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The effect of Nb interlayers on compaction of Mo/Mo silicide composites

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Abstract

Reactions during compaction of Mo/Mo silicide wires with and without Nb interlayers were qualitatively assessed in this work. It appeared that hot pressing at 1800 ℃/60 min/30 MPa in vacuum had not been sufficient to compact the Mo/Mo silicide wires in the absence of any additional interfacial layer. However, the development of silicide layers proceeded and the redistribution of elements towards equilibrium took place.

Hot pressing of Mo/Mo silicide + Nb wires yielded compact composites with little pores and cracks. Interfacial reactions resulted in the decomposition of $MoSi_2$ followed by forming of Nb_5Si_3 silicide.

Best results were achieved with 3 μm thick Nb foils, yielding compact interfaces with limited development of new phases. Low amount of Nb resulted in only partial decomposition of $MoSi_2$ to Mo_5Si_3 followed by forming of thin $(Nb, Mo)_5Si_3$ ternary silicide.

Key words: Mo silicides, Nb silicides, composite materials, Si infiltration, hot pressing

1. Introduction

Mo-Si system provides a family of Mo silicides, *i.e.* Mo_3Si, Mo_5Si_3 and $MoSi_2$ exhibiting different potentials for high temperature applications in terms of ductility and oxidation resistance.

Mo_3Si is the Mo-richest silicide phase. This phase forms through a peritectic reaction between liquid (25.72 at.% Si) and (Mo) at 2025 ℃ and the phase is nearly stoichiometric. Similarly as Mo_5Si_3, the Mo_3Si phase does not form protective silica, thus Mo_3Si is not regarded as oxidation resistant [1].

Mo_5Si_3 is an intermetallic compound with congruent melting temperature of 2180 ℃, density higher than that of $MoSi_2$ ($8.19\ \mathrm{g\,cm^{-3}}$) and tetragonal crystal structure. According to the Mo-Si phase diagram, Mo_5Si_3 is not a line compound, and the stoichiometry varies within the range of 2–3 at.%. The oxidation resistance of Mo_5Si_3 is significantly inferior to $MoSi_2$, however, the boron additions to Mo_5Si_3 greatly improve the oxidation resistance due to the formation of a protective borosilicate glass [2].

$MoSi_2$ is the most extensively studied phase exhibiting high temperature stability and oxidation resistance. Its melting temperature is 2020 ℃ and at the temperature of 1900 ℃ it undergoes a polymorphic transformation from low-temperature tetragonal form (α-$MoSi_2$) to high-temperature hexagonal form (β-$MoSi_2$). The intermediate phase appears to be nearly stoichiometric, with a homogeneity range of < 0.2 at.% Si. Molybdenum disilicide is well-known for its excellent oxidation and corrosion resistant properties at high temperatures. It has been established that the excellent oxidation resistance of $MoSi_2$ at high temperatures is attributed to the formation of self-healing, glassy silica (SiO_2) layer [3].

$MoSi_2$ can be best described as a borderline

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*Corresponding author: tel.: (+421) 2 49268 228; fax: (+421) 2 49268 312; e-mail address: lucia.sencekova@savba.sk ceramic-intermetallic compound. It possesses ceramic-like high-temperature oxidation resistance, and metallic-like electrical conductivity. This material exhibits mixture of covalent and metallic atomic bonding providing ceramic-like brittleness at room temperature, and metallic-like plasticity at elevated temperatures [4]. The main disadvantage of this intermetallic as possible structural material is its room temperature brittleness providing the fracture toughness of $3\,\mathrm{MPa\,m^{1/2}}$.

The favourable high temperature strength properties of the refractory metals including Mo are often offset by lower room temperature ductility, embrittlement after welding or joining, and in some cases inadequate oxidation resistance. Mo like W has relatively low oxygen solubility, but forms volatile oxides as the temperature increases. At lower temperatures, it can form stable and somewhat protective oxides, *e.g.* MoO_2, but once volatile products (MoO_3) begin to form, the amount of metal loss increases rapidly [5]. The volatility of these higher oxides represents a significant degradation mechanism.

Mo/Mo silicide composites based on metallic Mo skeleton protected by surface Mo silicides are expected to yield a synergic effect providing both improved toughness and high oxidation resistance. For this purpose liquid metal infiltration seems to be the most appropriate preparation technique.

