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EFFECT OF SOLIDIFICATION CONDITIONS ON MICROSTRUCTURE OF Ni_3Al/C COMPOSITE

The influence of the solidification conditions on the microstructure of an Ni_3Al/C composite, i.e. an engineering material in which the role of a lubricating phase, usually performed by reinforcing phases, is played by carbon, has been studied. When proper conditions are observed, a nickel-aluminium alloy composed in 87 wt. % of nickel and in 13 wt. % of aluminium, containing moreover carbon in an amount of 2.5 wt. %, forms in the solidification process a natural Ni_3Al/C "in situ" composite. The composite matrix is nickel aluminide characterised by very interesting functional properties, particularly high strength at elevated temperatures. An inspiration to these studies was the surprisingly similar microstructure observed in different types of cast iron and in the fundamentally different, in regard to chemical composition, structure and microstructure, nickel - aluminium alloy. The aim of the present study was to evaluate the effect of the solidification conditions on the shape of the precipitates of graphite particles. The morphologies of the graphite phases were examined and their chemical composition was determined.

Keywords: solidification, intermetallic phase, aluminides, "in-situ" composite

WPŁYW WARUNKÓW KRYSTALIZACJI NA MIKROSTRUKTURĘ KOMPOZYTU Ni_3Al/C

W pracy przedstawiono wpływ warunków krystalizacji na mikrostrukturę kompozytu Ni_3Al/C. W materiale tym osnowę stanowi aluminid niklu Ni_3Al wykazujący atrakcyjne właściwości wytrzymałościowe w wysokich temperaturach, a fazą smarującą jest grafit. Do wytworzenia osnowy kompozytu wykorzystano nikiel i aluminium o udziale atomowym odpowiadającym stechiometrii fazy Ni_3Al. Wytopy prowadzono w piecu próżniowym w atmosferze argonu. Fazę smarującą otrzymano wprowadzając do ciekłego stopu 2.5% wagowych grafitu. W celu zapewnienia różnych warunków krystalizacji przygotowane stopy odlewano do różnych form, tj. molochitowej, kokili chłodzonej na powietrzu, kokili chłodzonej ciekłym azotem. Jeden ze stopów pozostawiono w tyglu w celu uzyskania bardzo wolnej krystalizacji. Proces krzepnięcia stopów rejestrowano, wykorzystując standardową analizę termiczną. Przeprowadzone badania metalograficzne wykazały obecność w mikrostrukturze wydzieleń grafitu płatkowego i sferoidalnego oraz ich kombinacji. W przypadku dużych prędkości krystalizacji 25 i 100 K/s obserwowano w mikrostrukturze przewagę grafitu kulkowego. Mała prędkość chłodzenia 1 i 5 K/s sprzyjała krystalizacji grafitu płatkowego. Zaobserwowano również występowanie typowej eutektyki grafitowej przy prędkości 15 K/s.

Słowa kluczowe: krystalizacja, faza międzymetaliczna, aluminidy, kompozyt „in-situ"

INTRODUCTION

Composites cover a very large and diverse group of structural materials. The term "composite" means material formed by fast bonding of at least two chemically different materials (lubricating or reinforcing phase and a matrix) in a way such that despite a well-preserved phase boundary, the individual constituents form a satisfactory and continuous system with a possibly uniform distribution of the reinforcing phase in the matrix [1].

The matrix in composite materials can be metals, ceramics or plastics. The role that the matrix is supposed to play is to evenly distribute the reinforcing phases in it and produce deformation under the effect of loads so that it will make a "path" for the stresses through which they can move to the reinforcing or lubricating phase constituents.

The matrix of MMCs are alloys commonly used in mass production and offering *per se* the required properties - mechanical, technological and operational. The metal matrix of composites can be iron and its alloys, nickel alloys, non-ferrous metals and their alloys, especially aluminium, magnesium, copper, silver, tin, lead, titanium, and finally intermetallic compounds (Ni_3Al, NiAl, Ti_3Al, TiAl, $MoSi_2$) and superalloys.

In this paper, a completely new engineering material will be presented which, in light of the above statements, can be called a natural composite. It is the nickel aluminide Ni_3Al/C, in which the role of a lubricating phase is performed by graphite, whose shape depends on the solidification conditions.

