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ON THE CHARACTER OF MATRIX-REINFORCING PARTICLE PHASE BOUNDARIES IN MeC and MeB (Me= W, Zr, Ti, Nb, Ta) IN-SITU COMPOSITES

CHARAKTER GRANIC MIĘDZYFAZOWYCH OSNOWA-CZĄSTKA WZMACNIAJĄCA W KOMPOZYTACH "in situ" MeC i MeB (Me= W, Zr, Ti, Nb, Ta)

In metal matrix composites (MMCs), the character of the matrix-reinforcing particle phase boundaries has very important effect on the utilisation properties of these materials. For some composites like Al/TiC, Al/TiB$_2$, Ni$_3$Al/TiC, AlSi/SiC and Za27/NiAl, the properties of these phase boundaries were discussed in detail in study [1]. From this study it follows that during the in-situ composite synthesis by SHSB route, the solidification process results in the formation of large internal stresses, due to differences that have been observed to exist in the values of the coefficients of thermal expansion and elastic modulus between the matrix and reinforcing particles [2,3]. According to A. Mortensen [4], the differences in the thermal expansion that occur between the matrix and the reinforcing phase increase the density of dislocations in the structure, which may lead to the formation of microcracks. Besides these effects, alien phases, formed additionally in the process of composite synthesis, may appear at the phase boundaries. These are usually the undesired phases, weakening the bond that should exist between the matrix and the reinforcing particle. Both alien precipitates and the stresses have an important effect on the character of the phase boundaries and, indirectly, on the mechanical properties of composites fabricated by SHSB route [5,6,7]. The application of modern research methods, e.g. high-resolution electron microscopy (HREM), enables better understanding of the phenomena taking place at the matrix-reinforcing particle phase boundary. This study describes the investigations that have been carried out to prove the presence of internal stresses in the in situ composites. They are meant to complete the results presented in [1]. The main aim of the present study was to investigate the character of the matrix-ceramic particle phase boundary in, fabricated by the SHSB method, new composites from the group of the "in situ" materials, i.e. Ni$_3$Al/WC, Ni$_3$Al/ZrC, Ni$_3$Al/NbC, Ni$_3$Al/NbB [8] as well as Ni$_3$Al/TaC and Ni$_3$Al/TaB. Like in [1], also in this case, the techniques used in investigations included electron microscopy, scanning microscopy and X-ray microanalysis.

Charakter granic międzyfazowych osnowa – cząstka w kompozytach metalowych typu MMCs ma zasadniczy wpływ na właściwości użytkowe tych materiałów. Charakter tych granic dla niektórych kompozytów: Al/TiC, Al/TiB$_2$, Ni$_3$Al/TiC, Al-Si/SiC oraz Za27/NiAl zostały szczegółowo przedstawione w pracy [1]. Wynika z niej, że przy syntezie kompozytów "in situ" metodą SHSB, po procesie krystalizacji, powstają duże naprężenia wewnętrzne wynikające z różnic wartości współczynników rozszerzalności termicznej, oraz modułów sprężystości osnowy i cząstek wzmacniających [2,3]. Według A. Mortensena [4] to niedopasowanie rozszerzalności cieplnej pomiędzy osnową a umocnieniem jest przyczyną wzrostu gęstości dyslokacji w strukturze, co w następstwie może prowadzić do powstawania mikropęknięć. Oprócz tego na granicy rozdziału, mogą pojawiać się obce fazy, powstające dodatkowo w procesie syntezy kompozytu. Są to fazy zwykle niepożądane, osłabiające wiązanie osnowa -cząstka wzmacniająca. Zarówno obce wydzielenia jak i naprężenia mają decydujący wpływ na charakter granicy fazowej czyli pośrednio na właściwości mechaniczne otrzymywanych tą metodą kompozytów [5,6,7]. Zastosowanie nowoczesnych metod badawczych, m.in. wysokorozdzielczej mikroskopii elektronowej HREM, pozwala poznać opisane zjawiska na granicy międzyfazowej osnowa-cząstka wzmacniająca. W niniejszej pracy przedstawiono badania potwierdzające występowanie naprężeń wewnętrznych w kompozytach "in situ". Uzupełniają one wyniki badań prezentowanych w pracy [1]. Głównym celem prezentowanej pracy jest badanie charakteru granic osnowa – cząstka ceramiczna w wytworzonych metodą SHSB, innych, nowych materiałach kompozytowych, z grupy kompozytów "in situ" t.j. Ni$_3$Al/WC, Ni$_3$Al/ZrC, Ni$_3$Al/NbC, Ni$_3$Al/NbB [8] oraz Ni$_3$Al/TaC i Ni$_3$Al/TaB. Podobnie jak w pracy [1], do badań wykorzystano metody mikroskopii elektronowej, mikroskopii skaningowej i mikroanalizy rentgenowskiej.