The Si (*l*) – Mo (*s*) reaction forms Mo silicides what is accompanied by volume changes inducing either internal stresses (volume increase) or formation of pores (volume decrease). Comparison of particular molar volumes for Si ($11.088\,\mathrm{cm^3\,mol^{-1}}$), Mo ($9.39\,\mathrm{cm^3\,mol^{-1}}$) and $MoSi_2$ ($24.14\,\mathrm{cm^3\,mol^{-1}}$) indicates that formation of molybdenum disilicide results in 23.5 % decrease in volume of the constituents Mo + 2Si. Moreover, the mismatch in coefficients of thermal expansion α ($\alpha_{\mathrm{Si}} = 4.8 \times 10^{-6}\,\mathrm{K^{-1}}$; $\alpha_{\mathrm{Mo}} = 2.6 \times 10^{-6}\,\mathrm{K^{-1}}$; $\alpha_{\mathrm{Mo5Si3}} = 5.2\text{–}11.5 \times 10^{-6}\,\mathrm{K^{-1}}$ and $\alpha_{\mathrm{MoSi2}} = 8.2\text{–}9.4 \times 10^{-6}\,\mathrm{K^{-1}}$) contributes to the generation of internal stresses with potential forming of cracks. Additional compaction directed towards elimination of pores and cracks is therefore necessary particularly for composites aimed as potential load bearing structures.

This, however, is a problem due to extremely high temperature strength of $MoSi_2$ [6]. It appears that compaction temperatures exceeding 1800 ℃ are to be employed. This is not only impractical but may be also followed by undesired transformation of $MoSi_2$ phase into lower Mo silicides. Therefore the demand to perform the compaction at lower temperatures is quite apparent. One of possible solutions might be the employment of some bonding agent interconnecting the solid and undeformable Mo silicide interfaces and decreasing the compaction temperature to reasonable values.

In order to reduce the brittle-to-ductile transition temperature, $MoSi_2$ can be alloyed [7]. The aim is to weaken the Mo-Si bonds more than Si-Si bonds, so that the plastic deformation is preferred over cleavage. The first principles calculations involved the determination of a "disembrittlement parameter" for $MoSi_2$, which is the ratio of the surface energy to the unstable stacking fault energy. These calculations suggested that alloying additions of Mg, V, Nb, Tc, and Al to the $MoSi_2$ crystal structure might enhance ductility [8].

It was observed that the addition of the ductile Nb contributed to toughening of $MoSi_2$ matrix [9]. The composite $MoSi_2$/20vol.%Nb particles had a work of rupture much larger than that of the matrix. Observations of the fracture surface revealed the ductile rupture of the Nb particles. The toughening can thus be primarily attributed to the plastic work done upon stretching the constrained ductile ligaments. Interfacial reaction between $MoSi_2$ and Nb was recognized forming different silicides including Nb_5Si_3, $(Nb, Mo)_5Si_3$, $(Mo, Nb)_5Si_3$ and Mo_5Si_3 phases.

With respect to these facts Nb undoubtedly appears to be a promising bonding agent for Mo/Mo silicide composites. The reactions of Nb with Mo/Mo silicide composites are qualitatively analysed in this work.

2. Experimental

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 ℃. Monocrystalline Si with high purity (99.99999 %) was used for infiltration. As-infiltrated composite was formed by Mo wires with surface silicide ($MoSi_2$, Mo_5Si_3) layers and the inter-wire locations were filled with remaining Si.

The infiltrated composite samples were subsequently annealed at 1600 ℃ for 30 min in vacuum 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 hot pressing compaction at 1800 ℃/60 min/30 MPa in vacuum 30 Pa. Three different wire arrangements were experienced. These include Mo/Mo silicide wires hot pressed without any interlayer, Mo/Mo silicide wires densely packed with Nb wires ($\varnothing = 1 \pm 0.02$ mm) with purity 99.70 % (annealed, purchased from Plansee Reute), and Mo/Mo silicide wires separated by 3 μm thick Nb foils.

