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INFLUENCE OF HEAT TREATMENT ON THE STRUCTURE AND MECHANICAL PROPERTIES OF Ni_3Al – BASED ALLOYS

WPŁYW OBRÓBKI CIEPLNEJ NA STRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE STOPÓW NA OSNOWIE FAZY MIĘDZYMETALICZNEJ Ni_3Al

This study investigates two Ni_3Al – based intermetallic alloys containing differing amounts of zirconium, boron and chromium. Gradual homogenisation was accomplished through long-lasting annealing, up to 100 hours, at 1000°C or 1200°C in air or argon atmospheres. A higher level of homogeneity of the cast without chromium alloy was obtained in comparable heat treatment conditions. Annealing temperature has an essential influence on the homogenisation process of the investigated alloys. This influence is much more essential than annealing time and environmental conditions. These treatment conditions are critical for microstructure, as well as the properties of the investigated alloys.

For matched conditions of plastic working an optimum level of strain hardening was obtained . This did not cause a loss of cohesion in the investigated alloys, but it was sufficient to start a recrystallisation process. The fine-grained structure of the investigated alloys is responsible for the improvement in their mechanical properties.

Keywords: intermetallic alloys, homogenisation, mechanical properties, recrystallisation, fractography, thin strips

W pracy przedstawiono badania dwóch stopów na osnowie fazy międzymetalicznej Ni_3Al o różnej zawartości cyrkonu, boru i chromu. Długotrwałe wygrzewanie w czasie do 100 godzin w temperaturze 1000°C i 1200°C w atmosferze powietrza lub argonu prowadzi do stopniowego ujednorodnienia składu fazowego badanych materiałów.
W porównywalnych warunkach obróbki cieplnej uzyskano, dla materiału bez zawartości chromu zdecydowanie większy poziom jednorodności. Stwierdzono, że temperatura wygrzewania ma istotnie większy wpływ niż czas procesu na strukturę i właściwości badanych stopów.

Ściśle określone parametry obróbki plastycznej pozwoliły na uzyskanie, bez utraty spójności, poziomu umocnienia wystarczającego do zajścia procesu rekrystalizacji w całej objętości badanych materiałów. Tak uzyskana, drobnoziarnista struktura osnowy badanych stopów istotnie polepsza ich własności wytrzymałościowe.

1. Introduction

Dynamic development of technology and miniaturization of systems and devices (among others: MEMS – Micro Electro – Mechanical Systems, MECS – Microtechnology – based Energy and Chemical Systems) lead to impeding of operational conditions of structural elements, often in the range exceeds the capabilities of currently used steels, as well as high-temperature creep-resistant alloys [1]. Implementation of advanced technologies is frequently limited by a lack of suitable structural materials that could meet necessary operational conditions. Because of their properties, this problem can be solved by alloys based on ordered intermetallic phases, such as Ni_3Al alloys [2-4].

When compared to a competitive group of nickel-based super-alloys, intermetallic Ni_3Al phase alloys exhibit high strength at high deformation velocity and elevated temperature, high resistance to oxidation and carbonisation at elevated temperatures, and much better fatigue strength so that they crack more slowly than other intermetals. Common application of these alloys has introduced quite a few technological drawbacks, mainly related to insufficient plasticity and a tendency to brittle cracking [2-4].

So far, alloys based on intermetallic Ni_3Al phase have many applications in the automotive and aircraft

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industries and in metallurgical engineering. They are used mainly in elements for turbocompressors, valves, valve-seats and cylinder sleeves of combustion engines. These include AP Cummins Engine Company and PCC Airfoils. These alloys are also used in die blocks and press-forming dies and in fittings in furnaces for thermochemical treatment, such as at General Motors and Oak Ridge National Laboratory. After directed crystallisation, alloys can be used for the blades of reaction engines by General Electric and the Beijing Institute of Aeronautical Materials [2-4,10].

This paper is devoted to the analysis of intermetallic Ni_3Al phase alloys after heat treatment with the aim of improving plasticity. Two gravity cast alloys were selected for testing. Their differences in chemical composition determine their properties, especially plastic deformability.

2. Experimental procedure

Two alloys based on intermetallic Ni_3Al phase were investigated. The first alloy (**Ni_3Al (Zr, B)**) contains in the form Ni-22.13Al-0.26Zr-0.1B. The second alloy **Ni_3Al (Cr, Zr,B)** contains in the form Ni – 22,21Al – 7,39Cr – 0,41Zr – 0,19B (at.%).

