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Joining of Mo and $MoSi_2$ and their interaction with nickel

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Abstract

Joining of Mo and $MoSi_2$ with Mo and/or $MoSi_2$ by brazing with nickel was studied. Molybdenum disilicide was prepared by the reaction of liquid silicon with the Mo substrate at the temperature of 1530 °C and 3 min. Wetting of both Mo substrate and $MoSi_2$ was measured by sessile drop method; wetting angles were very low (close to zero). Products of interaction of Mo and/or $MoSi_2$ with Ni were studied by electron microscopy with energy-dispersive spectroscopy (EDS) and X-ray diffraction methods (XRD). Shear strength of the joints was measured by push-off method. The Mo-Ni-Mo system produced a joint with no cracking or porosity with the shear strength 134.5 MPa. $MoSi_2$-Ni-$MoSi_2$ joint due to different thermal expansion of materials being joined exhibited porous interface and catastrophic cracking through Mo_5Si_3 with the shear strength 37.0 MPa.

K e y w o r d s: molybdenum disilicide, wetting, joining, shear strength

1. Introduction

Development of better and more responsible products and facilities involves demand of new materials with improved properties. It concerns above all parts performing under extreme conditions like high temperature, environment and/or enormous loading as for example turbines used as jet engines, gas injection tubes, and more others. Refractory metals such as molybdenum and niobium commonly coated with $MoSi_2$ thick film belong to this kind of materials. According to the Mo-Si phase diagram there are three Mo silicides exhibiting different potentials for high temperature applications in terms of oxidation resistance and ductility. Mo_3Si is of cubic crystal structure and is formed peritectically by a reaction between liquid Si and Mo at 2025 °C. Mo_5Si_3 is an intermetallic compound with tetragonal crystal structure and melting temperature 2180 °C. Melting temperature of $MoSi_2$ is 2020 °C and at the temperature of 1900 °C it undergoes a polymorphic transformation from low temperature tetragonal form (α-$MoSi_2$) to high-temperature hexagonal form (β-$MoSi_2$). $MoSi_2$ is most interesting industrially for its excellent oxidation and corrosion resistant properties at high temperatures. It is capable of forming a thin self-healing protective layer of silica on the surface when exposed to an oxidizing atmosphere up to 1800 °C [1]. Molybdenum disilicide has great potential as a high-temperature structural material. $MoSi_2$ is characterized by excellent oxidation resistance, high melting point, good electrical and thermal conductivities and stability in a variety of corrosive environment [2]. It has relatively low density and moderately good high-temperature strength. Molybdenum disilicide is very attractive for high-temperature applications such as furnace components, gas injection tubes, protective coating, engine [3].

There are many routes how to prepare molybdenum disilicide. Chemical vapour deposition of Si on Mo substrate from the $SiCl_4$-H_2 gas mixture at 1000 °C was used for study of grow kinetics of the Mo-silicide layers [4]. Wiltner et al. studied various parameters on the completeness of silicide forming reactions when preparing silicides by powder metallurgical

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method [5]. Another route to produce molybdenum disilicides is known as self-propagating high temperature synthesis or combustion synthesis [6]. This method consists of using high exotermicity of its formation reaction. Stoloff [7] gives an overview of powder processing of silicides and their composites. Hot pressing is the least complicated powder consolidation method. Higher temperatures are needed to press pre-alloyed powders to reach full density. Typical temperatures for hot pressing are in the range 1600–1850 ℃ for unalloyed $MoSi_2$. Another method is hot isostatic pressing (HIP) which can be employed as the primary consolidated method. Temperatures for HIPing generally are in the range 1350–1700 ℃ for $MoSi_2$. Reaction sintering is simple method with which un-alloyed powders are mixed, and an exothermic reaction is allowed. Displacement reactions and mechanical alloying are solid state processes. In the first method, solid state process involves a chemical reaction that leads to the formation of fully dense silicides. Mechanical alloying is typically carried out in a high energy ball mill and may involve either pre-alloyed or elemental powders. $MoSi_2$ discs were prepared by the reaction of liquid Si on Mo substrate at 1530 ℃ for 3 min in vacuum $\sim 10^{-1}$ Pa.

