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The structural study of Ti-Si-C alloys produced by mechanical alloying method

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ABSTRACT

Purpose: The aim of this paper is to determine the influence of the alloying time and composition on the structure of Ti-Si-C alloy.

Design/methodology/approach: The powders of the Ti-Si-C alloys were obtained by mechanical alloying method in a planetary Fritsh Pulverisette 5 mill under inert argon atmosphere. In order to investigate the structure scanning electron microscopy, transmission electron microscopy and optical microscopy were used. Phase transformations during mechanical alloying process were determined by means of diffractometer. The distribution of particle sizes of powder materials was determined by a laser analyser.

Findings: The application of the mechanical alloying method gives opportunity to produce nanocrystalline and amorphous phase. The laboratory test show that, by using this method, one can produce alloys with intentional chemical constitution and desirable structure.

Research limitations/implications: : The powder metallurgy techniques make it possible to obtain Ti-Si-C massive materials by means of milling, followed by compacting and sintering. All of the experiments presented in this article are made on a laboratory scale. Further investigations should be concentrated on the developing of powder sintering method.

Originality/value: This scientific research will be helpful for the composition plan for higher Ti_3SiC_2 content of powder synthesis. The synthesis of Ti-Si-C powder gives opportunity for the development of dispersion-strengthened alloys. The Ti-Si-C alloys have been considered to be potentially important for high temperature applications as either a structural or functional material.

Keywords: Metallic alloys; Ti-Si-C alloy; Mechanical alloying; Powder metallurgy

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Materials

1. Introduction

The mechanical alloying (MA) technique is an important method to produce equilibrium and non-equilibrium phases from elemental powders. This method enables us to obtain supersaturated solid solution, intermetallic phases, crystalline and amorphous phases, also those which cannot be obtained by standard techniques. Mechanical alloying is a complex process, that require optimizing of many parameters to achieve desirable

Table 1.
Purity, particle size and chemical composition

Elements		Purity [%]	Granulation [mesh]	Granulation [μm]	mass. [%]	at. [%]
A	Ti	99.5	60-100	149-250	73.38	50
	Si	99.5	325	44	14.35	16.6
	C	99.8	325	44	12.27	33.4
B	Ti	99.5	60-100	149-250	83.10	70
	Si	99.5	325	44	13.92	20
	C	99.8	325	44	2.98	10

material. The productivity of this technique depends on the process control agent, temperature of the process, ball to powder weight ratio, time of milling process, particle sizes of a mixture, the mill type, atmosphere. The essence of the mechanical alloying process is the collision of the still balls with powder particles and the interaction of the powder particles. During this process the change of the chemical composition and material microstructure occurs [1-11].

Ternary compound Ti_3SiC_2 is a promising candidate for high temperature applications as either a structural or a functional material. It is characterized by good electrical and thermal conductivity. It is machinable, unusually damage tolerant and resistant to thermal shock. It possesses good high temperature mechanical properties and oxidation resistance. Titanium silicon carbide system (Ti_3SiC_2) is the only stoichiometric ternary phase. This materials is of interest due to its unique characteristic like thermal and chemical resistance with low hardness and high stiffness. This suggests that Ti-Si-C alloys possibly could be used as new matrix materials: Ti_3SiC_2-based composites, for example TiC-Ti_3SiC_2 for high temperature applications [12-20].

Lately, different methods have been employed for the production of bulk Ti_3SiC_2 materials, for example: chemical reaction, chemical vapour deposition, arc-melting, reactive sintering, HIP, SHS-HIP, pulse discharge sintering.

It is advisable to develop a method for the synthesis of a single Ti_3SiC_2 powder phase with a simple process. Up to now, the content of Ti_3SiC_2 in the synthesized powder reaches not more than 95.8 %. It is difficult to obtain monolithic Ti_3SiC_2. Some secondary phases such as TiC_x, $TiSi_2$, $Ti_5Si_3C_x$ and the other phases tend to occur. The Ti_3SiC_2 phase content is different depending on the process. The optimal temperature range for the formation of interesting phase was 1210-1300 °C, above 1300 °C the content of Ti_3SiC_2 decreased significantly with temperature [21-30]

The main purpose of this research is to synthesize Ti_3SiC_2 (A-alloy) and Ti_7Si_2C (B-alloy) powders by using the mechanical alloying technique at relatively lower temperature.

2. Experimental procedure

The aim of the present work is the characterization of the milled Ti-Si-C alloys using XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), optical microscopy and laser analysis methods.