Material was obtained by shell casting without directional solidification. While in as-cast condition, the samples were annealed in a temperature range of 1000 to 1200°C for 50 to 100 hours in air or argon. Analysis of the alloy microstructures was carried out using scanning electron microscopy as well as light microscopy, with elements of quantitative metallography. The samples were analysed by electrodischarge machining to measure mechanical properties including microhardness, and static tensile and impact tests were applied as well.

Microhardness tests were carried out using the Vickers method with a load of 0.98 N applied for 10 s. Measurements were performed 10 times for each kind of phase. Tensile tests were performed in air at room temperature and at a constant strain rate of $10^{-3}s^{-1}$ using an Instron 8501 machine.

Impact bending tests were performed according to the EN 10045-1 standard in order to determine the influence of microstructure on the materials' ability to absorb energy. Samples of 10 x 5 mm transverse sections with a V notch were used for tests. The tests were carried out at a temperature of 23°C using an Instron-Wolpert impact hammer at an energy of 300 J and a dropping speed of 5.5 m/s.

The tested material was cold worked and recrystallisation-annealed in order to analyse the improvement in plasticity of the investigated alloys, via refinement of the matrix structure.

3. Results of investigations

Intermetallic **Ni_3Al (Zr, B)** in as-cast condition exhibits a diphase dendritic structure (Fig. 1b) that contains [11-13]:

- coarse dendritic crystallites of average equivalent diameter on the order of 4 mm. The crystallites are of the ordered secondary solid solution, based on a Ni_3Al intermetallic phase (known as gamma prime phase (γ')) as an alloy matrix
- interdendritic zones filled with a mixture of γ' phase and disordered solid solution of aluminium in nickel lattice (known as gamma phase (γ)).

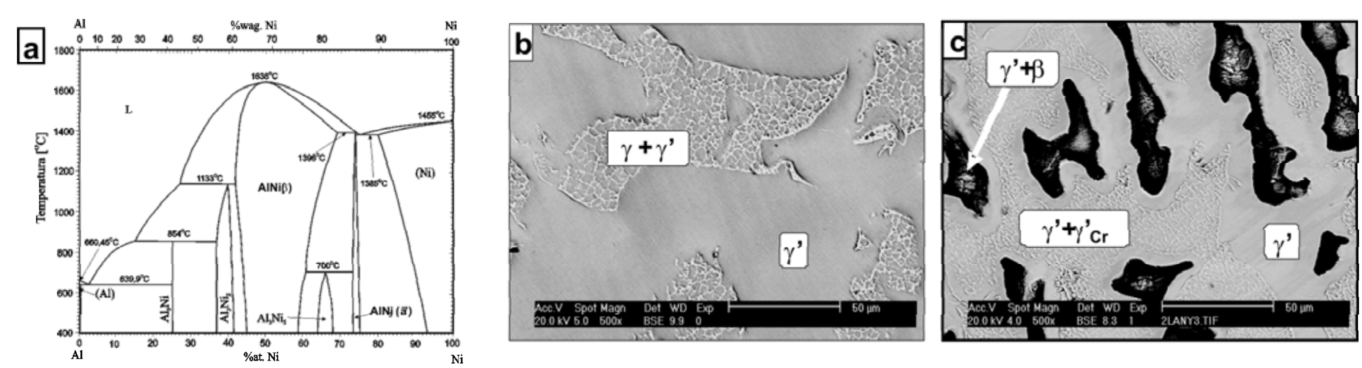

Fig. 1. Phase diagram (a) and SEM microstructures of as-cast condition of intermetallic alloys based on: b) Ni_3Al (Zr, B) and c) Ni_3Al (Cr, Zr, B)

Intermetallic **Ni_3Al (Cr, Zr, B)** in as-cast condition exhibits a complex, triphase dendritic structure that builds up the following structure (Fig. 1c) [11-13]:

- γ' phase type of stoichiometric Ni_3Al white zones as the basic component of the matrix,
- a mixture of $\gamma' + \beta$ (NiAl type) intermetallic phas-

es, with dark zones with lamellar morphology filling interdendritic zones,

- a mixture of γ'_{Cr} + γ' phases, where γ'_{Cr} phase is a γ' type but considerably enriched in chromium, or gray zones, as a second component of the matrix.