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1. Introduction

Cast "in situ" metal matrix composites are advanced materials assigned for numerous structural applications. Their characteristic feature is that they are fabricated in a single-stage process, the final product is of a near-net-shape, and as such requires nearly no machining. Compared with standard alloys, composites offer numerous additional benefits, to mention only high mechanical properties, advantageous strength-mass ratio, and ductility at high temperatures [9,10.]

In-situ composites combine high strength with the rigidity of the reinforcing particles (in this study, mainly ceramic materials), forming very strong bonds with the matrix. In the "in situ" process, pure, non-oxidised and free from the precipitates of alien phases, matrix-reinforcing particle phase boundaries are formed. In composites, both the matrix as well as the reinforcing particles preserve their original physical and chemical properties, but bonded together offer a combination of mechanical properties unattainable if used separately. The extending field of composite application raises the question of their utilisation properties, strong-

ly dependent on the phase boundary characteristics. The problem requires very early consideration, even at the stage of composite designing. Very important are different aspects of the phase boundary structure, understood not only as a geometrical contact surface between the matrix and the ceramic material, but as an area (a volume) within which the chemical, physical and mechanical properties undergo some changes at the stage of the composite synthesis and the following performance [11]. In the process of composite synthesis, the boundaries characterised by different degrees of coherence are formed. They may also have different defects. At phase boundaries, the products of chemical reactions taking place between various constituents of a ceramic particle and the metallic matrix may also appear and, as a consequence, reduce the composite strength. Therefore the quality of bonds at the phase boundary is of primary importance for the properties of the fabricated composite material. In MMCs, different types of the reinforcing particles are used. The majority of them can be produced by the method of "in situ" synthesis, e.g. by the SHSB route (Table 1).

TABLE 1

Types of the reinforcing particles in MMCs.[9]

oxides:	Al_2O_3, MgO, SiO_2, ZrO_2, HfO_2, TiO_2, CeO_2, Cr_2O_3
carbides:	TiC, SiC, ZrC, B_4C, Al_4C_3, Cr_3C_2, TaC, MoC, WC, NbC
nitrides:	BN, TiN, ZrN, Si_3N_4, Al_2N_2,
borides:	TiB_2, ZrB_2, SiB_3, TaB_2, MoB, NbB
aluminides:	NiAl , FeAl , Ni_3Al, Fe_3Al

2. The reactivity of composite matrix-reinforcing phase system

The composite matrix, which is aluminium or aluminium alloy (in the case of this study – the Al-Ni alloy solidifying as an intermetallic phase Ni_3Al), can enter into chemical reaction with the reinforcing phases and form various compounds that will have disadvantageous effect on the mechanical properties and/or corrosion resistance. The reinforcing phases may behave as stable in one matrix and as unstable in another. For example, silicon carbide SiC is chemically stable in magnesium alloys and unstable in aluminium alloys. Used as a reinforcing phase, alumina Al_2O_3 is chemically stable in aluminium composites. Nevertheless, replacing SiC particles with Al_2O_3 cannot fully solve the problem, because Al_2O_3 particles are hardly wettable by aluminium and its alloys. Therefore it is necessary to coat the Al_2O_3 particles with lithium or magnesium, which considerably

increases the cost of fabrication of such materials. One of the most serious difficulties in designing of composites is the choice of proper reinforcing phase. Among other properties, it should be thermodynamically stable in the matrix and offer good wetting properties. In composites, two types of effects may occur at the phase boundary – the effect of purely physical nature, i.e. wetting of the reinforcing phase by molten metal, and the effect of physico-chemical nature when wetting is accompanied by chemical reactions occurring between the phases. In the composite fabrication process, the problem most serious is how to overcome the wettability barrier, that is, to create the conditions under which, in the melt – reinforcing phase system, the contact angle Θ will be smaller than $\pi/2$. In practice, this can be achieved through the following operations:

♦ annealing of the reinforcing particles before introducing them to metal melt; this operation reduces the metal surface energy as well as the angle Θ,

◆ coating of particles; the coating-enveloped particle does not enter into direct contact with the melt, and only the intermediate coating layer is exposed to the wetting effect. As a matrix, aluminium offers numerous possibilities for the application of various barrier coatings. In most cases, the reinforcing particles are coated with nickel to produce a layer of aluminides of the $NiAl_3$ and Ni_2Al_3 type, which are wetted by the metal matrix. Metals like Fe, Ti, Cu, Ag and Cr are also used sometimes for coatings,

◆ adding some special elements, like lithium or magnesium, to the melt to reduce the liquid metal surface tension and energy at the molten metal – reinforcing particle phase boundary, or to produce an intermediate layer on the surface of the particles,

◆ "in situ" synthesis of composites.