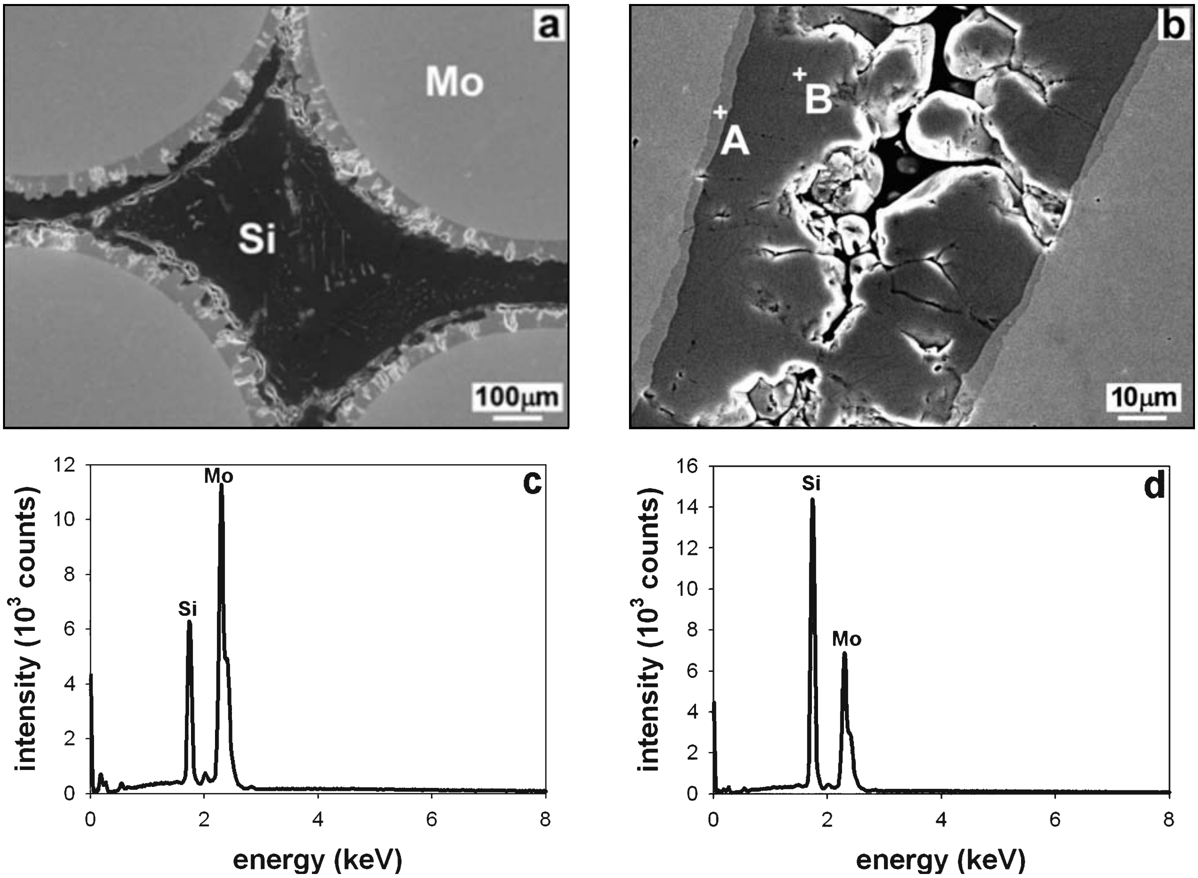

Fig. 1. SE micrographs of Mo wires infiltrated with Si (a), adjacent Mo wires with surface Mo silicide layers (b), EDX spectra corresponding to Mo_5Si_3 in A (c) and $MoSi_2$ in B (d).

As-compacted composites were cut and prepared for structural observations in a standard procedure including the embedding into conductive graphite and mineral filled phenolic thermoset – Konductomet, followed by grinding up to the grain size 2500 and final polishing using diamond pastes with 10; 5; 3 and 1 μm grain size.

Electron microscopy observations were performed using JEOL JSM6610 scanning electron microscope and field emission scanning electron microscope JEOL 7600F. Structural studies were performed using secondary electron (SE) and backscattered electron (BSE) microscopy observations.

Energy-dispersive (EDS) and wave dispersive spectroscopy (WDS) were employed for chemical analysis using Oxford EDX and WDX systems (INCA Energy and INCA Synergy$^+$). Point analysis, line scans and X-ray elemental mapping were employed to reveal the chemical composition of samples.

3. Results

As-infiltrated Mo wires are presented in Fig. 1. Structural observations revealed that columnar crystals of $MoSi_2$ and a thin continuous layer of Mo_5Si_3 silicides were formed on the surface of Mo wires. The thickness of the $MoSi_2$ layer was approximately 40 μm whereas the thickness of Mo_5Si_3 layer did not exceed 5 μm.