Homogenisation of the **Ni_3Al (Zr, B)** alloy at a temperature of 1000°C for up to 100 hours in an air atmosphere leads to partial phase homogenisation. This shows up as a gradual decrease of the superficial fraction of diphase zones ($\gamma + \gamma$'). After 100 hours of annealing, this fraction amounts to 20% (see Fig.2b).

When annealing at a temperature of 1200°C in both air and argon atmospheres, total homogenisation of the alloy structure to the γ' phase occurs after only 50 hours (see Figs. 1b and 2a). Thus, the annealing temperature plays a more important role than the annealing time for the phase composition homogenisation of the investigated alloy.

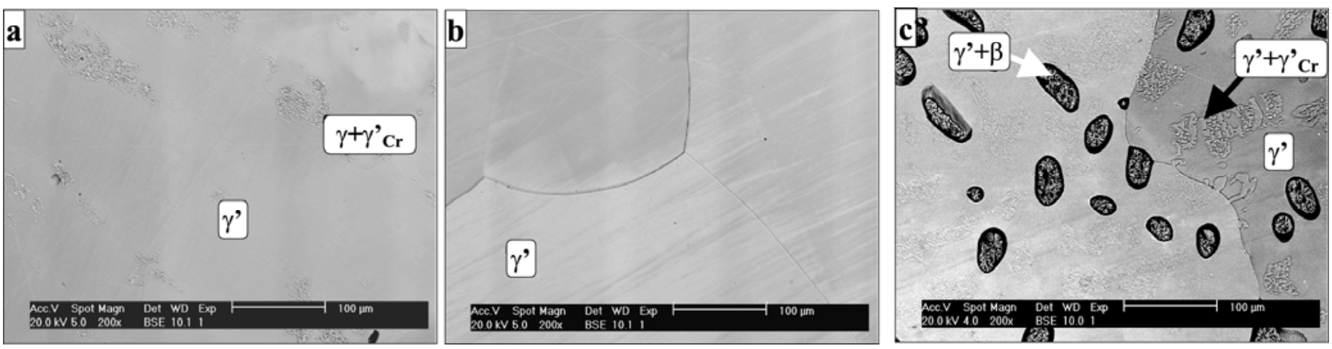

Fig. 2. SEM microstructures of investigated intermetallic alloys: a) Ni_3Al (Zr, B) after homogenisation at 1000°C/100h/air, b) Ni_3Al (Zr, B) after homogenisation at 1200°C/50h/argon and c) Ni_3Al (Cr, Zr, B) after homogenisation at 1200°C/100h/argon

Homogenisation annealing of the **Ni_3Al (Cr Zr, B) alloy**, when carried out for up to 100 hours at temperatures of 1000°C and 1200°C in air or argon atmospheres, gave rise to little change in the morphology and dimensions of the interdendritic zones occupied by diphase (γ' + β) areas (compare Figs. 1c and 2c). There was also a reduction in the level of strengthening of individual structural phases, with significant increase in microhardness of microregions filled by a mixture of (γ' + β) phases. This occurs from approximately 400 HV0,1 to 540 HV0,1 after annealing in an air atmosphere at a temperature of 1200°C. This phenomenon is caused by the environment. The authors of works [5-7] connected such behaviour with the effect of the oxygen atoms, which diffuse at high temperature along the grain boundaries.

Static tensile test (room temperature, air atmosphere)

In order to determine the influence of heat treatment on the mechanical properties of the investigated alloys, a static tensile test for limiting material conditions was performed as follows:

- **Ni_3Al (Zr, B) alloy** – casting and annealing for 100 hours at a temperature of 1200 °C, in argon atmosphere,
- **Ni_3Al (Cr Zr, B) alloy** – casting and annealing for 100 hours at a temperature of 900 °C in an argon atmosphere, and annealing for 100 hours at a temperature of 1000°C in an air atmosphere.

A **Ni_3Al (Zr, B) alloy**, in as-cast condition, is characterised by 7% relative elongation for 340 MPa tensile yield strength and an ultimate tensile strength limit of 540 MPa (Table 1). Homogenisation for 100 hours at a temperature of 1200°C in an argon atmosphere gives an improvement in alloy plasticity. The results indicate a 10% decrease in yield point, down to 300 MPa, and a greater than twofold increase in relative elongation. When compared to the as-cast condition, a 40% increase in the material tensile strength was observed in the processed alloy. Tension graphs for materials without a physical yield point were obtained.