The problem already mentioned, inherently related with the system of ductile matrix – hard ceramic particle, is the presence of mechanical stresses, due to differences in the coefficients of thermal expansion observed in this system. As outlined in [1], the ceramic material present in the composite is the source of stresses that can be released through, among others, the formation of lattice-type defects in the matrix.

In the case of Al/MeC and Ni_3Al/MeC composites, in spite of the carbide particles growing in a liquid matrix, probably as early as at the stage of cooling in the solid phase, the stresses caused by these particles can easily generate dislocations in the composite matrix.

As a matter of fact, most of the examined MeC particles suffered from these defects. The explanation should be sought in the presence of thermal stresses formed during the exothermic reaction of synthesis of the titanium carbide in liquid aluminium

3. Own investigations

The results of the studies on the character of phase boundaries in a group of the new composites like Ni_3Al/WC, Ni_3Al/ZrC, Ni_3Al/NbC and Ni_3Al/NbB, Ni_3Al/TaC, Ni_3Al/TaB, and of the complementary studies using electron microscopy, conducted on the Ni_3Al/TiC and Ni_3Al/TiB composites, were presented. For their synthesis, the SHSB method, i.e. the method of self-propagating exothermic reaction of synthesis proceeding in a briquette of mixed metallic and non-metallic powder placed in the bath of molten metal, was used. The method was described in detail in [9].

Ni_3Al/TiC composite

Thin foils of the Ni_3Al/TiC composite were prepared, and examinations of the phase boundary were carried out by electron microscopy and energy dispersive X-ray spectroscopy (EDS). Networks of dislocations in the composite matrix and stresses in the precipitates of titanium carbide were observed (Fig.1). No alien precipitates were present on the phase boundary - this fact was confirmed by the results of investigations using standard X-ray microanalysis (Fig.2)
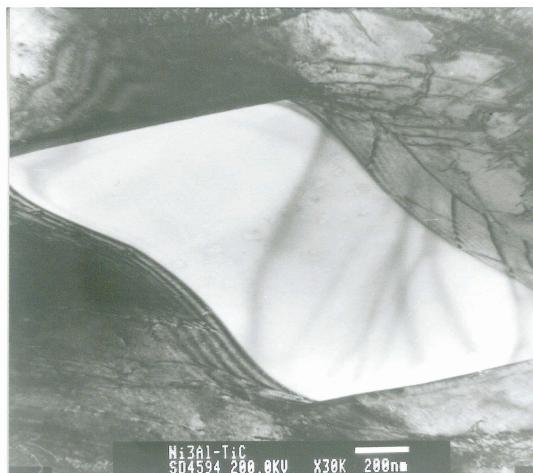

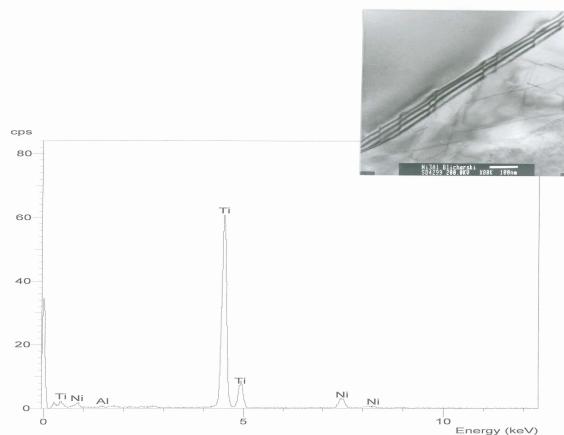Fig. 1. Microscopic image of phase boundary in Ni_3Al/TiC composite

Fig. 2. EDS spectrum of Ni_3Al – titanium carbide phase boundary

Ni_3Al/TiB_2 composite

As in the case described above, thin foils of the Ni_3Al/TiB_2 composite were also prepared and photographs of the phase boundary were taken. Both photographs (Fig 3, 4) have revealed the presence of dislocations in the matrix and of stresses in the reinforcing phase.

Similar effects were observed in all the in-situ composites subjected to SHSB synthesis. To document the effect of unfavourable internal stresses present in composite materials on their structure, fractures formed in the composites of Ni_3Al/MeC and Ni_3Al/MeB were examined,

using for this purpose a JEOL JSM 5500 LM scanning microscope. The results of these examinations are shown in Figs. 5-9. From the photographs it follows that, due to the application of large shear or tensile forces resulting in fracture, the energy of the internal stresses, accumulated on phase boundaries and inside pure ceramic phases, gets liberated.