The mechanical alloying process of the pure titanium, silicon and carbon powders was realized. Characteristic of powders used to manufacturing materials is given in Table 1. The mechanical alloying process was carried out in a high-energy planetary ball mill Fritsch Pulverisette 5. In this process wasn't added process control agent. The ball to powder weight ratio was 8:1. In order to prevent powder impurities, the samples were sealed in the vial under argon atmosphere. The powders were ground for 200 hours.

The microscopic observation of the shape and size of the powdered material particles was carried out by means of the Philips XL 30 scanning electron microscope, within the magnification of 1200 and 4800 times. The microscopic observation of the powder particles and grains were executed by means of transmission electron microscope of the JEM 2000 FX of JEOL firm with accelerating voltage 200kV. The optical microscopy Leica MEF4A was used. Powder sample were analyzed by energy dispersion spectroscopy, too.

The changes of the phase constitution were tested by means of the Philips PW 1140 X-ray diffractometer with CoKa radiation (35kV, 30mA) and a diffracted beam, graphite monochromator. The XRPD data have been collected in steps of 0.05° 2θ and a counting time of 10 seconds per step.

The measurements of particles size were carried out by means of the laser analyzer "Analysette 22" made by the Fritsch company. The laser analyzer of particle size "Analysette 22" is the apparatus designed to define the distribution of sizes of solid particles, in the range of 0.1-1250 μm.

3. Results

The as-milled powders consist of a fine mixture of crystalline and amorphous phases. Intermediate phases Ti_5Si_3 and TiC were found during the reaction. The Ti_3SiC_2 grains growth from the TiC particles was also observed.

The diffraction pattern of Ti-Si-C type mixture, after 200 hours of mechanical alloying is shown in the Figures 1-2. The X-ray diffraction pattern of titanium-silicon-carbon alloys powders showed the dependence of changes in the phase composition versus the titanium concentration. There are only the diffraction lines of TiC, Ti_3SiC_2 and Fe which can be seen in the pattern (Fig.1). The presence of iron is the residue after the preparation process. The mechanical alloying process was made in a steel container with steel balls. The diffraction pattern of Ti_7Si_2C recorded for the powder after 200 hrs shows the peaks characteristic for TiC and Ti_5Si_3 only. When the milling time increases to 200 hrs, all peaks become wider and their intensity decreases. The widening of curves probably is connected with the size reduction in the powder grains, appearance of solid solution and presence of stresses resulting from the intensive plastic strains occurring during the MA process.

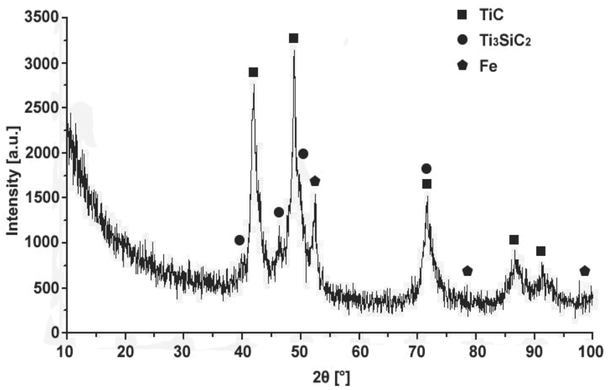

Fig. 1. The X-ray diffraction patterns of (A) Ti_3SiC_2 powder alloy after 200 hrs of mechanical alloying

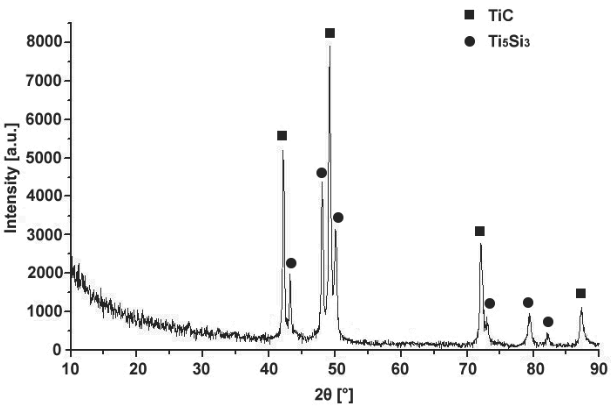

Fig. 2. The X-ray diffraction patterns of (B) Ti_7Si_2C powder alloy after 200 hrs of mechanical alloying

