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ScienceDirect
Journal of the European Ceramic Society 30 (2010) 2947–2953
www.elsevier.com/locate/jeurceramsoc

Sintering of powders in the $CrSi_2$–$Ti(Ta)Si_2$ systems depending on the methods for synthesis

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Available online 22 June 2010

Abstract

Composite materials based on refractory silicides, in particular their solid solutions, are widely used in many areas of engineering for parts of heating elements and heat resistance protective coatings. This paper presents the findings obtained in the study of peculiarities of solid-phase interaction during synthesis of $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ solid solutions depending on the synthesis conditions. The effect of the powder dispersity on compaction of targets from $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ powders has been studied, and it has been established that the use of nanosized powders complicates the process of pressing. Also, sintering of targets from nanosized $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ powders was studied. The sintered targets were established to have a small grain size and uniform porosity all over the volume. Thanks to small closed porosity, the targets exhibit high heat resistance under thermal shock.

Keywords: Sintering; Grain size; Thermal shock resistance; Silicide; Target

1. Introduction

The progress in any branch of current industry is greatly determined by the availability of materials able to operate under extreme conditions. Today it is difficult to find areas of science or engineering that do not use refractory compounds such as carbides, borides, and silicides, characterized by high melting temperature and high heat, wear, and corrosion resistances.[1–4] Composite materials on the basis of refractory compounds are widely used in many areas of engineering for parts of engines, jets, dies, armour shells, cutting tools, etc. They provide better conditions for preservation of nanostructure and thus for the achievement of high hardness, impact toughness, corrosion and abrasion resistance as compared to one-component systems. A marked increase in heat resistance is observed in complex silicide systems, especially in the case of forming solid solutions.[5–8] Refractoriness of silicides is determined by the possibility of surface film formation from complex silicates, which protect against penetration of oxygen.

The solid solution of chromium and titanium disilicides as a material for thin-film heating elements has made it possible to use the latter in unpackaged microdevices[9] up to 1350 °C in air. Such elements endure multichanges in temperature when used in antenna radiators in open space. The ion-plasma magnetron spraying of targets permits fabrication of 5 nm thick nanolayers whose composition completely corresponds to that of the targets.

Refractory materials are traditionally synthesized via solid-phase reactions between the elements at high temperatures. To reduce the temperatures of these reactions and to achieve a nanosized state of the product, intense milling can be used, owing to which formation of new phases is possible:

(i) via mechanosynthesis thanks to activation of one or several chemical reactions, formation of nuclei in the course of mechanical treatment or growth from an amorphous state, decomposition and phase transitions[10–12];
(ii) at reduced temperatures of the subsequent synthesis thanks to prior activation of the initial components (mechanical activation).[13]

A marked progress in synthesis of refractory compounds via mechanical activation has been achieved over the past decades. Mechanical activation of reactions of low temperature synthesis has a number of essential advantages over the traditional methods for thermal synthesis.[14,15]

In this work, mechanosynthesis and low temperature synthesis of prior mechanically activated initial mixtures were chosen

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doi:10.1016/j.jeurceramsoc.2010.05.026

for production of powders of chromium disilicide solid solutions.

2. Experimental

In elaboration of technology for production of nanodisperse powders of the $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ solid solutions via a solid-phase synthesis depending on the process conditions, the following initial components were used: microsized powders of silicon (99.998% Si, $S_{sp} = 1.7\ m^2/g$; Svitlovodsk Plant of Hard Alloys, Ukraine), electrolytic chromium PEPCr-1/280 (98.7% Cr; $S_{sp} = 1.3\ m^2/g$; Firm "Polema", Russia), tantalum VV-3 (99.96% Ta; $S_{sp} = 1.8\ m^2/g$; Ulba Metallurgical Plant, Republic of Kazakhstan), and titanium PTOM (98.3% Ti; $S_{sp} = 0.9\ m^2/g$; Firm "Polema", Russia) for both mechanosynthesis and low temperature synthesis of prior mechanically activated mixtures.

