Polskie Towarzystwo Materiałów Kompozytowych
Polish Society of Composite Materials

Kompozyty 11: 3 (2011) 225-229

KOMPOZYTY
COMPOSITES

Tomasz Durejko, Adrian Strąk, Stanisław Lipiński*

Military University of Technology, Department of Chemistry and New Technologies, Department of Advanced Materials and Technologies, ul. Kaliskiego 2, 00-908 Warsaw, Poland
** Corresponding author. E-mail: slipinski@wat.edu.pl*

Otrzymano (Received) 04.03.2011

STRUCTURAL STABILITY OF SINTERED FE40AL COMPOSITES DOPEEDWITH Al_2O_3 NANOCERAMICS

Temperature and time of heat treatment influence on the structural stability of Fe40Al intermetallic alloy with and without addition of alumina ceramics was investigated. Low energy milling in a ball mill was applied for material manufacturing. The batches were formed by cold-consolidation at 300 MPa pressure. Initial sintering was carried out at 1050˚C under 40 MPa of charge for 15 minutes in vacuum. The last step of Fe40Al sinters (with and without alumina nanoceramics addition, manufacturing was essential sintering). The process was carried out in tube oven with constant ambient gas flow (argon atmosphere) at 1200˚C for 1 hour. On classically prepared metallographic cross-section of samples with various additions of alumina nanoceramics, analysis of structure was carried out after initial and essential sintering. For all the technological options stereological investigations of grain size descriptions were done after full cycle of heat treatment. Material was cyclically heated at 800 and 1000˚C in air atmosphere for 150 h. Obtained results reveals that long heating of the Fe40Al intermetallic alloy based sinters leads to gradual grain growth of the matrix. Changes in grain size showed that doping with alumina nanoceramics in Fe40Al inhibits grain growth.

Keywords: powders metallurgy, structural stability, ODS sinters

STABILNOŚĆ STRUKTURALNA SPIEKANYCH KOMPOZYTÓW Fe40Al DOMIESZKOWANYCH NANOMETRYCZNĄ CERAMIKĄ Al_2O_3

W pracy przedstawiono wpływ temperatury i czasu wygrzewania na stabilność strukturalną spieków na osnowie fazy międzymetalicznej Fe40Al bez i z dodatkiem nanoceramiki Al_2O_3. Podczas wytwarzania materiału do badań, w celu wprowadzenia nanoceramiki do objętości cząstek proszku żelaza, stosowano niskoenergetyczne mielenie w młynku kulowym. Wypraski konsolidowano na zimno pod ciśnieniem 300 MPa, a następnie spiekano wstępnie w próżni, w temperaturze 1050˚C pod obciążeniem 40 MPa, w czasie 15min. Ostatnim etapem wytwarzania spieków Fe40Al bez oraz z dodatkiem nanoceramiki Al_2O_3 było spiekanie zasadnicze. Proces ten zrealizowano w piecu rurowym ze stałym przepływem gazu ochronnego (argonu) w temperaturze 1200˚C w czasie 1 godziny. Na klasycznie przygotowanych zgładach metalograficznych materiałów z różnym dodatkiem nanoceramiki przeprowadzono analizę struktury po spiekaniu wstępnym i zasadniczym. Dla wszystkich wytypowanych wariantów technologicznych, po pełnym cyklu obróbki cieplnej, przeprowadzono badania stereologiczne w celu określenia wielkości ziarna. Materiał badawczy poddano cyklicznemu wygrzewaniu w temperaturze 800 i 1000°C, w atmosferze powietrza w czasie do 150 h w piecu oporowym. Uzyskane wyniki badań wskazały, że długotrwałe wygrzewanie badanych spieków na osnowie fazy międzymetalicznej Fe40Al prowadzi do stopniowego rozrostu ziaren osnowy - procesu będącego konsekwencją dążenia materiału do obniżenia energii swobodnej. Na podstawie analizy zmian wielkości ziarna stwierdzono, że dodatek nanoceramiki Al_2O_3 w spiekach Fe40Al hamuje rozrost ziarna, wpływając korzystnie na stabilność strukturalną badanego materiału.