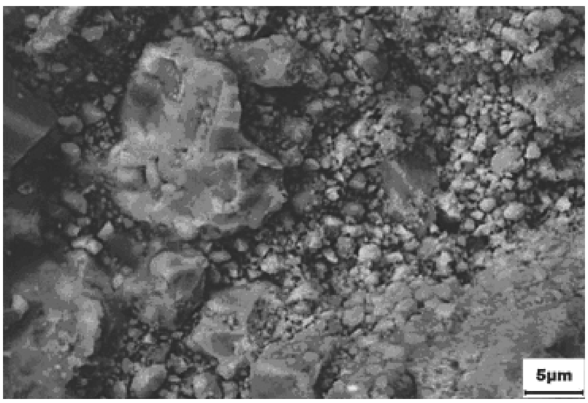

Fig. 3. Structure of powder's mixture of Ti_3SiC_2 alloy after 200hrs of mechanical alloying (SEM, 2400x)

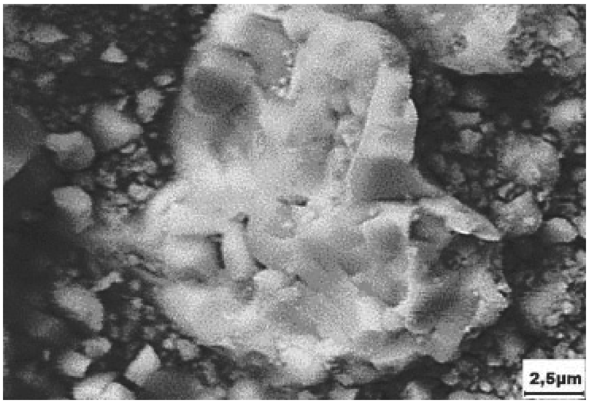

Fig. 4. Structure of powder's mixture of Ti_3SiC_2 alloy after 200hrs of mechanical alloying (SEM, 4800x)

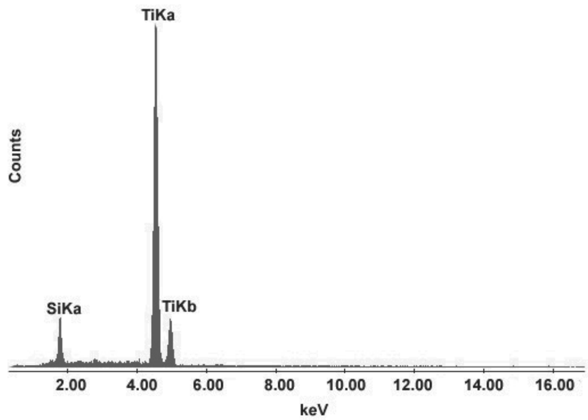

Fig. 5. Plot of the X-ray dispersive energy spectrometer measurement from the Ti_3SiC_2 alloy after 200hrs of mechanical alloying process (area in Fig. 3)

The Ti_3SiC_2 and Ti_7Si_2C alloys were researched in scanning microscope to analyze structure and chemical composition of the obtained material. The pictures show Ti_3SiC_2 and Ti_7Si_2C alloy particles after 200hrs of grinding.

The particle agglomerates are visible in the Fig. 3 and Fig. 4. The scanning microscopy research showed the presence of non-homogeneity particles in researched materials. The experiments showed great variety of particle sizes. The shape of the particles is irregular.

The Ti_3SiC_2 alloy was also checked with EDS attachment to identify chemical composition of chosen areas. Chemical analysis of this area shows the presence of titanium and silicon. The curve of the X-ray dispersive of Ti_3SiC_2 alloy after 200h of MA is presented in Fig. 5.

Ti_7Si_2C alloy obtained in the process of MA after 200hrs shows the structure and chemical composition similar to Ti_3SiC_2 alloy. The sample consists of both big particles of the powder and great number of small ones.

The pictures (Fig. 6, Fig. 7) present the sequence of magnification of the areas with the Ti_7Si_2C alloy particles. The particle of the powder presented in the pictures, undergoing chemical analysis also shows the presence of titanium and silicon (Fig. 8). The pictures show irregular shape of Ti_7Si_2C powder particles consisting of smaller particles after 200hrs. Agglomerates of Ti_7Si_2C powder particles after mechanical alloying are presented in Fig. 7.