Investigation of the effect of prior mechanical activation of reaction mixtures on the kinetics of a solid-phase synthesis of solid solutions was carried out in comparison with the kinetic regularities for high-temperature solid-phase interaction of microsized initial powders in the Cr–Ta–Si and Cr–Ti–Si systems before established by the authors.[16,17]

Processes of mechanical activation of powdered mixtures and mechanosynthesis were performed in a high-energy planetary mill of the AIR type (roller activator- miller AIR-0.015 with three 500 cm^3 drums rotating with a speed of 1370 rev/min at a centripetal axis acceleration of 250 m/s^2; produced by the firm "Gidrotsvetmet", Russia) in an argon atmosphere at a drum rotation speed of 1450 rev/min with the acceleration 25 g under the conditions already established in previous works.[18,19] In order to avoid contamination of products with the reactor material, the steel drums and milling bodies were prior charged with silicon particles.

The solid-phase synthesis of microsized and mechanically activated briquetted mixtures was performed in a vacuum electric resistance furnace SNVE-1.3.1/16IZ (Moscow Plant of Electrothermal Equipment, Russia) in a vacuum of $\approx 1 \times 10^{-3}$ Pa in the temperature range 400–1300 °C.

Also, the effect of the size factor on the processes of pressing and sintering of compacted bodies (targets) was studied. Target pressing was performed from micro- and nanosized powders of the $Cr_{0.5}Ti_{0.5}Si_2$ and $Cr_{0.9}Ta_{0.1}Si_2$ solid solutions using a hydraulic press PD-476 (Orenburg Plant of Hydraulic Presses, Russia) under a load of 160 t. The pressed target preforms were sintered in the electric vacuum furnace at a vacuum of 1×10^{-3} Pa in the temperature range 900–1500 °C.

The products of solid-phase synthesis were examined using an XRD method with filtered Cu-radiation. The error in the lattice parameter calculations was 0.001 nm.

The particle size was measured using a laser counter on a Zetasizer apparatus (Zetasizer 1000HSA Malvern Instruments Ltd, United Kingdom) by the photon correlation spectroscopy in the Buromin water solution. The average particle size was determined on the basis of six measurements with 15 min intervals. The error did not exceed 8–10%.

Table 1
The mechanosynthesis products depending on the composition of initial components for a milling time of 90 min and a powder-to-balls mass ratio of 1:20.

Initial components	Phase composition of synthesis products
Cr, Si	$CrSi_2$
Ta, Si	$TaSi_2$
Cr, Si, Ta	Cr_3Si, Cr_5Si_3, $CrSi_2$, Ta_5Si_3, $TaSi_2$
$CrSi_2$, Ta, Si	$CrSi_2$, $TaSi_2$
$CrSi_2$, $TaSi_2$	$CrSi_2$, $TaSi_2$

The morphology features of the powders obtained were examined using SEM analysis on an X-ray microanalyzer Superprobe 733 (JEOL, Japan).

3. Results and discussion

3.1. Peculiarities of solid-phase interaction depending on the synthesis conditions

The peculiarities of solid solution formation in the complex silicide $CrSi_2$–Ti(Ta)Si_2 systems were studied depending on the state of initial components and conditions of solid-phase synthesis performed under the action of temperature factor and high-energy mechanical milling. As revealed, the regularities of solid solution formation in these systems are similar, therefore in the present paper data are presented for one of them, namely for the solid solution $Cr_{0.9}Ta_{0.1}Si_2$.

Formation of solid solutions as a result of high-energy milling was studied for various initial mixtures such as Cr + Ta + Si; $CrSi_2$ + Ta + Si, and $CrSi_2$ + $TaSi_2$.

The XRD data show that mechanosynthesis of these mixtures does not result in the formation of solid solutions, and the solid-phase interaction products are dispersed composite powders containing a mixture of higher and lower silicide phases in the case of mechanosynthesis of simple elements and a mixture of disilicides in the case of using prior synthesized nanosized powders (Table 1).