Inter-wire locations were filled with the rest of Si interconnecting the Mo/Mo silicide wires. This silicon had to be restrained in order to stabilize the composite structure for high temperature applications.

It appeared that post infiltration annealing at 1600 ℃/30 min was sufficient to transform the rest of Si into silicides. The removal of rest Si resulted into disintegration of wire preform into individual Mo/Mo silicide wires subjected to final compaction.

3.1. Compaction without interlayer

Structure of Mo/Mo silicide composite prepared by hot pressing without any interlayer is presented in Fig. 2. It can be seen that hot pressing at 1800 ℃/60 min/30 MPa in vacuum 30 Pa was not sufficient to restrain the pores particularly in inter-wire locations. Mo wires were deformed to some extent but it was not enough to close the pores. The thickness of $MoSi_2$ increased to about 100 due to the supply

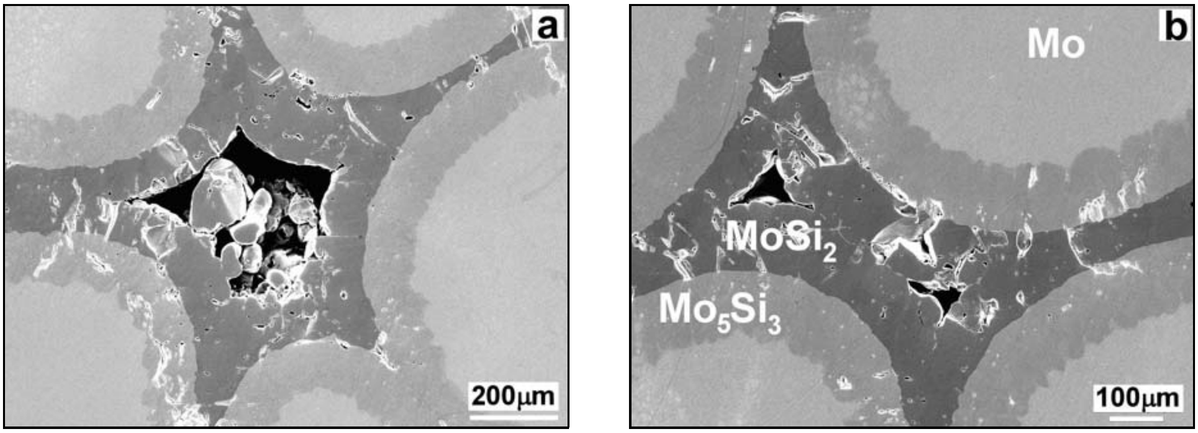

Fig. 2. SE micrographs of residual pores after hot pressing (1800 °C/60 min/30 MPa) of Mo/Mo silicide wires (a), (b).

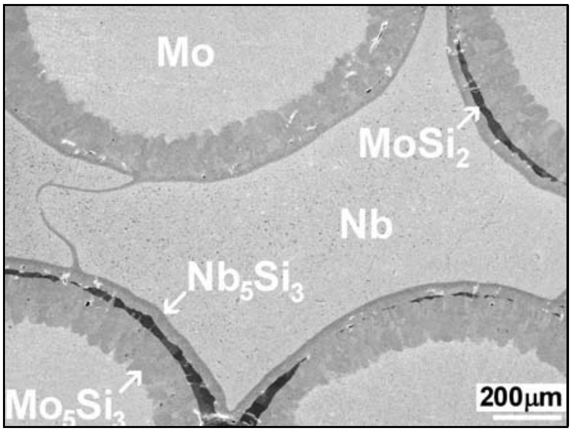

Fig. 3. SE micrograph of hot-pressed Mo/Mo silicide + Nb wire arrangements.

of Si from inter-wire locations. The Mo_5Si_3 layers increased significantly to thicknesses over 100 µm due to solid state diffusion pushing the system towards equilibrium.

There is a very good bonding between Mo and Mo_5Si_3 layer, cracks and pores are more frequently observed in $MoSi_2$. These were not eliminated in spite of applying high temperature throughout the whole hot pressing run.

3.2. Compaction with Nb wires

Structure of Mo/Mo silicide wires hot pressed with Nb wires is shown in Fig. 3. As can be seen initial cylindrical shapes of Nb wires underwent intense plastic deformation. No cracks or large voids were recognized in the structure of compacted composite.