One of the possibilities how to exploit the specific properties of both molybdenum silicide as a matrix and molybdenum as reinforcing component is to develop new class of high temperature composite material. This combination may provide a synergic effect yielding a material with excellent oxidation resistance and high strength, ductility and creep resistance [8].

In order for the materials generating parts of the aforementioned applications they must first be joined to other materials or to itself. To do so it is important to achieve good wetting of the components by the brazing metal and to know the products of the interaction between the braze and material to be joined and their influence on the joint properties.

Conzone et al. [9] investigated joining $MoSi_2$ to 316 L stainless steel using active brazing techniques. They used niobium and nickel as intermediate layers with copper-silver eutectic at moderate temperatures. Crack free joint was produced with niobium because of closeness of its coefficient of thermal expansion (CTE) with the one of Cu-Ag eutectic alloy. Vaidya et al. [2] joined $MoSi_2$ to itself using aluminium as a brazing material.

The aim of this paper is to know the wetting conditions of molybdenum and molybdenum disilicide by nickel and to determine the shear strength of the Mo and/or $MoSi_2$ joined with Ni braze and the products of the interaction of the components with the braze. Nickel is a material that lowers reaction rate of silicon with molybdenum. Also it increases the bonding of individual grains of molybdenum disilicide. According to Mo-Ni phase diagram there are three intermediate phases. MoNi has a tetragonal unit cell and forms at 1350 ℃, and $MoNi_3$ and $MoNi_4$ form at 890 and 840 ℃, respectively. $MoNi_3$ has a c.p. hexagonal and $MoNi_4$ has an ordered b.c. tetragonal unit cell. There is practically no solid solubility of Ni in Mo. Nickel solid solution extends to 34 wt.% Mo at 1100 ℃.

2. Experimental procedure

Mo sheet of a thickness of 1 mm was obtained commercially and was cut into form of disc with a diameter of 15 mm. Mo was cleaned ultrasonically in alcohol and piece of silicon of the amount around 0.02 g was placed on Mo substrate and inserted into the furnace. Molybdenum disilicide rises by the reaction of liquid silicon with Mo substrate in the furnace at 1530 ℃ during 3 min in vacuum of the order of 10^{-1} Pa. Another silicide, Mo_5Si_3, develops between the Mo substrate and $MoSi_2$. Existence of $MoSi_2$ and Mo_5Si_3 on Mo substrate in the cross-section after melting of Si was checked by X-ray diffraction. No free silicon was found. $MoSi_2$ samples were prepared in this way for all further experiments. As a brazing material Ni foil (thickness 50 μm) was used. Nickel was used as a bonding agent for compaction of Mo silicides [8].

Wetting of Mo and $MoSi_2$ by nickel was studied by the sessile drop method. For wetting experiments nickel in cube form with edge of ~ 4 mm length was put on a molybdenum substrate and placed into the furnace at 1360 ℃ up to 10 min. Photos of the nickel drops were taken with digital camera. Wetting of $MoSi_2$ was under way at the same temperature and time as of molybdenum and in vacuum of the order of 10^{-1} Pa.

After the drop solidified, specimens for further studies were cut perpendicularly to reveal the cross-section. Cross-sections of the specimens were metallographically prepared. The microstructure of the interfaces between Mo and/or $MoSi_2$ and nickel were studied by scanning electron microscopy using an energy-dispersive X-ray analyser (EDS). X-ray diffraction (Cu Kα) was used to test the existence of molybdenum disilicide and to identify the products of reaction at the interface between substrates and brazing metal.