The investigation of high-temperature solid-phase interaction in vacuum of microsized powders of initial components in comparison with mechanically activated reaction mixtures made it possible to reveal the kinetics features of solid solution formation in this system.

The change in the phase composition depending on the synthesis temperature, which was evaluated from the integral intensities of the diffraction lines corresponding to the initial components, intermediate individual silicide phases and final products, is demonstrated in Fig. 1.

The established regularities of interaction reveal the influence of the state of initial components on the kinetics of solid-phase interaction. Mechanically activated mixtures are characterized by higher rate of interaction accompanied with lower temperatures of both the start and completeness of the process. Solid solution is formed by a reaction diffusion mechanism through successive formation of individual silicides from lower to higher ones followed by their interaction (homogenization). At the latter stage diffusion processes prevail.

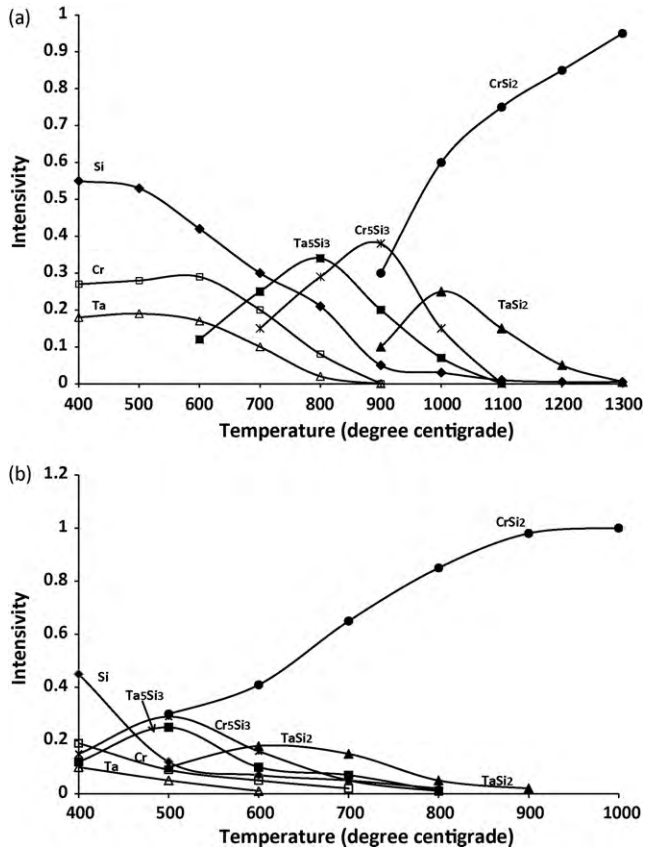

Fig. 1. Integral intensities of diffraction maxima for the initial, intermediate and final phases depending on the vacuum synthesis temperature: (a) micro- and (b) nanopowders.

The characteristics of the obtained solid solution powders against the method for their production (Table 2) indicate that the use of low temperature synthesis of prior activated initial components permits one to produce a nanosized powder of solid solution with high enough reproducibility of the element composition. Herein undesirable iron impurities (contamination from the milling bodies during mechanical processing) do not excess 1 mass%. Mechanosynthesis cannot yield solid solutions (instead it produces a nanosized composite powder which is a mixture of individual higher silicides) and does not provide preservation of the element composition. Furthermore, contamination with iron reaches 3 mass%. In contrast, the high temperature synthesis guarantees preservation of the element composition of material as well as its purity despite the additional milling. The increased content of oxygen in nanodisperse powders of solid solution obtained via solid-phase synthesis of mechanically activated mixtures at 1000 °C in vacuum may be related to absorption of oxygen during their discharge out of the furnace to air owing to the high absorptivity of nanodisperse powders. The absence of Novotny's phases (hexagonal Me_5Si_3 phase stabilized with oxygen impurities) in the intermediate products of solid-phase interaction in vacuum also confirms this suggestion.

The estimation (by PCS method) of the particle size of solid solutions produced via low temperature synthesis of prior mechanically activated initial mixtures shows their nanoscale (Table 2).