Słowa kluczowe: metalurgia proszków, stabilność strukturalna, spieki ODS

INTRODUCTION

Material selection is usually a compromise between its properties (tensile strength, plasticity, crack resistance, working temperature) and costs of production (raw material, manufacturing technique) [1]. Economical aspect is a major issue in the case of material selection for elements dedicated to work at elevated temperature, typically, heat-resistant materials have major impact on energy saving in the aircraft engine. It is a result of direct dependency of combustion chamber temperature from engines efficiency. Gas turbines blades are working at about 900^{o}C, what allows to obtain about 30% of heat thermal efficiency. Application of more advanced materials with special protective coatings preserving material from gas corrosion improves heat resistance of the blades, so higher temperature in the combustion chamber can be obtained (1200^{o}C) what assures increase of thermal efficiency of the engine up to 50% [2].

Temperature of work is crucial for the energetic blocks efficiency. Natural environment protection and simultaneous increasing need for energy makes energetic industry to apply new materials, increasing its resistance against oxidation and creep up to 600°C [3].

Constant increase of working temperature is linked to the existence of materials, which can face the requirements. It is possible only thanks to the new, high temperature alloys, which development is a impulse to do intensive research in this matter. The options connected with metallic materials are running out, so new materials, coatings technologies and intermetallic based composite may be here a chance.

Alloys from Fe-Al phase diagram applied as a matrix for modern structural materials are undoubtly a great change from material and also economical point of view.

A great chance for commercial development of the Fe-Al intermetallic phases is their application in the form of fine-grained sinters. Intermetallics in that form have much better mechanical properties in comparison to the same as-cast materials. Additionally, their structural stability and ease in formation of passive oxide coatings at the materials surface determine them to high temperature applications.

Advanced, dedicated to industrial application FeAl intermetallic alloys have alloying elements, including boron, chromium, zirconium, molybdenum and others. Addition of ceramics in a form of alumina particles is significant while the alloys will be working at elevated temperature. Investigations of mutual interactions between the intermetallic matrix and oxide particles would allow to assess their influence on the properties of the material, including heat-resistance and structural stability.

MATERIALS AND INVESIGATION METHODS

Sinters based on Fe40Al phase with and without alumina nano-ceramics, were obtained from technically pure powders of elemental components - iron (99.9%), aluminum (99.5%) were purchased from Alfa Easer GmbH & Co KG. Nanometric Al_2O_3 (99.5%) powder was purchased from Nanostructured & Amorphous Materials Inc. Powder had narrow distribution of particle size, for Fe 10÷54 μm, Al 38÷44 μm and n-Al_2O_3 27÷43 nm. On the basis of references and own results Fe40Al sinters were chosen for experiments without and with 0.5, 1, 1.5, 2 and 5% vol. addition of Al_2O_3 nano-ceramics (Tab. 1) [4, 5].

Iron and n-Al_2O_3 composite powders was obtained by low-energy milling of iron powder with nanometric alumina powder in FRITSCH planetary mill. Next aluminum powder (batch composition 60/40% at. iron to aluminum) was added to the pure iron powder and obtained composite Fe-n-Al_2O_3 powders (Tab. 1).

This step was conducted in glove box with ambient atmosphere. As obtained powder composites after homogenizing mixing in turbulent mill were consolidated at 300 MPa. Initial sintering was conducted at 1050°C and under load of 40 MPa for 15 minutes in vacuum. The last step of the Fe40Al sinters manufacturing was the essential sintering.