Particular attention was paid to Mo-silicide/Nb interface to reveal the influence of Nb on consolidation of silicides. The interface is shown and further analysed in Fig. 4. As can be seen from corresponding EDX spectra, Nb reacted with $MoSi_2$ and formed Nb_5Si_3 phase neighbouring Mo_5Si_3 and Mo_3Si layers with variable thicknesses. Only rests of $MoSi_2$ phase were locally observed (dark phase in Fig. 3) indicating that it had been consumed due to reaction with Nb.

In this location no ternary Mo-Nb-Si phases could be observed. Consolidation via Nb wires formed a compact bonding between Mo and Nb silicides indicating that Nb might successfully fulfil the role of desired bonding agent.

3.3. Compaction with Nb foils

Generally, as far as the interfacial bonding is a matter of concern, any huge formation of new phases is undesirable as they may affect the overall stability of the explored material. Therefore a consolidation attempt with quite little Nb was made. Particularly two Nb foils with the thickness of 3 µm were inserted between Mo/Mo silicide wires and compacted in the same way as in previous experiments.

The interface between two Mo wires developed after hot pressing at 1800 °C/60 min/30 MPa is shown in Fig. 5. It appeared that already very small amount of Nb was able to form compact bonding between Mo silicide layers. However, the phase composition is due to lack of Nb slightly different. The corresponding EDX analysis confirmed the Mo_3Si phase (E) between pure Mo wire and thicker Mo_5Si_3 (D) layer on both Mo-wires. Due to the diffusion of Si into Nb, $MoSi_2$ (C) was depleted in Si and partially transformed to lower silicide Mo_5Si_3 (B). Finally Nb foils transformed to $(Nb, Mo)_5Si_3$ (A). The chemical composition as determined by semi-quantitative EDS analysis corresponds to: 44.99 at.% Nb; 19.64 at.% Si; 35.46 at.% Mo.

Black dots in the interfacial zone are not pores but fine silicon oxide particles. It is assumed that oxygen originates from the surface of thin Nb foils.