Fig. 2 demonstrates the electron micrographs taken from products of mechanosynthesis and solid-phase syntheses in vacuum, both high temperature (upon milling) and low temperature (without milling) ones, which confirm that powders obtained by mechanosynthesis and low temperature synthesis are finely-disperse.

The performed experiments permitted establishment of the following peculiarities of solid solution formation depending on

Table 2
Specification of powders obtained by different methods.

Solid solution	Method of production	XRD data		Data of chemical analysis						Average particle size
		Phase composition	Lattice parameter, nm	Cr	Ta	Ti	Si	O	Fe	
$Cr_{0.9}Ta_{0.1}Si_2$	High temperature synthesis from microsized powders	$CrSi_2$	$a = 0.446$ $c = 0.639$	37.63	14.53	–	46.47	0.32	0.21	<50 μm
	Low temperature synthesis of activated powders	$CrSi_2$	$a = 0.446$ $c = 0.637$	36.95	14.47	–	46.22	1.48	0.67	230 nm
	Mechanosynthesis	$CrSi_2$ $TaSi_2$	–	35.81	13.95	–	44.85	2.31	2.91	150 nm
$Cr_{0.5}Ti_{0.5}Si_2$	High temperature synthesis from microsized powders	$CrSi_2$	$a = 0.458$ $c = 0.642$	24.29	–	22.17	52.94	0.27	0.16	<50 μm
	Low temperature synthesis of activated powders	$CrSi_2$	$a = 0.459$ $c = 0.641$	23.64	–	21.98	52.19	1.53	0.62	190 nm
	Mechanosynthesis	$CrSi_2$ $TiSi_2$	–	22.94	–	20.18	50.75	2.67	3.15	170 nm

For comparison: the lattice parameters of stoichiometric $CrSi_2$: $a = 0.443$, $c = 0.636$.