Two molybdenum discs, one of diameter 10 mm, the other of 15 mm to be able to measure the shear strength of the joint by the push-off method, were joined using Ni-foil in the furnace at the joining temperature 1360 ℃ during 10 min. Similar diameters of Mo discs as the substrate were used also for joining $MoSi_2$ at the same temperature and reflow time. After joining, the joint was cut perpendicularly to the Mo plane and metallographically prepared for study of the interface between Mo and/or $MoSi_2$ and nickel. The microstructure was studied similarly as were the interaction products of Mo-Ni by electron microscopy with EDX analyser. Three prepared joints were ex-

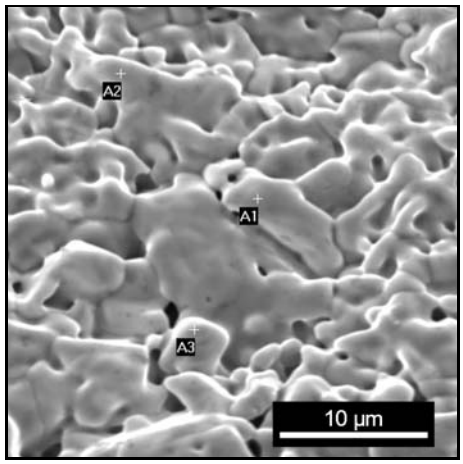

Fig. 1. Microstructure of $MoSi_2$ after the reaction of Si with Mo (1530 °C, 3 min).

Table 1. Concentration of Si and Mo in A_i points (at.%), Fig. 1

Points	Element		Possible phase
	Si	Mo	
A1	70.0	30.0	$MoSi_2$
A2	67.5	32.5	$MoSi_2$
A3	68.5	31.5	$MoSi_2$

posed to the measuring of shear strength using push-off method, the fourth joint was used for microstructural study. Loading rate was 1 mm min^{-1}.

3. Results and discussion

3.1. Molybdenum disilicide production

Figure 1 shows SEM image of $MoSi_2$ after the reaction of Si with Mo. The composition of several particles measured by energy dispersive X-ray analyser is given in Table 1. Figure 2 shows SEM image of such prepared specimen after cutting perpendicularly to the Mo plane and after metallographical treatment. The existence of $MoSi_2$ was also verified by X-ray diffraction of the reaction product (Fig. 3). Except $MoSi_2$ that forms the uppermost layer of the specimen, there is a layer of Mo_5Si_3 that lies between the Mo substrate and Mo disilicide. The Mo substrate has been removed from the sample prior to the XRD analysis in order to maximize the cross-section area of the topmost layers. The interface between molybdenum and Mo_5Si_3 layer forms a discontinuity, which can be due to different thermal expansion. ($CTE_{Mo} = 2.6 \times 10^{-6}\,K^{-1}$,