TABLE 1. **Chemical composition of choosen sinters based on Fe40Al phase**

TABELA 1. **Skład chemiczny wybranych do badań spieków na osnowie fazy międzymetalicznej Fe40Al**

Sinters based on FeAl phase						
Fe [vol. %.]	60					
Al [vol. %.]	40					
nAl [vol. %.]	-	0.5	1	1.5	2	5

The process was conducted in a tube furnance under constant ambient gas flow (argon) at 1200°C for one hour. Samples for structural investigations were cut from sinters by electric discharge machining (perpendicularly to the pressing direction), mounted in a conducting resin and mechanically grinded on the Struers automatic polisher using diamond particles in alcohol suspension. Quantitative metallographic investigations were done by using Philips XL30/LaB_6 scanning electron microscope equipped in backscattered electrons detector (BSE), which allows to observe differences in the chemical composition ("compo" image), or topography ("topo" image). The microscope is also equipped in secondary electrons detector (SE) assuring constant in time, high quality of taken images and energy dispersive spectrometry (EDS) dedicated to chemical composition analysis. Documentation of the stereographical investigations was done by using optical microscope Nikon eclipse MA200 equipped in CCD camera. Grain size of the matrix were estimated by Nikon NIS-AR image analyzing software. An average equivalent grains diameter (ECD), for every technological variants after essential sintering and heating in air atmosphere were estimated on the basis at least 300 objects.

Samples for structural stability analyses were taken from sinters after full cycle of the heat treatment. Obtained cylindrical samples had d = 4±0.1 mm of diameter and about 3.5÷4 mm height. Directly before investigations the samples were polished with 1200 and 2400 grinding papers. Next they were flushed with ethanol in a ultrasonic washer. Next prepared material was heated at 800 and 1000°C in air atmosphere for 150 h in SNOL furnance. Four samples for every technological variant were prepared. After 25, 50, 100 and 150 hours the samples were taken out from the furnance and cooled in the air.

RESULTS AND DISCUSSION

Conducted microscope observation were supported by chemical micro-analysis results. Results show structural homogeneity of sinters already at the initial sintering. After chemical etching it was found that the sinters, independently from the nanoceramics content reveals

grain structure and dispersions of alumina in the grain boundaries (Fig. 1).

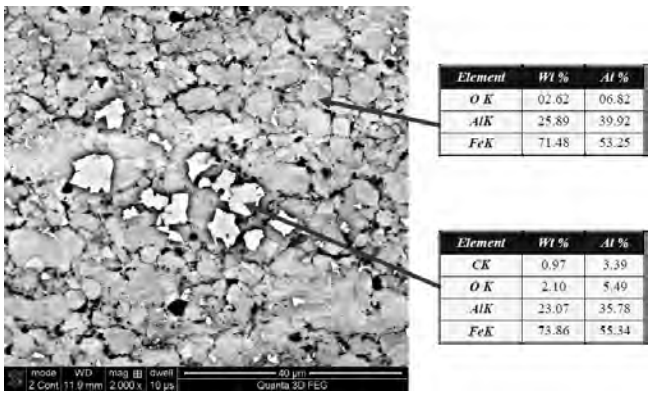

Fig. 1. Microstructure of the Fe40Al + 0.5% vol. Al_2O_3 alloy after initial sintering

Rys. 1. Mikrostruktura spieku na osnowie fazy międzymetalicznej Fe40Al + 0,5% obj. Al_2O_3 po spiekaniu wstępnym

High dispersion level of the alumina particles improves mass transport (does not make diffusion harder to occur) during sintering and may be in a final structure barrier for micro-cracks and their connection into the macro systems generated by load.

Increased content of carbon was found (point chemical analysis) in the brighter areas, among iron grains. On the basis of chemical analysis results it was estimated that there is a iron carbide, produced during initial sintering (samples before placing in the matrices were wrapped into the graphite tape). During sintering graphite, thanks to the provided heat, diffused towards sintered material, combining with iron resulting with appearance of iron carbide. X-ray diffraction patterns for give technological variant (Fe40Al with addition of 2% vol. Al_2O_3) confirmed EDS analysis results and presence of the iron carbide in the sinters structure (probably it is Fe_2C_5) [6].