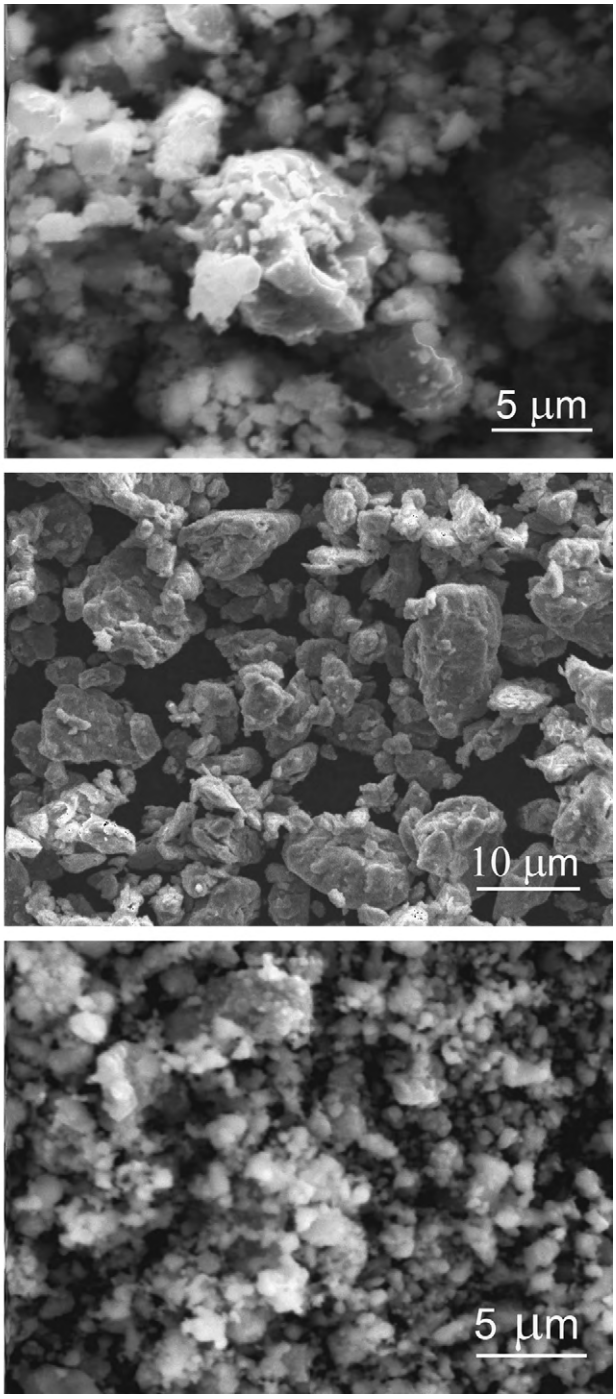

Fig. 2. Morphology of the products of (a) mechanosynthesis, (b) solid-phase interaction of microsized powders at 1300 °C, and (c) mechanically activated powders at 1000 °C.

the state of initial components and conditions of solid-phase synthesis, which, in turn, depend on the conditions of high-energy milling and temperature:

(i) solid solution formation in the course of solid-phase synthesis under heating occurs owing to reaction diffusion through intermediate stages of formation of individual silicide phases from lower to higher ones with subsequent their interaction;

(ii) preliminary mechanical activation markedly affects the solid-phase interaction: it decreases the temperature of both the start and the completeness of the interaction by 300–400 °C, which provides the possibility to produce non-milled nanosized powders of solid solutions, with the mechanism of solid solution formation being the same as in the case of microsized powders, that is, formation of individual silicide phases from lower to higher ones followed by dissolution of tantalum disilicide in the lattice of chromium disilicide (Fig. 1);

(iii) in a solid-phase synthesis which is due to intense milling and also proceeds via the mechanism of reaction diffusion at contacts between the initial components, a chemical reaction dominates with formation of disilicides as the most thermodynamically preferable compounds. Herein it is impossible produce solid solutions since homogenization needed for their formation is generally provided by diffusion processes and so requires higher temperature and longer process duration (Table 1).

3.2. Investigation of fabrication of targets from nanosized powders of the obtained solid solutions for magnetron sputtering

The previously developed process for fabrication of targets[20] includes synthesis of a material with desired composition, its pressing and sintering in vacuum. Since refractory compounds are characterized by great fraction of covalent chemical bonds, their sintering proceeds with the participation of diffusion processes and macro-movements. They are therefore sintered in the range of high temperatures, very close to the melting temperatures, namely $(0.92–0.98) \times T_m$. The use of such compounds in the nanodispersed state will allow one to increase the diffusion mobility of atoms and thus to activate sintering at reduced temperatures.

When fabricating targets from nanosized powders, in particular from solid solutions on the basis of chromium disilicide, a number of problems spring up which are related to the nanosized state of the material used, which have to be solved in order to obtain dense homogeneous articles free of layers and cracks throughout the target bulk.

Since powders of disilicide-based solid solutions, like other powders of refractory compounds, are brittle and hard materials with high elastic modulus, they exhibit no plastic deformation of particles under pressing. This determines their low densification and formability of powders, especially in the case of their nanosized state. A plasticizer can provide densification of powder thanks to mutual sliding of particles. It must be chemically indifferent towards the powder and able to be completely removed under the following sintering. A number of organic compounds can be used as such plasticizers, including a 5% resin solution in benzene, which was added to the nanosized powders of solid solutions along with minimal addition of carbon to the articles fabricated.

The process parameters for target pressing from nanosized powders were compared to those for microsized powders of the analogous solid solutions. With keeping in mind a far larger