In situ composites based on nickel and cobalt are characterised by high coefficients of creep and heat resistance, and as such are used for heavily loaded machine components operating at high temperatures, to mention as an example gas turbine blades [3]. Some in situ composites are characterised by unique physical properties (magnetoelectric effect). Among metal matrix composite materials, composites whose matrix is based on aluminium alloys deserve special attention. The introduction of graphite to aluminium alloys produces slide composites, abrasion resistant and offering high strength. Some trials to produce such materials have already been made [4, 5]. Graphite was introduced into aluminium by the methods of powder metallurgy, by "squeeze casting", and by the "vortex" process. Unfortunately, the Al-C system was found to be thermodynamically unstable, and aluminium carbides of the Al_4C_3 type were formed with a highly adverse effect on the Al / C composite strength and durability.

For many decades, the Fe-C alloys have been known and widely used. In alloys from this family, when proper carbon content and inoculation methods are observed, graphite can assume numerous and varied forms, to mention as an example the following ones:
- flakes
- rosettes
- vermicular shapes
- nodules
- temper carbon

Literature data indicate that, apart from iron, the graphite eutectic appears only in pure nickel - carbon and pure cobalt - carbon alloys [6]. It has not been observed to occur in any other metals or their alloys. So far, a successful attempt has been made to induce in this material the crystallisation of a graphite eutectic and of other morphological forms of graphite precipitates. [6-8].

Aluminides are intermetallic phases formed in Ni-Al, Fe-Al, Ti-Al systems. Nickel aluminides (NiAl, Ni_3Al) are widely used in various branches of industry, including aviation, power engineering and automotive applications. They are characterised by a complex of quite unusual properties, namely:
- resistance to oxidation and carburisation at temperatures of up to 1100°C,
- good high temperature tensile, fatigue and creep resistance,
- very good abrasion resistance at temperatures within the range of 400÷650°C,

The most typical and interesting property of aluminium alloys with nickel additions is the yield stress increase with temperature increase. This feature was the first one to draw attention to this particular material. [8-10]. Potential applications for alloys with nickel aluminide include:
- parts of furnaces for heat treatment (better resistance to carburisation, high temperature and thermal fatigue resistance),
- water, gas and steam turbines (excellent resistance to cavitation, and excellent resistance to erosion and oxidation),
- fasteners in aircraft (relatively low density and ease of obtaining required strength),
- car turbochargers (high fatigue strength and low density),
- pistons and valves (abrasion resistance) - bellows compensators operating in corrosive environment (good resistance to water corrosion),
- instrumentation (high-temperature strength and wear resistance induced by pre-oxidation),
- permanent moulds (ability to develop protective thermal shell jacket by subjecting element to high-temperature oxidation).

The presence of carbon in the structure of this material, assuming the form of various graphite shapes, is expected to further broaden the range of beneficial properties, including additionally an improved tribological behaviour and increased damping capacity. In the Laboratory of Crystallization and Composites, comprehensive studies have been undertaken on the microstructure of Ni-Al-C alloys using standard microscopy as well as scanning electron microscopy.

In the intermetallic Ni_3Al phase, graphite precipitates are formed during solidification and take the form of a lamellar, fibrous or nodular eutectic. In terms of energy, the nodular precipitates of graphite are an optimum form of this constituent. This means that to produce them, a minimum amount of energy is needed. During crystallisation, the system creates excess energy. This energy leads to a transformation of the graphite nuclei precipitates present at grain boundaries into other forms, mostly flaky nes.

Modern research methods do not allow direct tracing of the graphite solidification and crystallisation mechanism, even in well-known cast iron, not to mention the much more advanced material which Ni_3Al undoubtedly is. The hypothesis proposed in this article seems to well correspond to the results of the tests described below. It says that the slower the cooling process, the more flake graphite and the less nodular graphite is formed. This can be explained by the fact that during slow eutectic transformation, more graphite nodules get energy from the system and are converted to flakes.

RESULTS OF INVESTIGATIONS

The Ni-Al-C alloy was vacuum cast by the OPW method (cost-saving melting process) in a Balzers vacuum induction furnace, using the EXOMELT effect.

The alloy was cast in two different ways. First, in a ceramic molochite mould whose configuration shown in Figure 1 ensures very slow heat transfer, and second in a metal mould placed in a container with liquid nitrogen.

The temperature characteristics were plotted for both of these cases. A cumulative graph showing the course of the Ni-Al-C alloy crystallisation into an Ni_3Al/C composite is shown in Figure 2.

