plasticity of newly formed intermetallic phases. Of course it is highly demanded to consolidate the structure by subsequent compaction.

4.2. Structure of Mo/Mo silicide composite infiltrated with Ni and compacted by HIP

The Ni_2Si matrix is according to phase diagram stable up to 1239°C [7]. The applied HIP temperature of 1200°C was expected to be high enough to get the matrix into plastic condition, on the other hand, not very high in order to suppress the detrimental reactions leading to further decomposition of Mo silicides.

Structural observations revealed that HIP had moved the system further towards equilibrium. Additional diffusion led to the growth of ternary MoNiSi phase at the cost of Ni_2Si binary and Mo silicide phases. MoSi_2 is no more present and Mo_5Si_3 phase nearly disappeared.

Slightly different situation is in the region adjacent to Ta tube. Ni obviously reacted with Ta giving rise to reaction zone formed by a mixture of Ta_2Ni – $\text{Ta}_{6.5}\text{Ni}_{6.5}$ phases. The composition of this zone as determined by EDX is indicated in Fig. 7.

Due to the Ni-Ta reaction less Ni is available to react with Mo silicides. Therefore the Mo_5Si_3 layer and even some rests of MoSi_2 can be still recognized.

The improved structural integrity of the obtained composite is quite obvious. Unfortunately, it is at the cost of phase transformations leading to the decom-

position of MoSi₂. This is not quite desirable result as MoSi₂ exhibiting excellent oxidation resistance [4] plays an important role in the Mo/Mo silicide composite concept [5]. The examined compaction via Ni infiltration followed by HIP is expected to improve the mechanical properties of Mo/Mo silicide composites, due to reducing of numerous cracks, voids and other structural inhomogeneities. However, the oxidation resistance of MoNiSi and Ni₂Si phases should be further examined.

The extent of undesirable intense reaction of Ni with Mo silicides might be suppressed if other technologies inducing less Ni in the bonding process are employed.

5. Conclusions

Reactions during infiltration of Mo/Mo silicide wires with Ni and subsequent compaction with HIP were qualitatively assessed in this work.

Intense reactions of Ni with Mo/Mo silicide composites were recorded. The extent of these reactions is determined by the amount of available Ni.

Full range reaching from surface and subsurface reactions to dissolving of Mo/Mo silicide wires took place.

If excessive Ni is available, Mo and Mo silicides are dissolved with detrimental effect on the composite structure.

If less Ni is applied and the intimate contact of Ni with Mo/Mo silicides is shortened substantially, less intense reaction takes place providing the structure with MoSi₂ laths crystallized in Ni₂Si matrix and ternary MoNiSi appearing as intermediate phase between Mo₅Si₃ and Ni₂Si matrix.

HIP moves the system further to equilibrium. Additional diffusion leads to the growth of ternary MoNiSi phase at the cost of Ni₂Si binary and Mo silicide phases.

Ni reacts also with the Ta tube forming Ta₂Ni – Ta_{6,5}Ni_{6,5} phases. This locally reduces the activity of Ni what limits the dissolving of Mo silicides.

HIP undoubtedly improved the structural integrity of the Mo/Mo silicide/Ni composite, however, the oxidation resistance of newly formed phases, particularly MoNiSi and Ni₂Si, should be further examined.

Acknowledgements

This work was accomplished within the 7th framework programme project Micro and Nanocrystalline Silicide – Refractory Metals FGM for Materials Innovation in Transport Applications (Project acronym SILTRANS); grant agreement No. 229127. This work was co-funded by Slovak Research and Development Agency under the contract No. DO7RP-0023-09. The contribution of infrastructure purchased within the frame of the project No. 26240120006 Creating the centre of excellence for research and development of structural composite materials for mechanical and civil engineering and medical applications (ERDF) is highly appreciated.

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