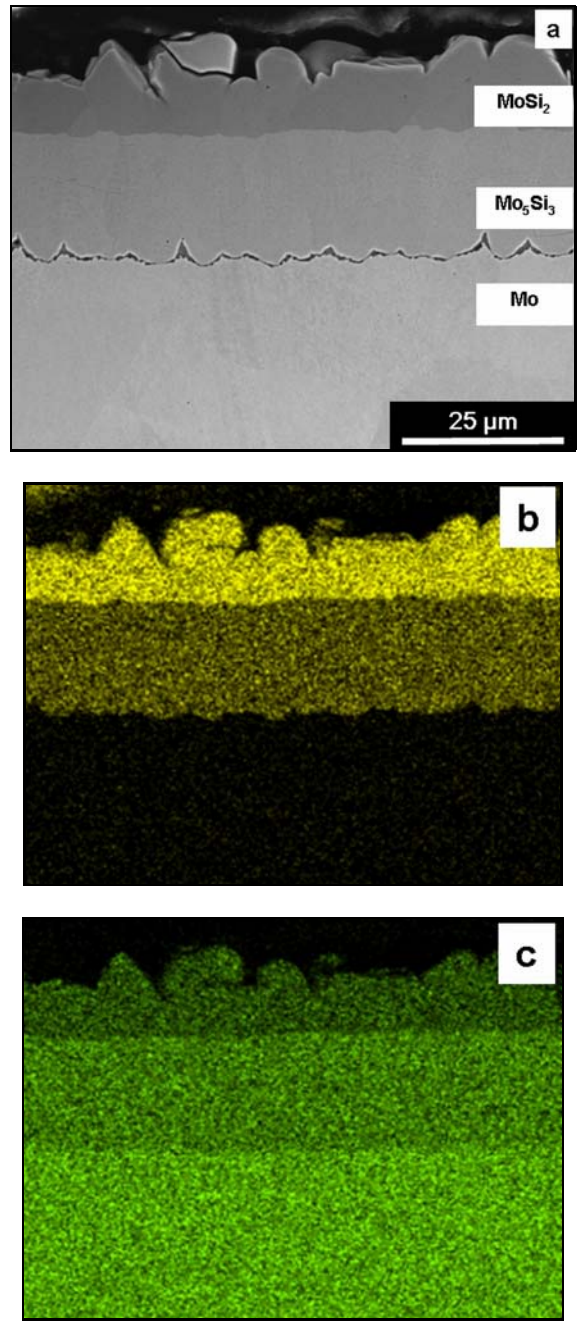

Fig. 2. SEM cross-section image (a) after reaction of Si with Mo substrate (1530 °C, 3 min) and X-ray maps of Si (b) and Mo (c).

$CTE_{Mo5Si3} = (5.2–11.5) \times 10^{-6}\,K^{-1}$). Iždinský et al. [10] infiltrated Mo wires by liquid silicon to produce Mo-$MoSi_2$ composite material. These reactions are accompanied by volume changes which can be eliminated by post infiltration compaction. The interface between Mo_5Si_3 and $MoSi_2$ forms a continuum. The amount of silicon placed on the Mo substrate is chosen so that no free Si remains on the surface of the topmost ($MoSi_2$) layer after the experiment; this is a

Table 2. Concentration of Mo, Ni in the Ni drop after wetting of Mo at 1360 °C and 10 min with Ni (at.%), Fig. 4

Element	Point No.							
	1	2	3	4	5	6	7	8
Mo	44.38	45.96	47.64	45.14	46.36	97.18	26.25	27.08
Ni	55.62	54.04	52.36	54.86	53.64	2.82	73.75	72.92
Possible phase	MoNi	MoNi	MoNi	MoNi	MoNi	Mo	$MoNi_3$	$MoNi_3$

Table 3. Concentration of Mo and Ni in the Mo-Ni-Mo joint (at.%), Fig. 5

Element	Point No.								
	1	2	3	4	5	6	7	8	9
Mo	48.96	47.49	47.49	37.77	48.39	29.42	28.20	29.86	37.04
Ni	51.04	52.51	51.70	62.23	51.61	70.58	71.80	70.14	62.96
Possible phase	MoNi	MoNi	MoNi	Mo + $MoNi_3$	MoNi	Mo + $MoNi_3$	Mo + $MoNi_3$	Mo + $MoNi_3$	Mo + $MoNi_3$

Table 4. Concentration of Mo, Ni in the Ni drop after wetting of $MoSi_2$ at 1360 °C and 10 min with Ni (at.%), Fig. 6

Element	Point No.					
	1	2	3	4	5	6
Si	33.22	36.78	36.36	37.11	35.24	–
Ni	32.09	0.85	2.76	0.00	2.32	–
Mo	34.69	62.37	60.88	62.89	62.44	100.00
Possible phase	$Mo(Ni,Si)_2$	–	–	–	–	Mo