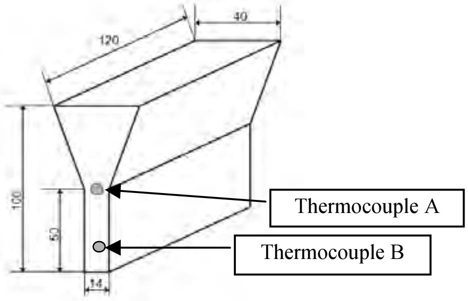

Fig. 1. Shape of ceramic mould and places marking location of thermocouples A and B

Rys. 1. Kształt formy ceramicznej i oznakowanie miejsc lokalizacji termopary A i B

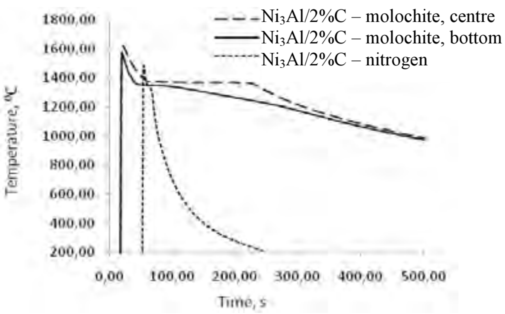

Fig. 2. Cumulative graph of thermal analysis for three cases of crystallisation under different solidification rates

Rys.2. Zbiorczy wykres analizy termicznej w trzech przypadkach krystalizacji

The dashed line marks the curve of the temperature characteristics for the solidification rate of about 1 K/s (thermocouple A in Figure 1); the solid line is an intermediate case of solidification rate at about 10÷15 K/s (thermocouple B in Figure 1), and finally the dotted line is the case of extra-rapid solidification at a rate of about 100 K/s. Figures 3 to 12 show the microstructures and morphologies of various forms of graphite in relation to the heat transfer rate.

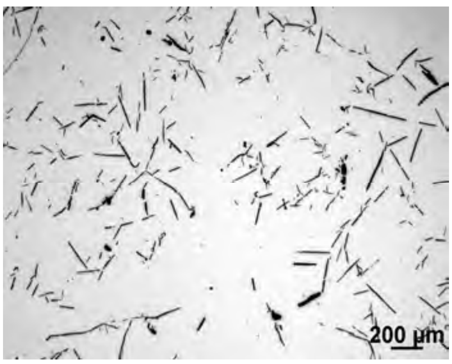

Fig. 3. Microscopic image of Ni_3Al/C composite sample surface with precipitates of lamellar graphite eutectic revealed by etching in "aqua regia". Sample cast in ceramic mould (area A), very slow cooling together with furnace at rate of about 1 K/s

Rys. 3. Obraz mikroskopowy powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską" wydzieleniami eutektyki grafitowej włóknistej (pow. 500x). Próbka odlewana do formy ceramicznej, chłodzenie bardzo powolne, wraz z piecem ok. 1 K/s

Fig. 4. Microscopic image of Ni_3Al/C composite sample surface with precipitates of nodular graphite eutectic revealed by etching in "aqua regia". Sample cast in metal mould, very rapid cooling in liquid nitrogen at rate of about 100 K/s

Rys. 4. Obraz mikroskopowy powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską" wydzieleniami eutektyki grafitowej włóknistej (pow. 500x).Próbka odlewana do formy metalowej, chłodzenie bardzo szybkie, w ciekłym azocie ok. 100 K/s

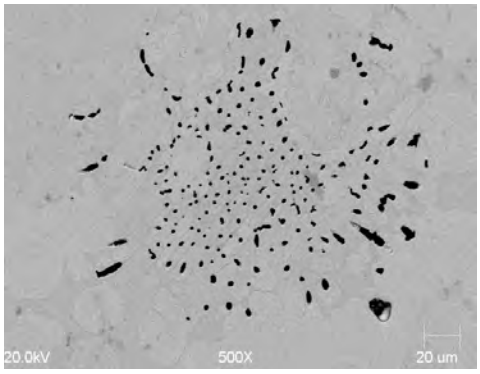

Fig. 5. Microscopic image of Ni_3Al/C composite sample surface with precipitates of fibrous graphite eutectic revealed by etching in "aqua regia" (magn. 500x). Sample cast in ceramic mould (area B), cooling at rate of about 15 K/s