As a result of this effect, a delamination occurs at the matrix-reinforcing particle phase boundary with fracture of crystals in the reinforcing phase.
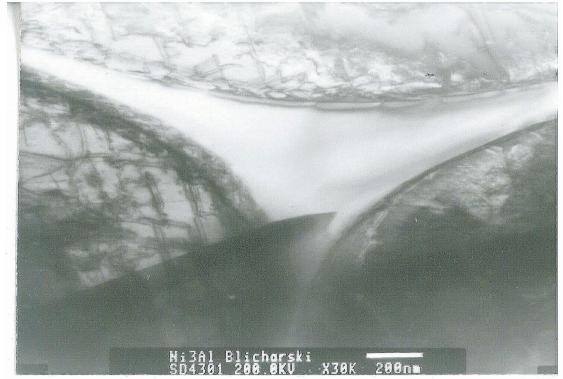
Fig. 3. Microscopic image of phase boundary in Ni_3Al/TiB_2 composite

Fig. 4. Microscopic image of phase boundary in Ni_3Al/TiB_2. composite. Note well visible dislocations present in the matrix material
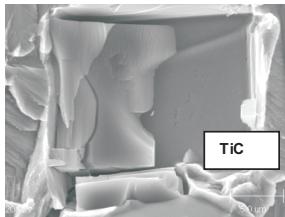
Fig.5. Scanning image of fracture in Ni_3Al/TiC composite. Note the destruction of phase boundary and of TiC crystal.
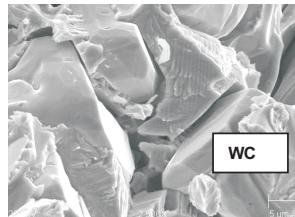
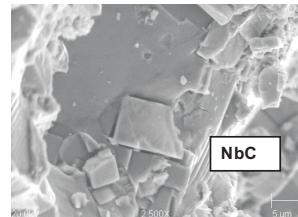Fig.6. Scanning image of fracture in Ni_3Al/WC composite. Note the destruction of phase boundary and of WC crystal

Fig.7. Scanning image of fracture in Ni_3Al/NbC composite. Note the destruction of phase boundary.

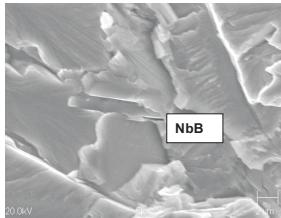

Fig.8. Scanning image of fracture in Ni_3Al/NbB composite. Note the destruction of phase boundary.

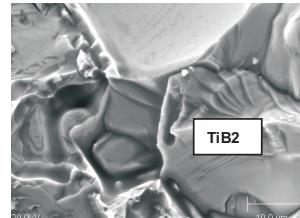Fig.9. Scanning image of fracture in Ni_3Al/TiB_2 composite. Note the destruction of phase boundary and of TiB_2 crystal.

Ni$_3$Al/WC composite

The fabricated composite was subjected to preliminary metallographic examinations. Its microstructure is shown in Fig. 10. The WC particles of dimensions reaching about 20μm are distributed in the interdendritic spaces of the matrix.

Next, a region of the Ni$_3$Al/WC composite matrix-reinforcing particle phase boundary was subjected to scanning analysis and X-ray microanalysis, shown in Fig. 11.

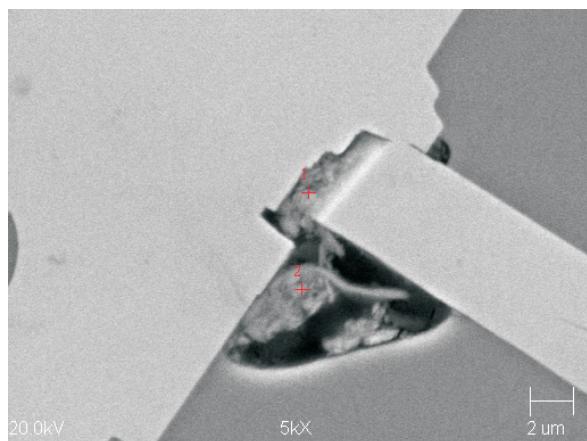Fig. 10. Scaning image of Ni$_3$Al/WC composite. 100x

Fig. 11. Scanning topographic image of the matrix-reinforcing particle phase boundary in Ni$_3$Al/WC composite. 5000x

No reactivity has been observed to exist between the matrix of the Ni$_3$Al composite and its WC reinforcing phase. The local chemical analysis performed in microregions of the phase boundary has confirmed this fact, indicating the existence of Ni$_3$Al phase and tungsten carbide WC only.