JEM 2000 FX microscopy was used to observe single Ti_3SiC_2 alloy particles. The obtained results point at great non-homogeneity of the chemical composition of the researched particles. The research showed the presence of joint crystallites which enables us to determine the size of single crystallite (Fig. 9). Chemical analysis of these particles proves content of titanium, silicon and little admixture of iron and copper (Fig. 10). The variety of particles shapes are presented in the Figure 11, and the next picture (Fig. 12) shows the shape of the single particle.

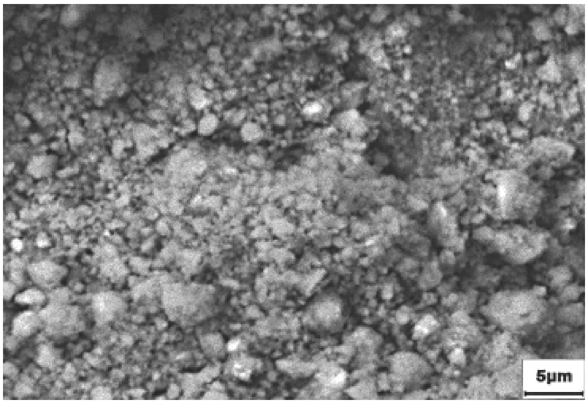

Fig. 6. Structure of powder's mixture of Ti_7Si_2C alloy after 200hrs of mechanical alloying (SEM, 2400x)

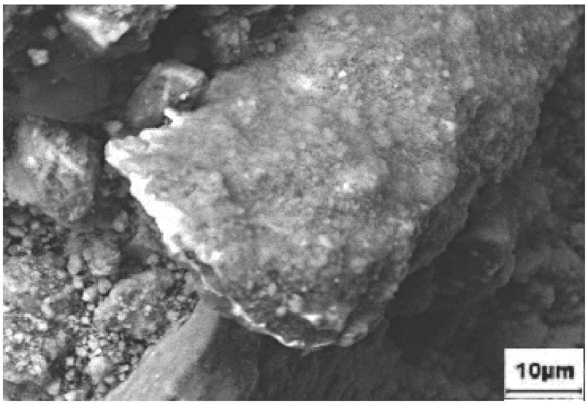

Fig. 7. Structure of powder's mixture of Ti_7Si_2C alloy after 200hrs of mechanical alloying (SEM, 1200x)

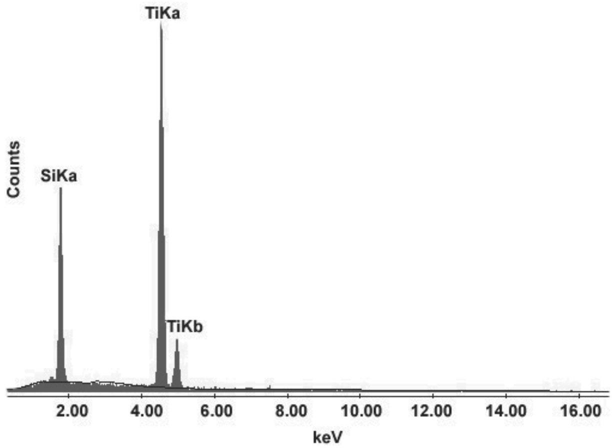

Fig. 8. Plot of the X-ray dispersive energy spectrometer measurement from the Ti_7Si_2C alloy after 200hrs of mechanical alloying process (area in Fig. 6)

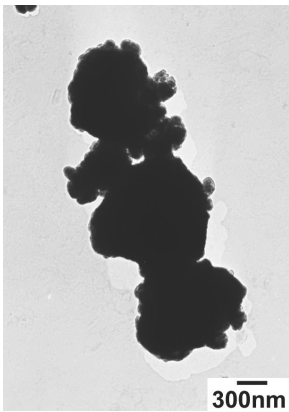

Fig. 9. TEM image of Ti_3SiC_2 alloy after 200hrs of mechanical alloying

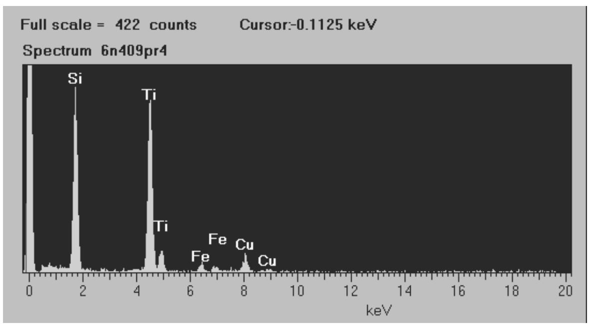

Fig. 10. Plot of the X-ray dispersive energy spectrometer measurement from the Ti_3SiC_2 alloy after 200hrs of mechanical alloying process (area in Fig. 9)

Research of TEM of Ti_3SiC_2 powder alloy shows the presence the titanium and silicon. The presence of copper in samples is the result of application of copper nets during research preparation (Fig. 15).