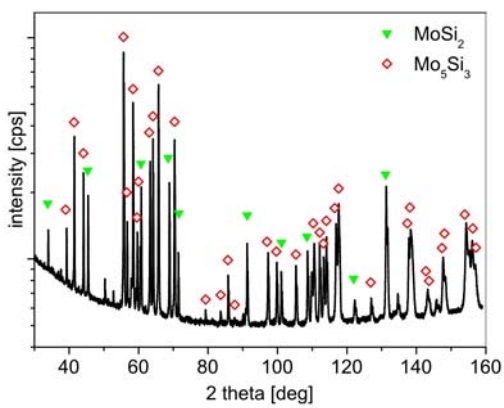

Fig. 3. X-ray diffraction pattern of $MoSi_2$ and Mo_5Si_3 phases ($\lambda_{CuK\alpha}$) after Si reaction with Mo at 1530 °C, 3 min.

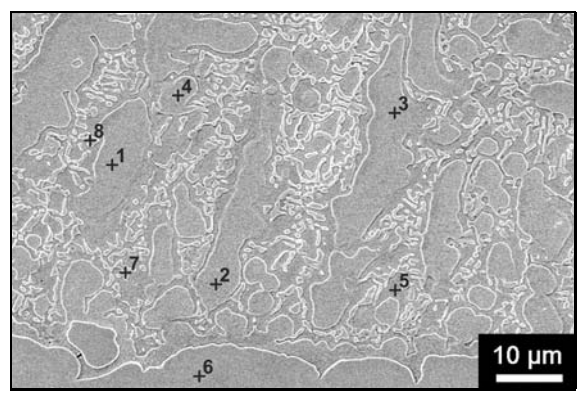

Fig. 4. Microstructure after wetting (1360 °C, 10 min) of Ni drop on Mo substrate.

consequence of significantly higher diffusion rate of Si than Mo in the Mo-Si system [11].

3.2. Wetting and products of interaction

At the contact of polycrystalline metal with a liquid metallic phase, the liquid can penetrate along the grain boundaries. Reaction in metal-metal wetting processes can involve dissolution of the substrate and the formation of intermetallic compounds [12]. Cube of Ni was melted on Mo as well as on $MoSi_2$ substrates at 1360 °C. After full melting nickel spilt over all surface of both substrates with wetting angle practically equal to zero. Because of very good wetting of both molybdenum and molybdenum disilicide at (low) temperatures by nickel there was no reason to test the wetting at higher temperatures.

Table 5. Concentration of Si, Ni and Mo in the $MoSi_2$-Ni-$MoSi_2$ joint (at. %), Fig. 7

Element	Point No.								
	9	10	11	12	13	14	15	16	17
Si	0.2	33.8	24.9	19.5	9.2	18.8	19.0	11.9	0.4
Ni	0.1	2.8	23.5	46.2	82.5	47.7	46.8	41.1	0.8
Mo	99.7	63.3	51.7	34.3	8.3	33.5	34.2	47.0	98.8
Possible phase	Mo	Mo_5Si_3	Mo(Si,Ni)	$Mo(Si,Ni)_2$	$(Mo,Si)Ni_4$	$Mo(Si,Ni)_2$	$Mo(Si,Ni)_2$	Mo(Si,Ni)	Mo