Ni$_3$Al/ZrC composite

As in the composite described above, also in this case, attention was focussed on the scanning analysis and X-ray microanalysis of the matrix-reinforcing particle phase boundary. The microstructure of the Ni$_3$Al/ZrC composite is shown in Fig. 12, while the results of an X-ray microanalysis of the matrix-reinforcing particle phase boundary are shown in Fig. 13
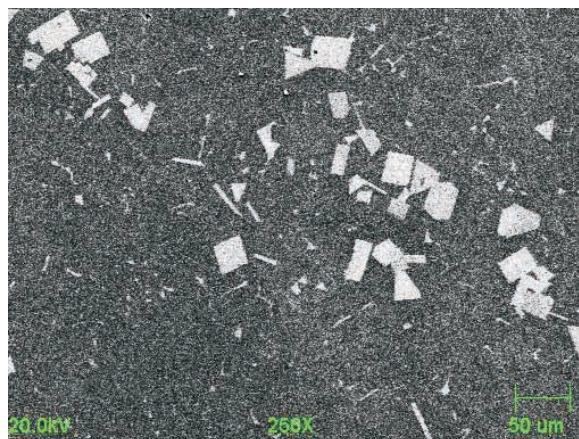

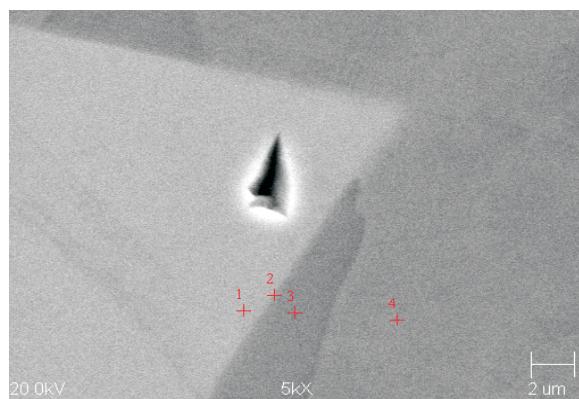Fig. 12. Scaning image of Ni$_3$Al/ZrC composite. 250x

Fig. 13. Scanning topographic image of the matrix-reinforcing particle phase boundary in Ni$_3$Al/ZrC composite. 5000x

In Ni$_3$Al/ZrC composite, local analysis was made at selected points of the phase boundary. The results are shown in Table 2.

TABLE 2

Chemical analysis in microregions of the matrix-reinforcing particle phase boundary in Ni$_3$Al/ZrC composite

Measuring point	Content C wt.%	Content Al wt.%	Content Ni wt.%	Content Zr wt.%
1	46,7	0,1	1,0	52,1
2	47,1	3,1	13,4	36,5
3	–	23,7	75,4	0,8
4	–	15,5	83,6	0,8

The examined particles of zirconium carbide ZrC are several times larger than the particles of WC carbides. Also in this case, total absence of chemical reactions at the matrix-reinforcing particle phase boundary has been reported.

Ni$_3$Al/NbC composite

The performed metallographic examinations have proved that niobium carbides NbC present in the composite appear in two different forms, i.e. as single particles (Fig.15) and, more frequently, as large *clusters* (Fig.14). The X-ray microanalysis did not show the presence of any products of the reaction at the matrix-reinforcing particle phase boundary other than the two basic phases, i.e. Ni$_3$Al and NbC. The results of chemical analysis confirm this fact (Table 3).
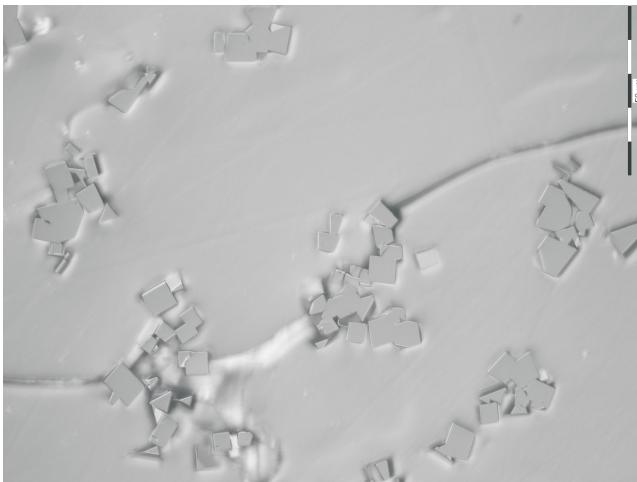