The research of TEM showed the presence of salt particles visible as transparent elements in the picture (Fig.11). The presence of salt is the residue after the preparation process and proves that it is not possible to get rid of impurities during the preparation of this material. The particles in the picture have similar chemical composition to composition of previous particles. The Ti_7Si_2C powder alloy research of higher content of titanium shows great similarities in shape and size to Ti_3SiC_2 alloy powder particles. The particles of researched sample are characterized with different size, which proves that the process of mechanical alloying should be prolonged. The analysis of particles presented in the picture showed non-homogeneity of chemical composition (Fig. 13-14, Fig. 16).

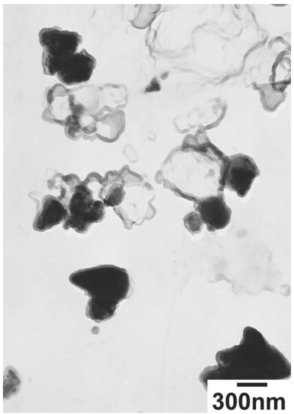

Fig. 11. TEM image of Ti_3SiC_2 alloy after 200hrs of mechanical alloying

Fig. 12. TEM image of Ti_3SiC_2 alloy after 200hrs of mechanical alloying

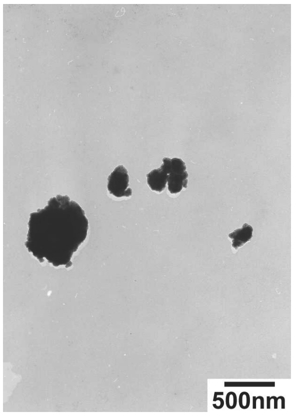

Fig. 13. TEM image of Ti_7Si_2C alloy after 200hrs of mechanical alloying

Fig. 14. TEM image of Ti_7SiC_2 alloy after 200hrs of mechanical alloying

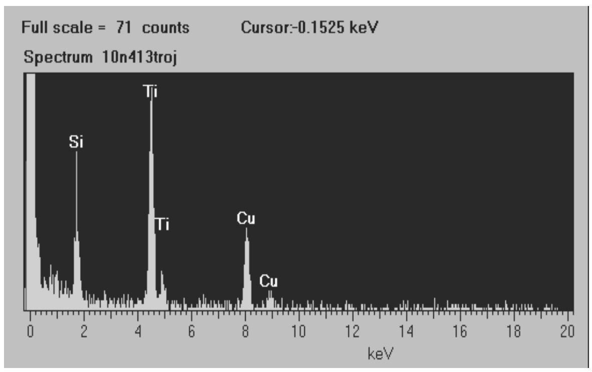

Fig. 15. Plot of the X-ray dispersive energy spectrometer measurement from the Ti_3SiC_2 alloy after 200hrs of mechanical alloying process (area in Fig. 12)

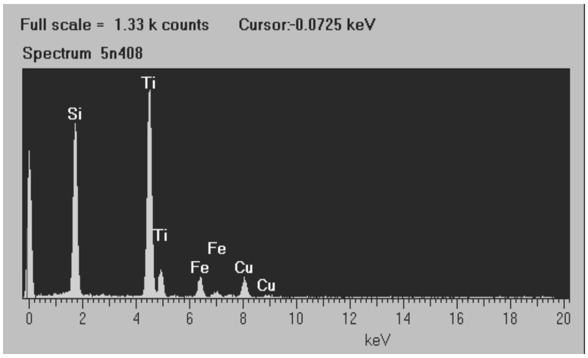

Fig. 16. Plot of the X-ray dispersive energy spectrometer measurement from the Ti_7Si_2C alloy after 200hrs of mechanical alloying process (area in Fig. 14)

The important determining factor about properties of Ti-based materials is the particle size. The investigation of particle size and their distributions were executed (Fig.17). The following parameters were determined: arithmetic mean diameter, geometric mean diameter, mode, median. Laser analysis of particle size distribution showed, that the biggest number of particles comprises in 9.68µm to 11.16µm range and amounts to 4.72%. Median is 4.79µm, mode – 10µm. Majority of particles includes in 0.15µm to 40.37µm range. From the test carried out on the laser analyzer it results that the particle size decreases together with the increased time of grinding. (Table 1 and Fig. 17).