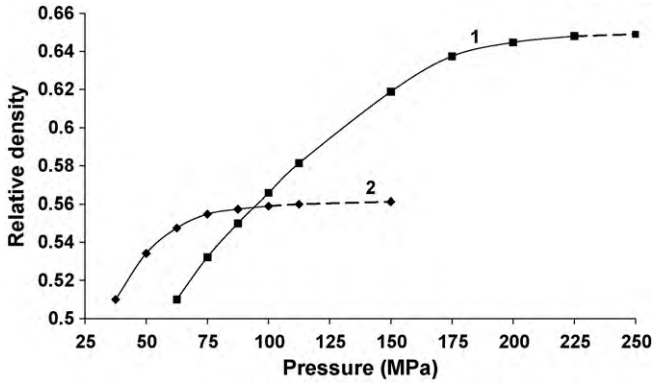

Fig. 3. The relative density of pressed 120 mm diameter targets from $Cr_{0.9}Ta_{0.1}Si_2$ powders against the applied pressure for (1) micro- and (2) nanosized powders.

specific surface area and a smaller particle size of nanosized powders, the required amount of plasticizer was experimentally determined to double that for compaction of microsized powders of the same composition. In spite of the fact that in pressing of refractory compound powders the general features of the pressure dependence of the relative density remain in each case the needed pressure was determined experimentally depending on the required shape and geometry of targets.

Because of the big aspect ratio (over 10), the targets required a two-sided pressing and a special fabrication process. In order to facilitate pressing and especially pressing-out, the die walls were prior lubricated with boron nitride.

The dependence of the relative density of compacted targets on the pressing pressure and dispersity of $Cr_{0.9}Ta_{0.1}Si_2$ powders is shown in Fig. 3.

The analysis of the experimental data on pressing of targets from the solid solution $Cr_{0.9}Ta_{0.1}Si_2$ has revealed that the state, morphology, structural and size factors as well as the load significantly influence the shaping. Taking into account the big volume and mass of compacts (about 300 g), loading during pressing was slow and step-by-step with a holding time under each load of 1–3 min. The load was removed slowly as well to prevent the post-action of the pressure and fracture of compacts. In order to raise the fluidity of the initial mixture for production of powder as dense as possible and uniformly distributed about the die, preliminary granulation of the powder was shown to be reasonable. An optimal granulometric composition was determined to be: 60% 100–160 μm and 40% below 100 μm.

Microsized powders were characterized by the dependence of the compact density on the applied pressure: the density monotonously increased with increasing the pressure. A maximum relative density (0.63–0.65%) was attained at a pressure of 180 MPa; its further increase over 200 MPa caused delamination of compact.

The compatibility of nanosized powders is much worse, which makes fabrication of high-quality dense compacts difficult. Such powders are compacted under far smaller pressures. High-quality compacts with a relative density of 0.55–0.58% without observable delamination can be made at 80–100 MPa. Delamination of nanosized powders at lower pressures compared to microsized powders is due to high internal friction, which is inversely proportional to the particle size. High residual stresses between particles and in the sample as a whole tend to relaxation inducing local deformations.

When studying sintering of the chromium disilicide-based solid solutions, a severe effect of the solid solution composition on the parameters of densification at the same fraction composition and pressing conditions was established. An increase in the content of the transition metal (Ti, Ta, or Mo), which replaces chromium atoms in the lattice, is accompanied with decreasing the portion of covalent bonds (compared to $CrSi_2$) and leads to increasing the diffusion mobility of atoms and thus to decreasing the temperature of intense shrinkage. The use of nanosized powders makes it possible to markedly reduce the sintering temperature thanks to the high activity of their surface due to the size factor. The features of diffusion mass transport under sintering are related to the great volume of the material located along grain boundaries and in ternary joints, that is, in areas with a defective crystalline lattice. According to the experimental data, the effective self-diffusion coefficients in nanosized materials at reduced temperatures are several orders of magnitude higher than those obtained by extrapolation of the data for high temperatures.[21]

Study of sintering of targets from solid solution powders in vacuum was carried out on samples pressed under optimal conditions with an initial porosity of 35–37% for microsized and 42–47% for nanosized powders. Processes of target sintering were elaborated in an electric vacuum furnace in the temperature range 1000–1500 °C. Criteria for estimation of sintering ability were porosity and relative shrinkage.