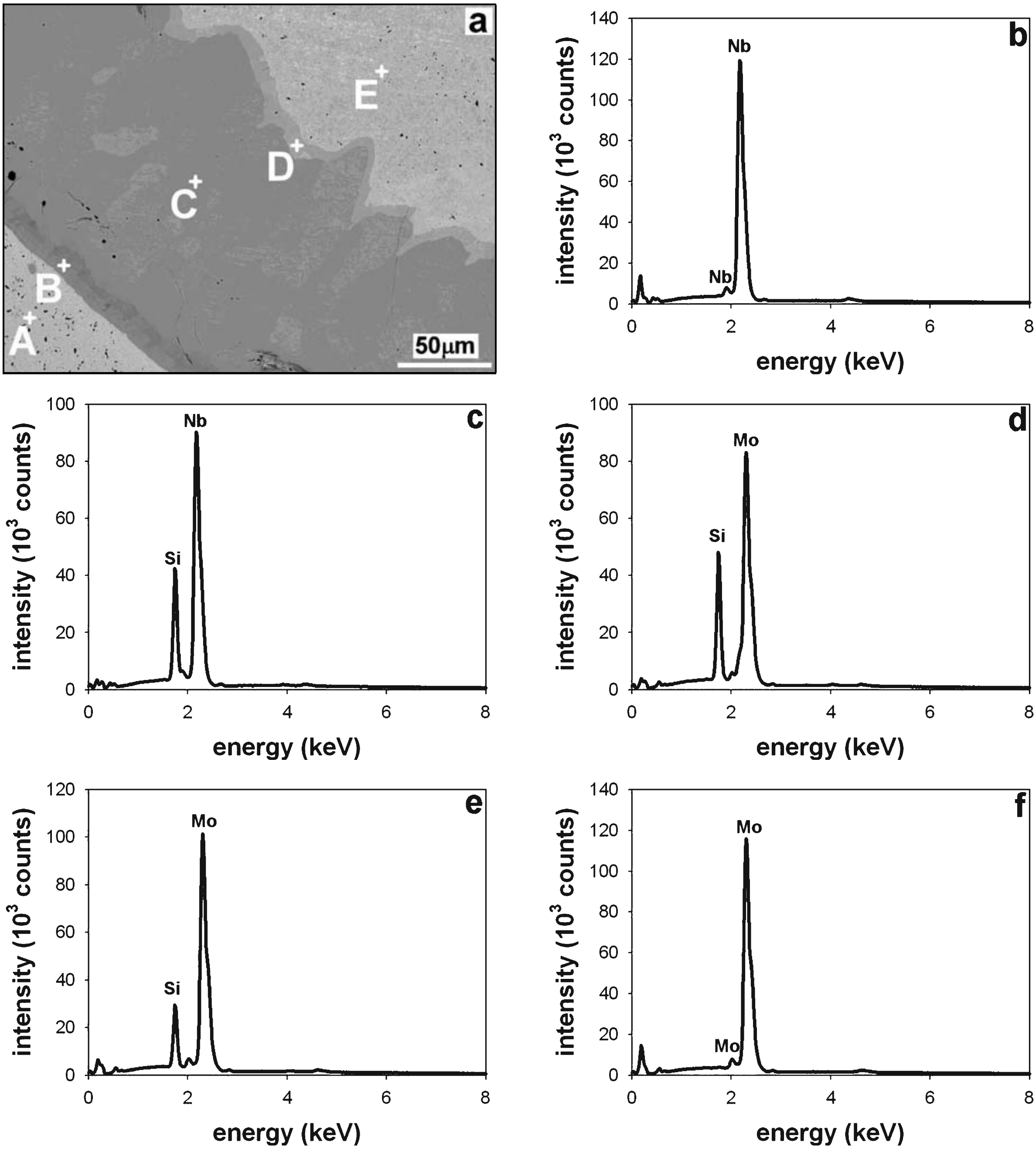

Fig. 4. BSE micrograph of Mo/Mo silicide/Nb wire interface (a) and EDX spectra corresponding to Nb in A (b); Nb_5Si_3 in B (c); Mo_5Si_3 in C (d); Mo_3Si in D (e); Mo in E (f).

4. Discussion

The compaction related to closing of pores in inter-wire locations and cracks requires some plasticity of Mo wires as well as of Mo silicides. The strength of $MoSi_2$ ($\sim$ 100 MPa at 1550 °C) is quite high particularly with respect to the available tooling (graphite). Therefore the highest temperature, as well as pressure (1800 °C/30 MPa), were applied for hot pressing to meet the necessary plasticity of the constituents.

It appeared that large pores and cracks survived the hot pressing at 1800 °C/60 min/30 MPa. Some wires exhibited some deformation but the achieved plasticity was obviously not sufficient to heal all pores and cracks.

The study of positive effect of Nb on consolidation of $MoSi_2$ powder [10] revealed that densification is most likely dominated by power low creep. This was accompanied by reaction between Nb and $MoSi_2$, which led to formation of reaction zone of (Nb, Mo)$_5$Si$_3$ and (Mo, Nb)$_5$Si$_3$ filled with Kirkendall voids.