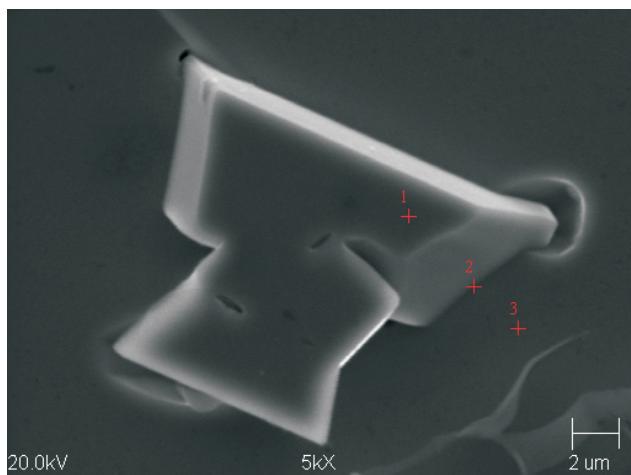Fig. 14. Microstructure of Ni$_3$Al/NbC composite. 500x

Fig. 15. Scanning topographic image of the matrix-reinforcing particle phase boundary in Ni$_3$Al/NbC composite. 5000x

TABLE 3

Chemical analysis in microregions of the matrix-reinforcing particle phase boundary in Ni$_3$Al/NbC composite

Measuring point	Content C wt.%	Content Al wt.%	Content Ni wt.%	Content Nb wt.%
1	47,7	0,01	1,7	50,5
2	46,5	0,5	4,1	48,8
3	–	13,4	84,1	2,4

Ni$_3$Al/NbB composite

At the next stage of the investigations, the Ni$_3$Al-based composite with particles of niobium boride was examined. Metallographic examinations have proved that the particles of NbB are by one order of magnitude smaller than those of the niobium carbides NbC; their shapes are also different (Figs. 15,17). Also in this particular case, the lack of any reactivity between the Ni$_3$Al matrix and the reinforcing phase of NbB has been reported.

The results of chemical analysis in microregions of the matrix-reinforcing particle phase boundary in Ni$_3$Al/NbB are shown in Table 4.
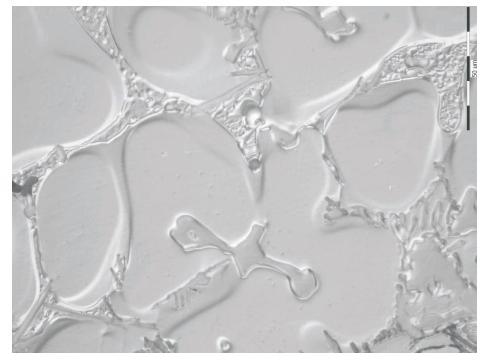

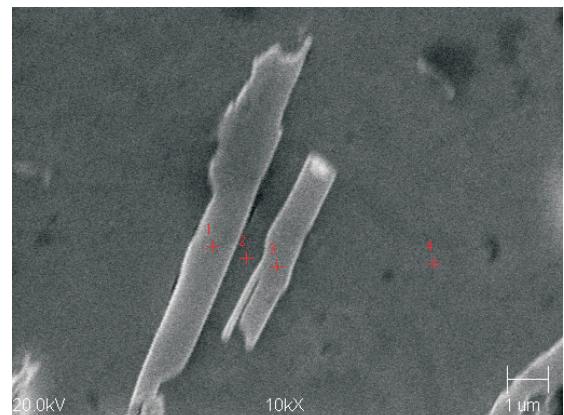Fig. 16. Microstructure of Ni$_3$Al/NbB composite. 500x

Fig. 17. Scanning topographic image of the matrix-reinforcing particle phase boundary in Ni$_3$Al/NbB composite.10000x

TABLE 4

Chemical analysis in microregions of the matrix-reinforcing particle phase boundary in Ni$_3$Al/NbB composite

Measuring point	Content **B** wt.%	Content **Al** wt.%	Content **Ni** wt.%	Content **Nb** wt.%
1	45,8	0,6	21,5	32,0
2	18,6	2,5	55,3	23,5
3	43,6	0,8	24,5	31,0
4	–	6,5	90,1	3,2

Finally, the composites of Ni$_3$Al/TaC and Ni$_3$Al/TaB were examined.