Vacuum during initial sintering and ambient gas (argon) during essential sintering allowed to limit oxygen access to the material. Reduction of oxygen content during the sintering process allowed to minimize quantity of "in situ" obtained Al_2O_3. Present ones originates from the oxygenized surface of powder particles and n-Al_2O_3 doping. Smaller amount of the oxides in the materials structure promotes homogenous distribution of the oxide in the grain boundaries.

Sinters structure after homogenizing heating in comparison with phase composition after initial sintering did not change significantly (Figs. 1 and 2).

In the case of materials doped with Al_2O_3 nanoceramics, it was found that alumina particles are present not only in the grain boundaries, but also in the bulk of the grains (Fig. 3) what is indirectly caused by low energetic milling of the composite Fe+nAl_2O_3 powders during preparation of initial batch material.

Theoretical density of manufactured Fe40Al materials with and without nanoceramics was estimated on the basis on the molar fraction of particular components, by using weighted average. For estimation of the real density of the sinters, hydrostatic weighing method was applied. Comparison of the densities of the analyzed materials shows experimental density decrease with nanoceramics content increase.

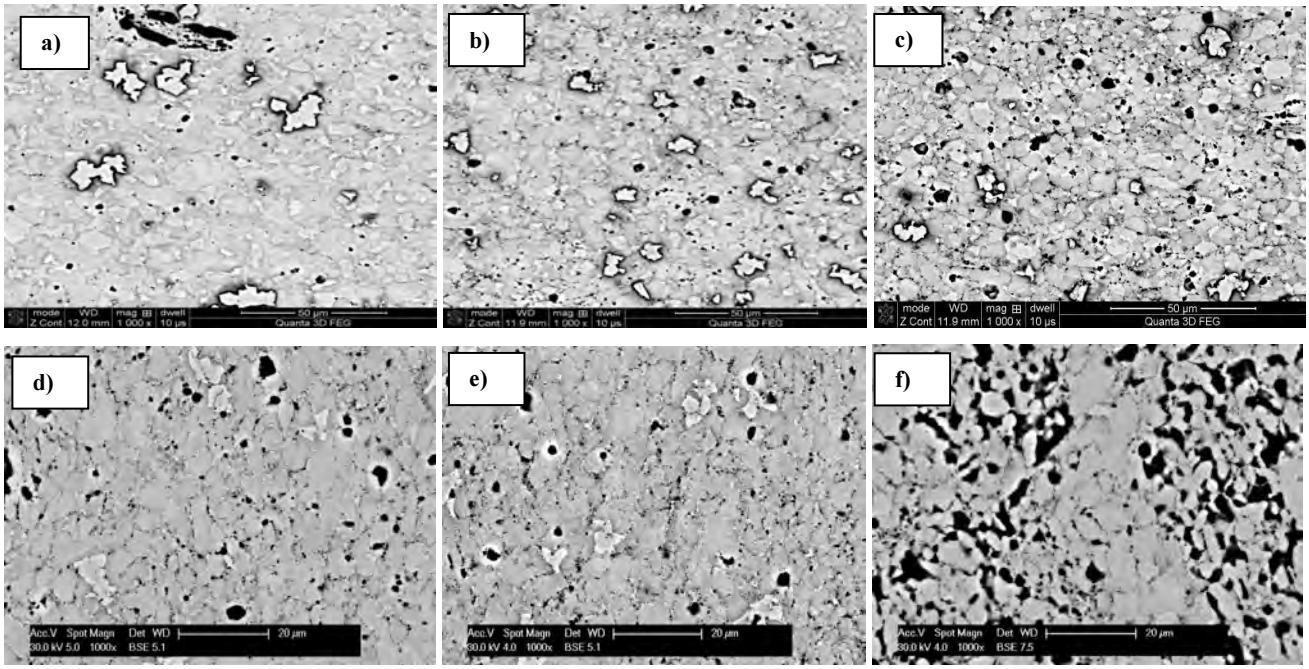

Fig. 2. Microstructure of the Fe40Al sinters after initial sintering: a) Fe40Al, b) Fe40Al + 0.5 vol. % Al_2O_3, c) Fe40Al + 1 vol. % Al_2O_3, d) Fe40Al + 1.5 vol. % Al_2O_3, e) Fe40Al + 2 vol. % Al_2O_3, f) Fe40Al + 5 vol. % Al_2O_3

Rys. 2. Mikrostruktura spieków na osnowie fazy Fe40Al po spiekaniu zasadniczym: a) Fe40Al, b) Fe40Al + 0,5% obj. Al_2O_3, c) Fe40Al + 1% obj. Al_2O_3, d) Fe40Al + 1,5% obj. Al_2O_3, e) Fe40Al + 2% obj. Al_2O_3, f) Fe40Al + 5% obj. Al_2O_3

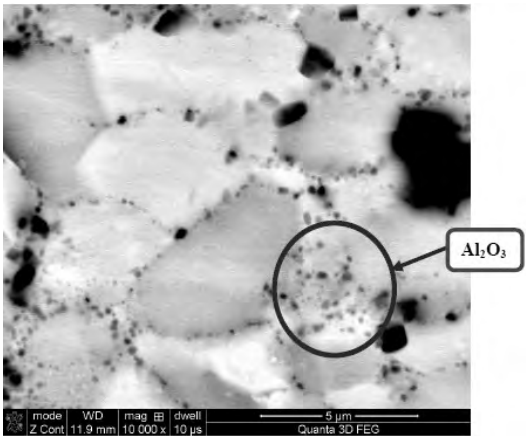