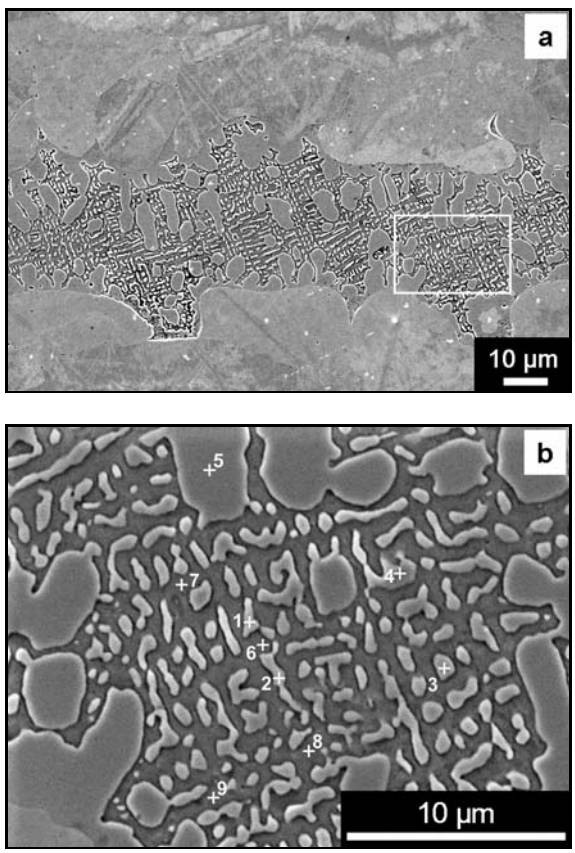

Fig. 5. Microstructure of Mo-Ni-Mo joint (a) and detail (white rectangle) with elements concentration (b).

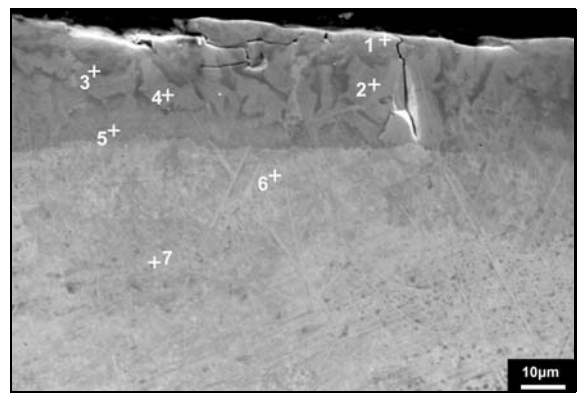

Fig. 6. Microstructure after wetting (1360 °C, 10 min) of Ni drop on $MoSi_2$ substrate.

3.2.1. Microstructure of Mo-Ni interface

Interface of Mo-Ni specimen prepared by cutting Mo substrate with Ni drop on the substrate was identified by SEM with EDS analyser. Figure 4 shows the interface between Mo substrate and Ni drop and Table 2 gives composition of Mo and Ni in the Ni drop measured by EDS analyser. Possible phases occurring in the microstructure can be phases MoNi (points 1–5), $MoNi_3$ (points 7, 8) and Mo (point 6) as a substrate.

Figure 5a shows a part of the Mo-Ni-Mo joint prepared at 1360 °C and 10 min; detailed view of the structure from the white rectangle with points, where compositional analysis by EDS was performed, is shown in Fig. 5b. Table 3 gives concentrations of the elements at the space between two Mo substrates joined with nickel braze. Possible phases occurring in this microstructure can be MoNi (points 1–3, 5) and $MoNi_3$ (points 4, 6–9). The interfaces between molybdenum and nickel in both cases, i.e., after wetting experiments as well as joining experiments, are continuous. The Mo-Ni-Mo interlayer system produced a joint with no cracking or porosity (Fig. 5a).

3.2.2. Microstructure of $MoSi_2$-Ni interface

Nickel in the form of a cube was put on the Mo substrate with $MoSi_2$ layer on it and melted at 1360 °C for 10 min similarly as in the case of Ni cube on Mo substrate. Because of very good wetting, nickel formed a thin layer on $MoSi_2$. Figure 6 reveals the section of the specimen perpendicularly to the substrate. Table 4 shows the concentration of the elements measured by energy dispersive X-ray analyser. Because of a very thin layer of nickel (lack of nickel due to its excellent wetting) it is possible to assume that the present structure is a mixture of $Mo(Ni,Si)_2$ or Mo(Ni,Si) with Mo.