Ni$_3$Al/TaC composite

The microstructure of Ni$_3$Al/TaC composite is shown in Figs. 18 to 21.
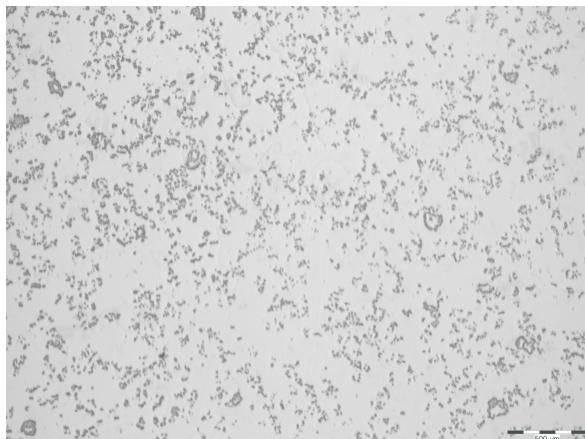
Fig. 18. Metallographic image of Ni$_3$Al/TaC composite specimen, 25x

Ni$_3$Al/TaB composite

For Ni$_3$Al matrix, the SHSB reaction of synthesis has
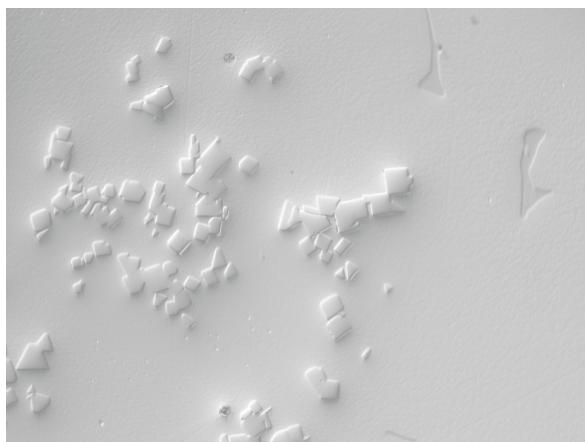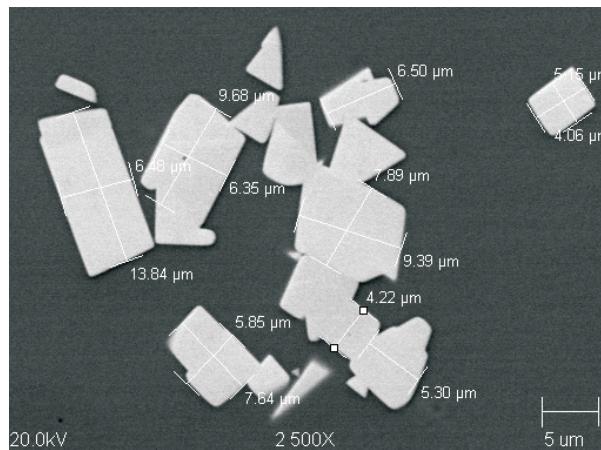
Fig. 19. Metallographic image of Ni$_3$Al/TaC composite specimen, 500x

Fig. 20. Microstructure of the Ni$_3$Al /TaC composite surface, 2500x; note the shape and dimensions of particles visible in the image
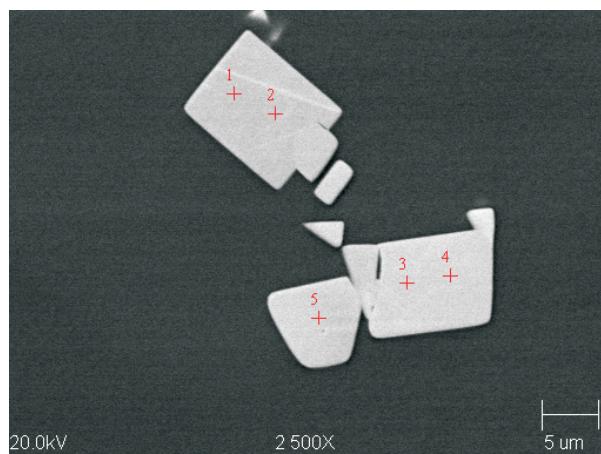

Fig. 21. Microstructure of the Ni$_3$Al /TaC composite surface. 2500x; note the points of local chemical analysis

Metallographic examinations have proved that tantalum carbides present in the composite occur in the form of large clusters (Fig.20) and are dispersed on the whole surface of the examined specimens. In Figs. 20 and 21, the dark background is the composite matrix, i.e. the intermetallic phase of Ni$_3$Al. The X-ray microanalysis did not show any products of reaction at the matrix – reinforcing particle phase boundary. For further verification, the chemical composition of the ceramic phases formed in the composite was examined by EDX on the specimen cross-section (at local points marked in Fig. 21); the obtained results were compiled in Table 5.

proved to be much less effective in the case of tantalum boride TaB than in the case of tantalum carbide