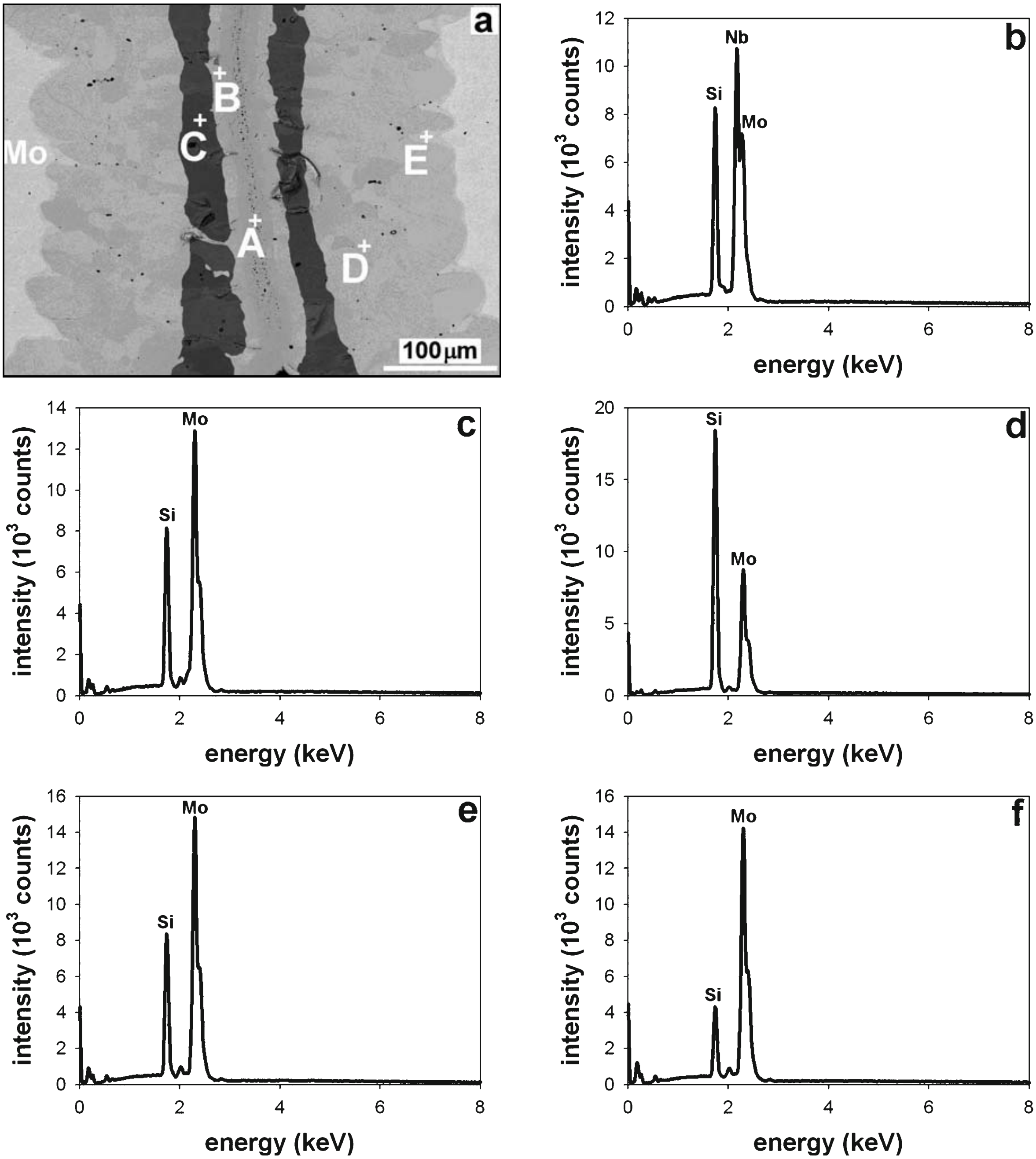

Fig. 5. BSE micrograph of the interface developed between two Mo/Mo silicide wires separated by Nb foils after hot pressing at 1800 °C/60 min/30 MPa (a); EDX spectra corresponding to (Nb, Mo)$_5$Si$_3$ in A (b); Mo$_5$Si$_3$ in B (c); MoSi$_2$ in C (d); Mo$_5$Si$_3$ in D (e); Mo$_3$Si in E (f).

Authors also detected the reduction of temperature required for the densification.

Therefore important contributions were expected from employing Nb in compaction of Mo/Mo silicide composites. These expectations were partially fulfilled. Nb wires exhibited very good plasticity and filled all inter-wire locations in their vicinity. The reaction products confirmed that Nb reacted with Si from Mo silicides and contributed to development of interfacial bonding on inter-atomic basis.

Mo-Si system is relatively simple from the analytical point of view. However, the differentiation between Nb and Mo in EDX spectra can be tricky due to similar energies of L lines Lα (Mo) = 2.2932 keV vs. Lα (Nb) = 2.1659 keV. Actually, there is a risk that Nb peak can be partially overlapped with Mo or vice versa. In order to confirm the presence of both elements WDS analysis was performed. WDX spectrum superimposed on EDX spectrum in Fig. 6 confirms that both Nb and Mo

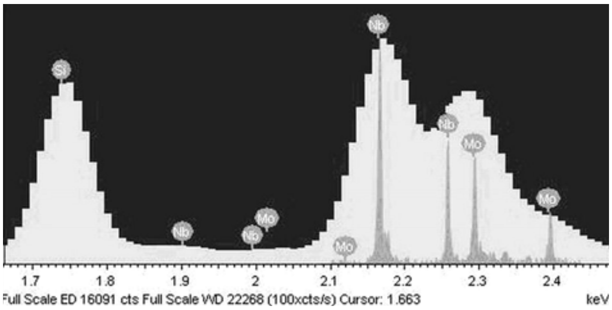

Fig. 6. WDX spectrum superimposed on EDX spectrum acquired from A in Fig. 5.

are present in the reaction zone indicated by A in Fig. 5.