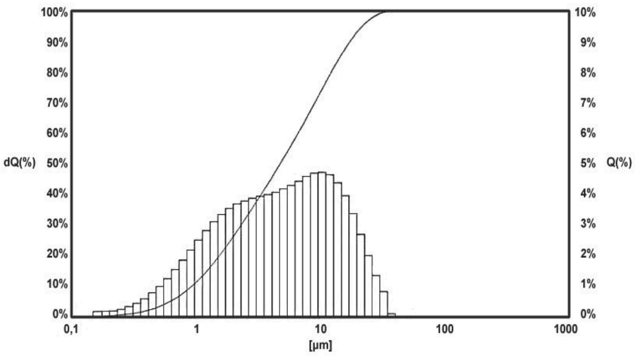

Fig. 17. Particle size distribution of studied Ti_3SiC_2 powder alloy after 200hrs of mechanical alloying

The cross-sectional microstructure evolution and particle size of Ti-Si-C powder alloy were investigated using optical microscopy. Typical images of the cross section of Ti_3SiC_2 and Ti_7Si_2C powder after 200hrs of mechanical alloying are shown in Fig. 18-19. The structure is characterized by the large and small particles. It is the result of applied milling parameters of MA process. The investigation results have shown that it is difficult to obtain high-homogeneity and finely divided of the powder particles.

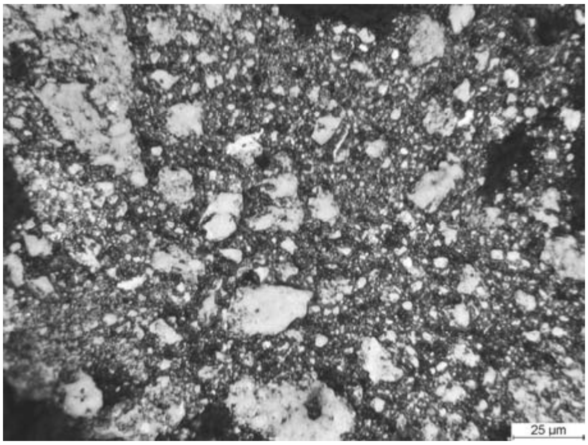

Fig. 18. Cross section of Ti_3SiC_2 alloy after 200hrs of mechanical alloying process (no etched, 400x)

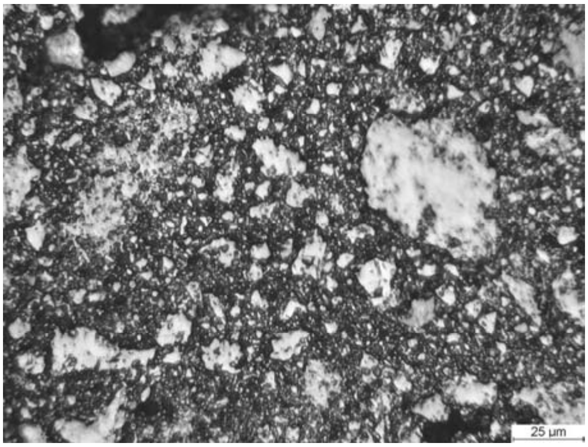

Fig. 19. Cross section of Ti_7Si_2C alloy after 200hrs of mechanical alloying process (no etched, 400x)

4. Conclusions

The way of synthesizing of Ti_3SiC_2 and Ti_7Si_2C powder alloys from elemental powders of Ti, Si, C by mechanical alloying method was studied for its productivity.

Results of research show, that the application of mechanical alloying technique to obtain Ti_3SiC_2 and Ti_7Si_2C alloys results in obtaining crystalline and amorphous structure. After 200 hrs of mechanical alloying process, the presence of TiC, Fe and Ti_3SiC_2 in smaller concentration of titanium alloy were found and in Ti_7Si_2C alloy, TiC and Ti_5Si_3 phases were found.

Microscopic observation showed reduce of particle size of the researched material. Non-regular shape of powder particles was observed. Particle agglomerates are visible in microscopic photos. On the basis of transmission electron microscopy research, non-homogeneous chemical composition particles were stated and few particles of less than 100 nm were observed.

We expect, that samples of the consolidated, tested materials will have higher mechanical properties than those of similar materials with microcrystalline size of grains.

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