TABLE 5

The results of chemical analysis of TaC particles in the Ni$_3$Al/TaC composite

Point no.	Content of elements							
	C		Al		Ni		Ta	
	[%] atomic	[%] weight	[%] atomic	[%] weight	[%] atomic	[%] weight	[%] atomic	[%] weight
1	89.2	36.9	0.0	0.0	0.8	1.7	9.8	61.2
2	89.1	36.5	0.1	0.1	0.7	1.4	10.0	61.9
3	88.9	36.3	0.1	0.1	0.7	1.4	10.0	62.0
4	89.1	36.6	0.0	0.0	0.7	1.6	9.9	61.6
5	89.5	37.4	0.0	0.0	0.8	1.7	9.6	60.7
6	–	–	24.9	24.9	75.0	86.7	–	–

TaC. Though the TaB precipitates were obtained in the matrix, the typical structure of a composite was not produced, because the tantalum boride TaB volume content was much lower than the required predetermined value. Difficulties appeared as early as at the stage of selecting a methodology that should be used in metallographic examinations undertakem to reveal the presence of this phase on the specimen surface. Because of a very low content of tantalum borides in the Ni$_3$Al/TaB composite examined by scanning microscopy, it was difficult to determine their location on the specimen cross-section. The structure of the produced material is shown in Figs. 22, 23 and 24.
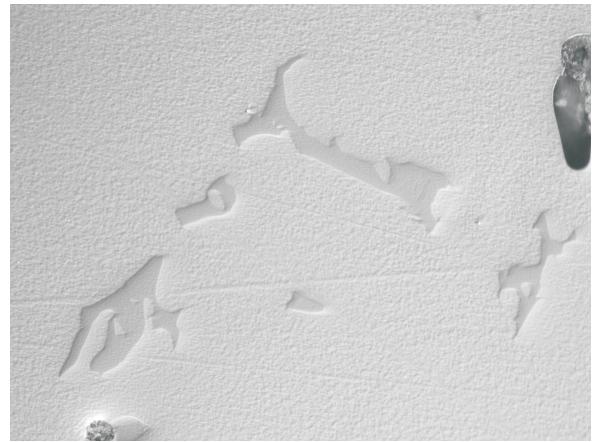

Fif. 23. Microstructure of the Ni$_3$Al /TaB composite surface, 500x
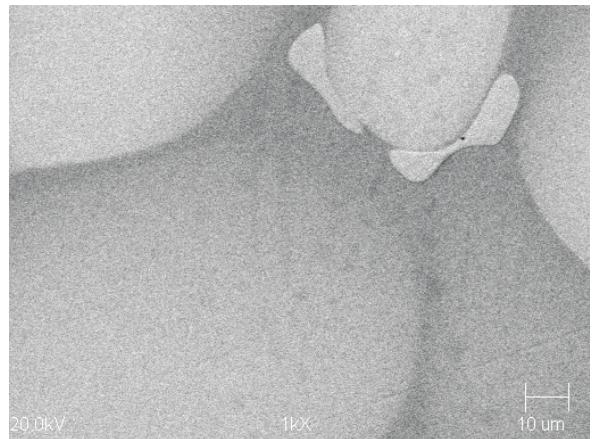

Fig. 24. Topographic image of the Ni$_3$Al /TaB composite surface, 1000x

Fig. 22. Microstructure of the Ni$_3$Al /TaB composite surface, 100x

Given the fact that the X-ray microanalysis of Ni$_3$Al/TaB composite failed to give the expected result, which was identification of tantalum borides, the determination of the TaB particles chemical composition and mean size has also proved to be impossible. Like in the case of Ni3Al/TaC composite, the specimen was also subjected to X-ray diffraction analysis, but attempts to determine the phase composition (except Ni3Al matrix) were unsuccessful. The method of SHSB synthesis has proved to be of no use in this particular case.

4. Conclusions

In Ni$_3$Al/TiC composites, the presence of stresses near the phase boundary and in the carbide crystals has been stated. No alien precipitates appeared at the matrix – TiC particle phase boundary, neither did the precipitates at the Ni$_3$Al - TiB$_2$ phase boundary. On the other hand, numerous dislocations near the phase boundaries were detected. In all composites fabricated by the "in situ" technique, the occurrence of dislocations in the metallic matrix and of stresses in the particles of the reinforcing phase was reported. The stresses were formed as a result of the difference in volume expansion of the metallic matrix and ceramic particles of the following types: WC, NbC, NbB, and ZrC. In the latter group of composites, i.e. Ni$_3$Al/TaC and Ni$_3$Al/TaB, the SHSB method has proved to be effective only for the Ni$_3$Al/TaC composite. In the case of this composite, the size of the particles was typical of the cast in situ composites reinforced with other metallic carbides, like Ti, W, or Nb. Generally speaking, no other products of the chemical reaction were detected at the matrix – reinforcing particle phase boundary for the whole group of Ni$_3$Al/MeC and Ni$_3$Al/MeB composites fabricated by SHSB technique.

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