Rys. 5. Obraz mikroskopowy powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską" wydzieleniami eutektyki grafitowej włóknistej (pow. 500x). Próbka odlewana do formy ceramicznej, chłodzenie ok. 15 K/s

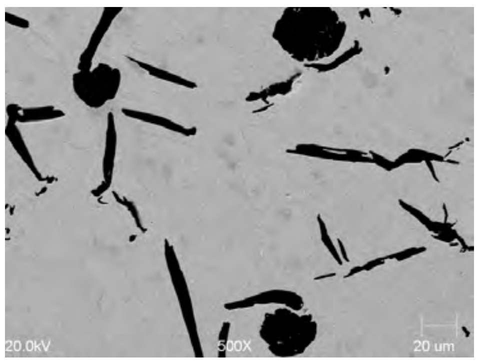

Fig. 6. Microscopic image of Ni_3Al/C composite sample surface with precipitates of fibrous graphite eutectic revealed by etching in "aqua regia" (magn. 500x). Sample cast in metal mould, rapid cooling at rate of about 25 K/s

Rys. 6. Obraz mikroskopowy powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską" wydzieleniami eutektyki grafitowej włóknistej (pow. 500x). Próbka odlewana do formy metalowej, szybkie chłodzenie ok. 25 K/s

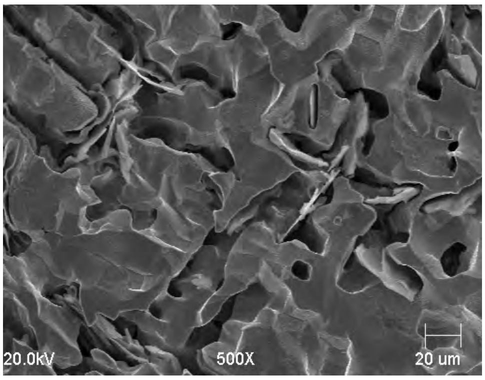

Fig. 7. SEM image of Ni_3Al/C composite sample surface with precipitates of flake graphite revealed by etching in ”aqua regia” (magn. 500x). Sample cast in ceramic mould, slow cooling at rate of about 5 K/s

Rys. 7. Obraz SE powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską” wydzieleniami płatków grafitu (pow. 500x). Próbka odlewana do formy ceramicznej, wolne chłodzenie ok. 5 K/s

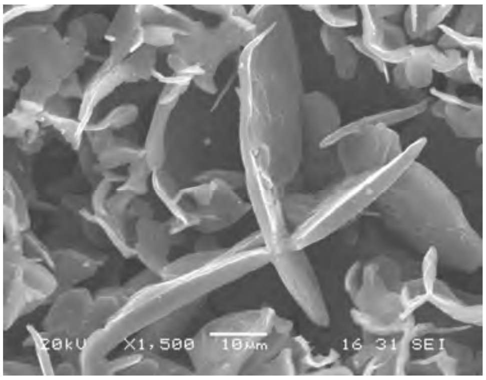

Fig. 8. SEM image of Ni_3Al/C composite sample surface with precipitates of flake graphite revealed by etching in ”aqua regia” (magn. 1500x). Sample cast in ceramic mould, slow cooling at rate of about 5 K/s

Rys. 8. Obraz SE powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską” wydzieleniami płatków grafitu (pow. 1500x). Próbka odlewana do formy ceramicznej, wolne chłodzenie ok. 5 K/s

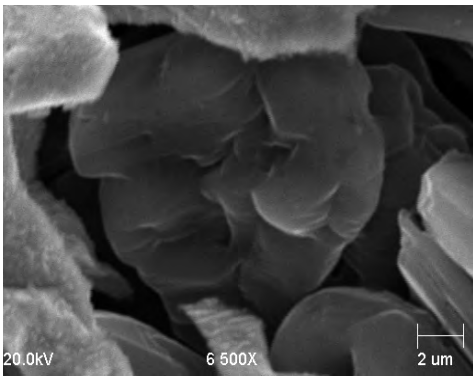

Fig. 9. SEM image of Ni_3Al/C composite sample surface with precipitates of nodular graphite revealed by etching in ”aqua regia” (magn. 6500x). Sample cast in metal mould, rapid cooling at rate of about 25 K/s