Figures 7a–d show SEM image of the $MoSi_2$-Ni-$MoSi_2$ joint and X-ray maps of the joint place. Composition in individual points as measured by energy dispersive X-ray analyser is given in Table 5. Possible phases occurring in the microstructure can be Mo

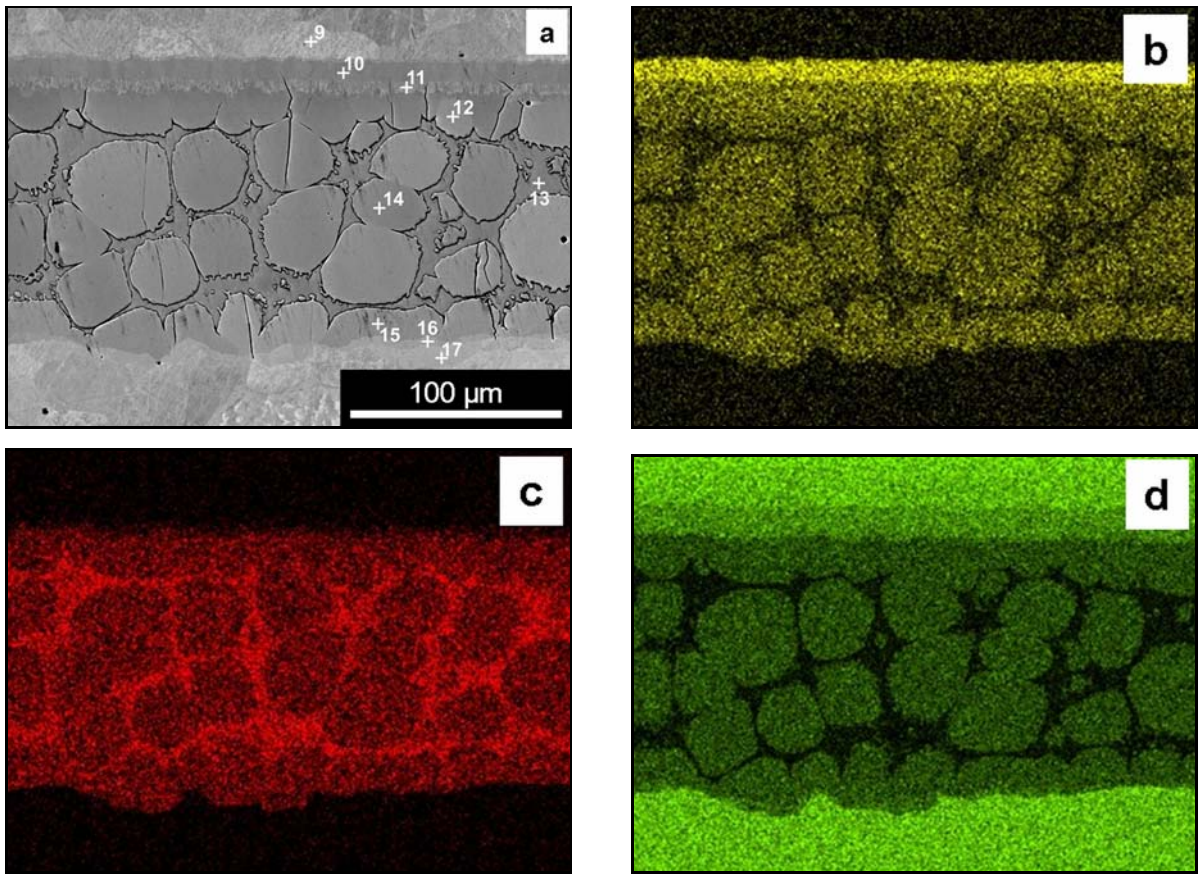

Fig. 7. Microstructure of $MoSi_2$-Ni-$MoSi_2$ joint (a) and X-ray maps of Si (b), Ni (c) and Mo (d).