Fig. 3. Fe40Al based sinters microstructure with 2% vol. addition of n-Al_2O_3 with dispersion-like distributed alumina nanoceramics

Rys. 3. Mikrostruktura spieku na osnowie fazy międzymetalicznej Fe40Al z dodatkiem 2% obj. nAl_2O_3 z dyspersyjnie rozmieszczoną nanoceramiką Al_2O_3 [6]

The highest value of porosity was stated for material with 5% vol. of nanoceramics (Tab. 2). Moreover it was found high degree of structures heterogeneity (Fig. 2f), being results of conglomerates formation obtained already at the low energetic milling. Further investigations of this variant were abandoned because of such results.

TABLE 2. **Summary of density and porosity of Fe40Al sinters with and without addition of Al_2O_3 nanoceramics**

TABELA 2. **Zestawienie gęstości i porowatości spieków Fe40Al bez i z dodatkiem nanoceramiki Al_2O_3**

Fe40Al			
nAl_2O_3 [% vol.]	Gęstość teoretyczna [g/cm^3]	Gęstość zmierzona [g/cm^3]	Porowatość [%]
brak	6.06	5.81	4.2
0,5	6.01	5.74	4.5
1	5.97	5.67	5.1
1,5	5.95	5.60	5.8
2	5.93	5.56	6.2
5	5.90	5.34	9.4

Remaining sinters, after full cycle of heat treatment, stereological investigations were done to assess average grain size. Average equivalent diameter ECD_A calculations were based on the base of at least 300 objects. Obtained values for particular variants were set in table 3.

TABLE 3. Average **grain size for Fe40Al sinters without and with addition of Al_2O_3 nanoceramics**

TABELA 3. **Średnia wartość wielkości ziarna dla spieków Fe40Al bez i z dodatkiem nanoceramiki Al_2O_3**

	Fe40Al				
nAl_2O_3 [% vol.]	brak	0,5	1	1,5	2
ECDa [µm]	3.9±1.69	3.8±1.42	3.40±1.43	3.40±1.30	3.8±1.42

Statistical analysis of grain size revealed slight decrease of ECD_A for materials with addition of 1% vol. and 1.5% vol. of nAl_2O_3. It can be stated that appropriate amount of the nano-alumina addition inhibited grains expansion during the initial and essential sintering.