The predominant factor which affects the rate of shrinkage is temperature. Preference to an isothermal or non-isothermal regime of sintering is based on the theoretic ideas about competition between the mechanisms of sintering and evolution of the microstructure of material. In the case of nanosized powders, the first two steps of sintering (formation of necks between particles and structure of cylindrical channel pores) proceed and finish under heating to the isothermal holding, which is advisable to be combined with the third step of sintering (formation of isolated pores) at the temperature, at which mechanisms of grain-boundary and volume diffusion, determining shrinkage, prevail. A proper choice of heating regime at the initial step and a homogeneous porous structure of pressed green body can depress grain growth. Using a fast heating is not always reasonable because of the tendency of nanosized powders to form agglomerates and the temperature gradient in the bulk under heating, which causes internal stresses and can result in the shape changing. Hence the effect of the heating rate on the sintering process is complicated enough, and sintering process conditions should be selected individually in each case.

In investigation of sintering of targets, particular attention was paid to the regime of temperature raising and lowering taking into account their dimensions and configuration (disk with an aspect ratio of 20:1) as well as a higher plasticizer content (in the case of nanosized powders), which suggests more intense gas evolution. It is especially important to raise temperature slowly in the range 350–600 °C (burning of plasticizer). In addition, process of recrystallization (expected to take place

Table 3
Sintering of pressed samples from the $Cr_{0.9}Ta_{0.1}Si_2$ solid solution (holding time 40 min).

Microsized powder			Nanosized powder after low-temperature synthesis		
Temperature of sintering, °C	Volume shrinkage, %	Porosity, %	Temperature of sintering, °C	Volume shrinkage, %	Porosity, %
1200	No shrinkage	43	950	No shrinkage	42
1250	1.7	35	1000	3.6	27
1300	3.9	27	1050	12.3	14
1350	5.8	21	1100	16.4	10
1400	8.1	19	1150	Deformation	11
1420	9.3	15	–	–	–
1450	Surface-melt	–	–	–	–

in the case of solid solution based on refractory compound in the interval (0.5–0.6) T_m) should be taken into account as well. As established experimentally, the heating rate in this temperature range should not exceed 10–20 deg/min. An isothermal holding should be conducted at 600 °C for 30 min, afterwards temperature should be raised faster (80–100 deg/min) up to the achievement of the temperature of active shrinkage. In order to smooth the temperature gradient about the target, an isothermal 30–40 min holding at the final sintering temperature is required. This sintering regime preserves high moving forces of sintering process, initially contained in a green body and not spent on the growth of pores and grains under the isothermal holding at 600 °C. An increase in the heating rate can cause the loss of the target shape. The following regime for target cooling was established experimentally: temperature reduction down to 600 °C (to temperatures lower than the temperature of possible recrystallization) as fast as possible and subsequent controlled slow cooling to room temperature with a rate of 5 deg/min. This made it possible to fabricate targets with no stresses.

The results of investigation of the effect of the temperature factor on the shrinkage of micro- and nanosized powders of solid solution on the basis of chromium disilicide are presented in Table 3.

A maximal shrinkage rate of silicide-based solid solutions was observed during the initial period (5–10 min) of isothermal holding. Elongation of this holding to 30–60 min did not change the porosity of sample, and only grain growth and change in the character of porosity were observed. At the initial sintering stages powder particles are separated from each other with pores and the contact surfaces are very small (porosity to 40%), but with increasing temperature and intense shrinkage the contact areas grow and pores become closed and rounded. The porosity of targets is 12–17% and 8–10% for micro- and nanosized powders, respectively. Under isothermal sintering, the particle size monotonously increases, which makes it possible to describe the sintering as a viscous flow caused by diffusion processes. However, the high shrinkage rate at the initial stage of isothermal holding cannot be prescribed to diffusion only and may also be due to deformation of particles and pulling them into pores as well as to their shrinkage sliding along grain boundaries under the action of the surface tension forces.

An analysis of the data in Table 3 reveals that for targets from microsized $Cr_{0.9}Ta_{0.1}Si_2$ powder, a maximum shrinkage (7.3%, porosity 12–17%) is reached at 1420 °C, and at 1450 °C samples are surface-melt, whereas for nanosized powders the temperature of maximal shrinkage is 16% and porosity reaches 10%.