T a b l e 6. Shear strength of the Mo-Ni-Mo and $MoSi_2$-Ni--$MoSi_2$ joints

	Mo-Ni-Mo	$MoSi_2$-Ni-$MoSi_2$
Shear strength of the joint (MPa)	134.5	37.0

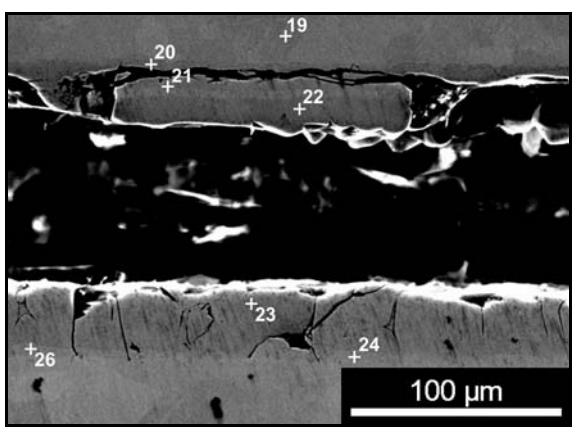

Fig. 8. Microstructure of $Mo(Si)_2$-Ni-$Mo(Si)_2$ joint after failure.

(substrate, points 9, 17), the interaction area includes Mo_5Si_3 layer (point 10) which does not contain nickel, the next layer contains Mo(Ni,Si) phase (point 11), phase with high amount of nickel containing about equal concentration of silicon and molybdenum (close to the phase $(Mo,Si)Ni_4$ (point 13). The grains in the middle of the figure are grains of $Mo(Si,Ni)_2$ phase (points 12, 14, 15).

3.3. Shear strength

Shear strength of the joints was measured of two types of joints: pure molybdenum and molybdenum disilicides by push-off method. Values are the average from three shear strength measurements. Table 6 shows the shear strength of both types of the joints. Shear strength of the Mo-Ni-Mo joint reaches 134.5 MPa. This system produces a joint with no cracking or porosity (Fig. 5a). Shear strength of $MoSi_2$-Ni-$MoSi_2$ joint is very low (37.0 MPa). Figure 8 shows the failure of the integrity of the joint. Points 20 and 21 (Table 7) reveal the crack in Mo_5Si_3 layer. Similar failure may start up already at the production of Mo disilicide (Fig. 2). Nickel interlayer system with molybdenum disilicides produced a joint with a porous interface and catastrophic cracking through Mo_5Si_3.

Table 7. Concentration of Si, Ni and Mo in the crack of $MoSi_2$-Ni-$MoSi_2$ joint (at.%), Fig. 8

Element	Point No.							
	19	20	21	22	23	24	25	26
Si	0.18	31.50	24.09	22.51	18.77	12.03	0.41	11.92
Ni	0.11	0.38	10.08	43.52	46.96	40.51	0.47	41.52
Mo	99.70	68.12	65.83	33.97	34.27	47.46	99.12	46.56
Possible phase	Mo	Mo_5Si_3	Mo_5Si_3	$Mo(Si,Ni)_2$	$Mo(Si,Ni)_2$	Mo(Ni.Si)	Mo	Mo(Ni,Si)

This cracking is a result of large stresses developing due to different thermal expansion of materials being joined.

4. Conclusions

Obtained results can be summarized as follows:

1. Molybdenum disilicide was prepared on the top of Mo substrate by the reaction of liquid Si with solid Mo at a reaction temperature 1530 ℃ and time 3 min.

2. Nickel after melting wets Mo and $MoSi_2$ with almost zero wetting angle.

3. Interaction products of Mo and Ni are composed of $MoNi_3$ and MoNi phases.

4. Interaction products of $MoSi_2$ and Ni are composed of Mo_5Si_3, Mo(Ni,Si), $(Mo,Si)Ni_4$, $Mo(Si,Ni)_2$ phases.

5. The Mo-Ni-Mo system produced a joint with no cracking or porosity. Its shear strength was 134.5 MPa.

6. $MoSi_2$-Ni-$MoSi_2$ produced a joint with a porous interface and cracking through Mo_5Si_3, and its shear strength was 37.0 MPa.

Acknowledgements

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