Obtained results shows that long heating of the investigated Fe40Al intermetallic alloys up to 150 hours at 800°C (Fig. 4) and 1000°C (Fig. 5) in the air leads to gradual matrix grains expansion.

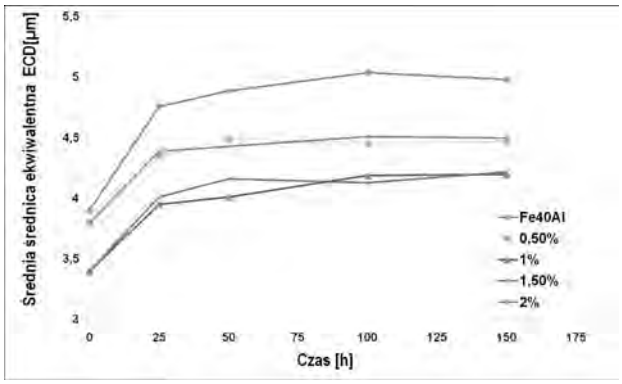

Fig. 4. Changes in grain size of the matrix of Fe40Al based sinters with addition of Al_2O_3 nanoceramics in various quantities 0.5, 1, 1.5 and 2% vol. after heating in air atmosphere for 150 hours at 800°C

Rys. 4. Zmiany wielkości ziarna osnowy badanych stopów na osnowie fazy międzymetalicznej Fe40Al bez oraz z dodatkiem nanoceramiki Al_2O_3 w ilości 0,5, 1, 1,5 i 2% obj. po wygrzewaniu w atmosferze powietrza, w czasie do 150 godzin, w temperaturze 800°C

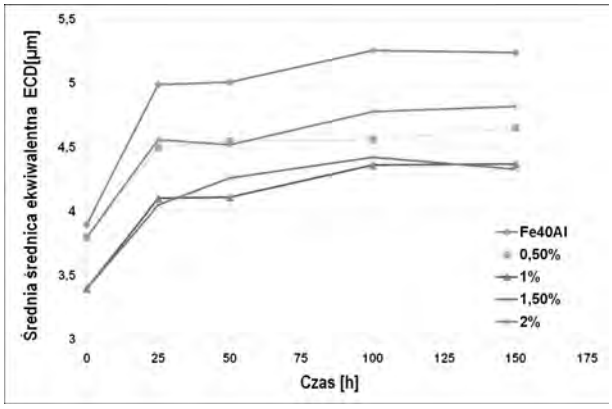

Fig. 5. Changes in grain size of the investigated Fe40Al intermetallic based alloys matrix without and with addition of Al_2O_3 nanoceramics in various quantities: 0.5, 1, 1.5 and 2% vol. after heating in air atmosphere for 150 hours at 1000°C

Rys. 5. Zmiany wielkości ziarna osnowy badanych stopów na osnowie fazy międzymetalicznej Fe40Al bez oraz z dodatkiem nanoceramiki Al_2O_3 w ilości 0,5, 1, 1,5 i 2% obj. po wygrzewaniu w atmosferze powietrza, w czasie do 150 godzin, w temperaturze 1000°C

After heating at 1000°C it was noticed that grain size expressed by ECD, independently from time of heating was higher than for the same alloys heated at 800°C. For all the investigated materials with respect to the initial grain size it was found that grains growth to the similar extent ranging from 15÷25% of the initial size.