Rys. 9. Obraz SE powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską” wydzieleniami grafitu sferoidalnego (pow. 6500x). Próbka odlewana do formy metalowej, szybkie chłodzenie ok. 25 K/s

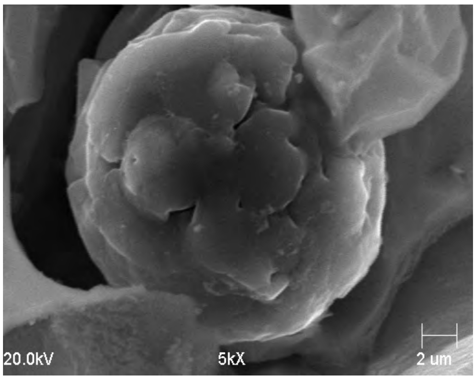

Fig. 10. SEM image of Ni_3Al/C composite sample surface with precipitates of nodular graphite revealed by etching in ”aqua regia”, (magn. 5000x). Sample cast in metal mould, rapid cooling at rate of about 25 K/s

Rys. 10. Obraz SE powierzchni próbki kompozytu Ni_3Al/C z uwidocznionymi przez trawienie „wodą królewską” wydzieleniami grafitu sferoidalnego (pow. 5000x). Próbka odlewana do formy metalowej, szybkie chłodzenie ok. 25 K/s

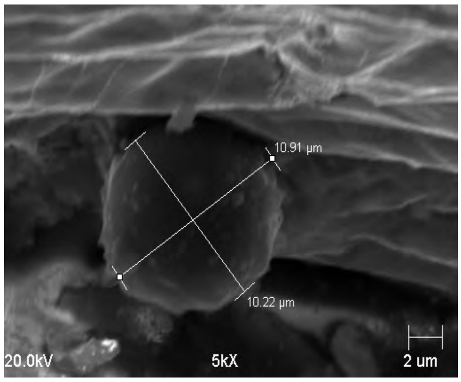

Fig. 11. SEM image of Ni_3Al/C composite sample surface with visible precipitates of nodular graphite (magn. 5000x). Sample cast in metal mould, very rapid cooling at rate of about 100 K/s

Rys. 11. Obraz SE powierzchni przełomu próbki kompozytu Ni_3Al/C z uwidocznionymi wydzieleniami grafitu sferoidalnego (pow. 5000x). Próbka odlewana do formy metalowej, bardzo szybkie chłodzenie ok. 100 K/s

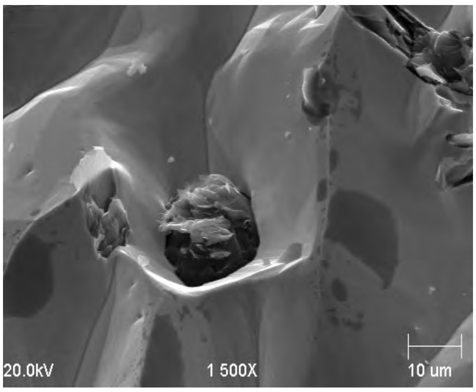

Fig. 12. SEM image of Ni_3Al/C composite sample surface with visible precipitates of nodular graphite (magn. 1500x). Sample cast in metal mould, very rapid cooling at rate of about 100 K/s

Rys. 12. Obraz SE powierzchni przełomu próbki kompozytu Ni_3Al/C z uwidocznionymi wydzieleniami grafitu sferoidalnego (pow. 1500x). Próbka odlewana do formy metalowej, bardzo szybkie chłodzenie ok. 100 K/s

CONCLUSIONS

- The solidification of an Ni_3Al/C composite occurs at a temperature typical of the graphite eutectic crystallisation in an Ni-C alloy at a temperature of 1375°C.
- The maximum solubility of carbon in an Ni-Al alloy at a temperature of 1600°C is 2.5 wt. % of carbon.
- An Ni-Al-C alloy crystallises as a natural Ni_3Al/C cast composite with lubricating and damping graphite phase whose morphology depends on the solidification rate.
- Under the conditions of slow solidification, i.e. at a rate of 1÷5 K/s, the precipitates of the lubricating phase present in the composite assume the form of a lamellar eutectic; in the range of 10÷15 K/s, various mixed forms occur from lamellae, through fibres up to irregular precipitates at the grain boundaries; rapid solidification from 25 to 100 K/s encourages the formation of nodular graphite.

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