Bonding with Nb foils provided best compaction results. It appeared that 3 μm thick Nb foils were sufficient to form satisfactory joint between Mo silicides. Based on the analytical results it can be understood that Si was diffusing into Nb foil forming thus diffusion bonding. The distribution of Nb and Mo across the interface can be revealed by WDS line scan as shown in Fig. 7. Actually WDS yields due to better signal to noise ratio more precise information about the distribution of elements than WDS. It can be seen that the width of the mutual Mo and Nb diffusion zone, *i.e.* zone of (Nb, Mo) mixed silicides is about 35 μm. Outside this zone no Nb is present. As the diameter of the X-ray generation volume at 15 kV acceleration voltage is according to [9] 0.43 μm for Mo and 0.52 μm for Nb, respectively, no serious overlapping of the excited volumes distorting the distribution of elements as revealed via linescans actually takes place. This, however, means that not only Si is diffusing into Nb but also Nb is diffusing into Mo silicides. The depletion of Si due to diffusion into Nb transforms the $MoSi_2$ into lower Mo_5Si_3 as can be seen in Fig. 5.

The intensity of Si in the interfacial zone is different particularly for Mo, Mo_3Si and Mo_5Si_3 phases. However, only slight intensity increase can be recognized in the Nb-Mo mixed zone. It can be therefore assumed, that part of Mo atoms was replaced by Nb in Mo_5Si_3 what does not necessarily need to result in formation of principally new phase but rather $(Nb, Mo)_5Si_3$ phase with continuously changing concentrations of mutually interchangeable Mo and Nb atoms.

5. Conclusions

Reactions during compaction of Mo/Mo silicide wires with and without Nb interlayers were qualitatively assessed in this work.

It appeared that hot pressing at 1800 ℃/60 min/30 MPa in vacuum was not sufficient to compact the Mo/Mo silicide wires in the absence of any additional interfacial layer.

The development of silicide layers proceeded and the redistribution of elements towards equilibrium took place during hot pressing.

Hot pressing of Mo/Mo silicide + Nb wires yielded compact composites with little pores and cracks.

Interfacial reactions resulted in the decomposition of $MoSi_2$ followed by forming of Nb_5Si_3 silicide.

Best results were achieved with 3 μm thick Nb foils, yielding compact interfaces with limited development of new phases.

Low amount of Nb resulted in only partial decomposition of $MoSi_2$ to Mo_5Si_3 followed by forming of thin $(Nb, Mo)_5Si_3$ ternary silicide.

Acknowledgements

This work was accomplished within the 7th framework

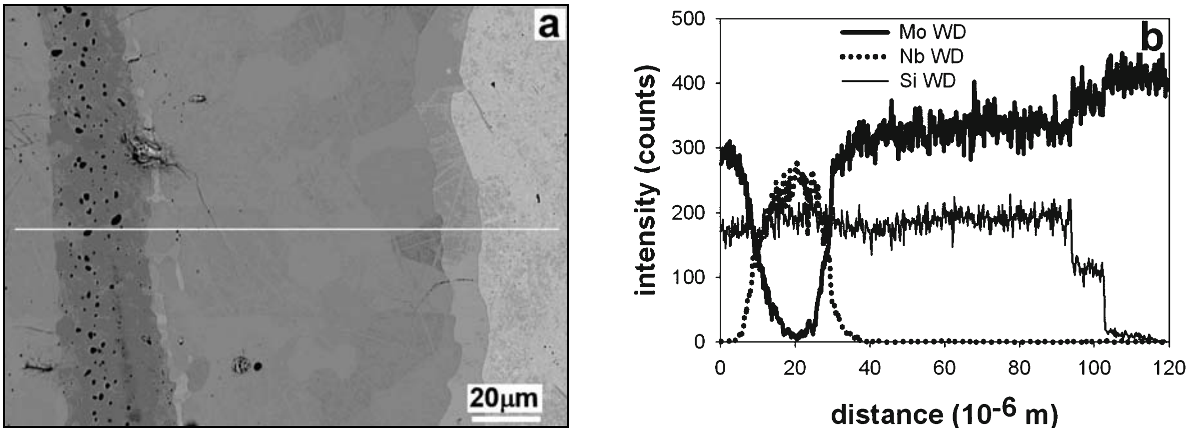

Fig. 7. BSE micrograph of the interface developed between two Mo/Mo silicide wires separated by Nb foils after hot pressing at 1800 °C/60 min/30 MPa: (a) WDS line scans (b) acquired along the white line in (a).

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