The metallographic examination of sections of sintered targets from micro- and nanosized $Cr_{0.9}Ta_{0.1}Si_2$ powders (Fig. 4) demonstrates a change in the character of porosity depending on the particle size. In both cases, a closed porosity can be observed, but the porosity structure is different. The microstructure of targets sintered from nanosized powder is characterized by homogeneous pore (by size and shape) distribution about the target bulk, whereas in the case of microsized powders, the tar-

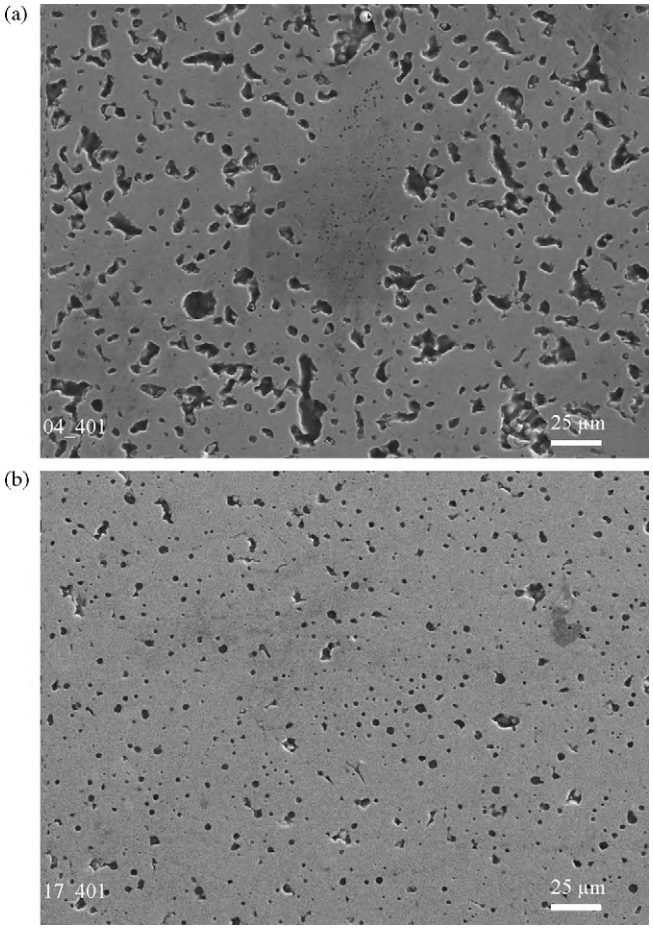

Fig. 4. Character of porosity and pore distribution in samples made from (a) micro- and (b) nanosized $Cr_{0.9}Ta_{0.1}Si_2$ powders.

get porosity is not uniform both by size and by shape. The pores are deep, elongated and of irregular shape.

The carried out investigation into the effect of the powder dispersity on the sintering of targets from $Cr_{0.9}Ta_{0.1}Si_2$ has established that the use of nanosized powder activates the sintering and reduces the temperature of maximal shrinkage by 300 °C. The samples have a closed porosity of about 10% with a uniform pore distribution all over the bulk. Thanks to a small closed porosity, targets exhibited high heat resistance during thermal shock tests.

4. Conclusions

The effect of the powder dispersity on shaping targets from $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ powders has been studied and it has been established that the use of nanosized powders complicates the process of pressing. Sintering of targets from nanosized $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ powders takes place at temperatures which are 250–300 °C lower than those for microsized powders.

The sintered targets from nanosized $Cr_{0.9}Ta_{0.1}Si_2$ and $Cr_{0.5}Ti_{0.5}Si_2$ powders have a smaller final porosity as compared to microsized powders. They have a small grain size and uniform porosity all over the bulk. The advantages of the nanosized powders studied guarantee manufacture of articles from them with high heat resistance.

Acknowledgement

The work was supported by the Science and Technology Centre in Ukraine (grant 3522).

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