Obtained results show that addition of Al_2O_3 nanoceramics to the Fe40Al sinters inhibits grains expansion (ECD_A independently from time and temperature of heating for Fe40Al without nanocermis has the greatest value). After 150 h of heating at 800 or 1000°C average grain size of the materials matrix was 5.0 and 5,3 μm respectively, what compared with the initial value of ECD (directly after full cycle of heat treatment) gives grains expansion at level of 22 and 25% respectively. The smallest value of matrix ECD was observed for Fe40Al + 1% vol. nAl_2O_3 sinter. For 800 and 1000°C it was 4.2 and 4.4 μm respectively. Slight dimensional changes of the structure are result of grain expansion inhibition by the dispersed particles of aluminum oxides, homogenously distributed in the grain boundaries and grains bulk.

Grain size analysis for other material variants it was noticed that for addition of 0.5 and 2% vol. of alumina nanoceramics, the ECD value was elevated. Doping with Al_2O_3 at 0.5% vol. level results with smaller number of boundaries limiting grains expansion. Although, while the sinter is doped with 2% vol. of Al_2O_3 has also increased ECD value, but this one origins from agglomerates formation during the low energetic milling of iron powder with Al_2O_3 nanoceramics.

A two-step character of structural changes was observed on the basis of the grain size changes as a function of heating time. In the first step, during first 25 hours, dynamic changes of grain size occur, during heating at 800 and 1000°C. In the second step, geometry changes rate is decreasing. At 800°C grain expansion stoped after 50 hours of heating for sinters with 0.5, 1.5 and 2% vol. of nAl_2O_3 and 100 hours for Fe40Al and Fe40Al + 1% vol. n-Al_2O_3 (Fig. 4). However, at 1000°C for all the materials variants the ECD value stabilizes after 100 h of heating. Heating lengthening up to 150 h reveals slight changes in matrix grain size.

RESULTS

Conducted research and analysis of obtained results allow to state that materials structure after initial and essential sintering gives materials with similar chemical and phase composition, so the technological process of Fe40Al sinters manufacturing may be limited to the one step sintering, with possible time lengthening.

Nanoceramics of Al_2O_3 addition to the Fe40Al intermetallic based materials causes structure fragmentation during the initial sintering. Cyclical heating at 800 and 1000°C causes the highest grain expansion in comparison to the Fe40Al as a reference material. Manufacturing of Fe40Al alloys with more than 2% vol. nAl_2O_3 addition is impossible with presented technology, because of conglomerates formation during the low energetic milling, what implies structural heterogeneities and high porosity of the sinters.

Structural stability investigations of the Fe40Al intermetallic alloy based sinter exhibits that doping with 1% vol. Al_2O_3 nanoceramics provides the best improvements in the high-temperature properties.

REFERENCES

[1] Meetham G.W., High temperature materials - a general review, Journal of Material Science 1991, 26, 853--860.

[2] Grabski M.W., Kozubowski J.A., (Material Science - genesis, the matter, perspectives) Inżynieria materiałowa - geneza istota perspektywy, Oficyna Wydawnicza Politechniki Warszawskiej 2003.

[3] Zielińska-Lipiec A., Czyrska-Filemonowicz A., Chromium steels for XXIst century energetic industries (Stale chromowe dla przemysłu energetycznego XXI wieku). Hutnik. 5.1999.

[4] Durejko T., Lipiński S., Abrasive wear of Fe-Al. graded materials (Analiza odporności na zużycie materiałów gradientowych typu Fe-Al.), Kompozyty 2010, 3, 195-199.

[5] Durejko T., Thesis Ph.D., Sintering parameters influence on the structure and properties of the FeAl based sinters (rozprawa doktorska „Analiza wpływu parametrów spiekania na strukturę i właściwości spieków na osnowie fazy FeAl"), Warszawa 2006.

[6] Strąk A., Structural stability of Fe40Al sinters with addition of oxide nanoceramics M.Sc. thesis (Stabilność strukturalna spieków na osnowie fazy Fe40Al z dodatkiem nanoceramiki tlenkowej), Praca magisterska, WAT 2010.