Tensile fracture analysis of as-cast and homogenised **Ni_3Al (Zr, B)** alloy showed a complex character. Zones of intercrystalline, often interdendritic, and transcrystalline cracking, with many fragments occurring due to cleavage cracking, were seen in a significant part of the plastic strained regions. These regions were larger for materials that had been homogenised (see Fig. 3).

Flat dendrite branches of the Ni_3Al phase, observed as dispersive matrices of (γ + γ') eutectic release, were seen during static fracture of coarse-grained as-cast samples (Fig. 3a). Sample fractures after homogenisation do not reveal symptoms related to dendritic structure. This confirms the effectiveness of the annealing process carried out at 1200°C for 100 hours in argon. Favourable effects were also seen with respect to material cracking after annealing (Fig. 3b).

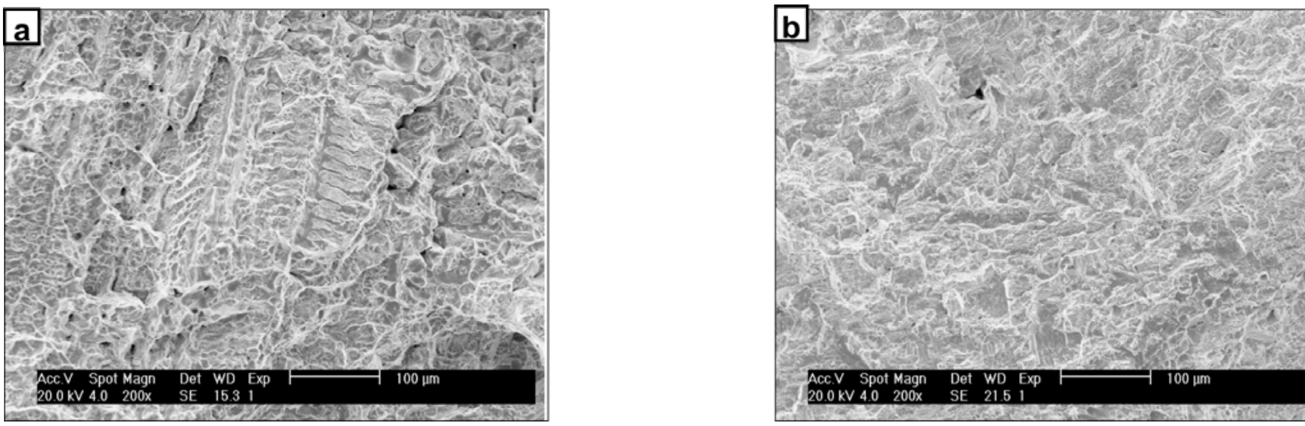

Fig. 3. The structure of fractures obtained in the static tensile tests for Ni_3Al (Zr, B) alloy at room temperature in air: a) as-cast condition, and b) after homogenization 1200°C/100h/argonium

A static tensile test of the **Ni_3Al (Cr, Zr, B)** alloy was performed at room temperature in an air atmosphere. It did not show a substantial change in a tensile strength for the as-cast alloy compared to the alloy annealed at 900°C/100h/air. However, the tensile strength value increased by about 65 MPa (10%) for the alloy annealed in argon.

Homogenisation at 1200°C/10h/argon reduced the relative yield point from 515 MPa for the alloy in as-cast condition to 380 MPa after annealing in air, and 380 MPa for the alloy annealed in argon. There was a simultaneous increase of relative elongation from 1% for the material in as-cast condition up to 5% for the material after homogenisation. Tension graphs, typical for brittle materials without a physical yield point, were obtained for the investigated material.

Microfractographic analysis revealed that the as-cast **Ni_3Al (Cr, Zr, B)** alloy fracture demonstrates a fairly typical, brittle character, with clear signs of cracking along crystallite boundaries as well as mixed cracking. A higher fraction of intercrystalline cracking was observed on fracture surfaces for samples after homogenisation in air. After homogenisation of the samples in argon, surface sections of 100-200 µm in size with clear cleavable failures were observed (Fig.4), apart from cracking along crystallite boundaries.

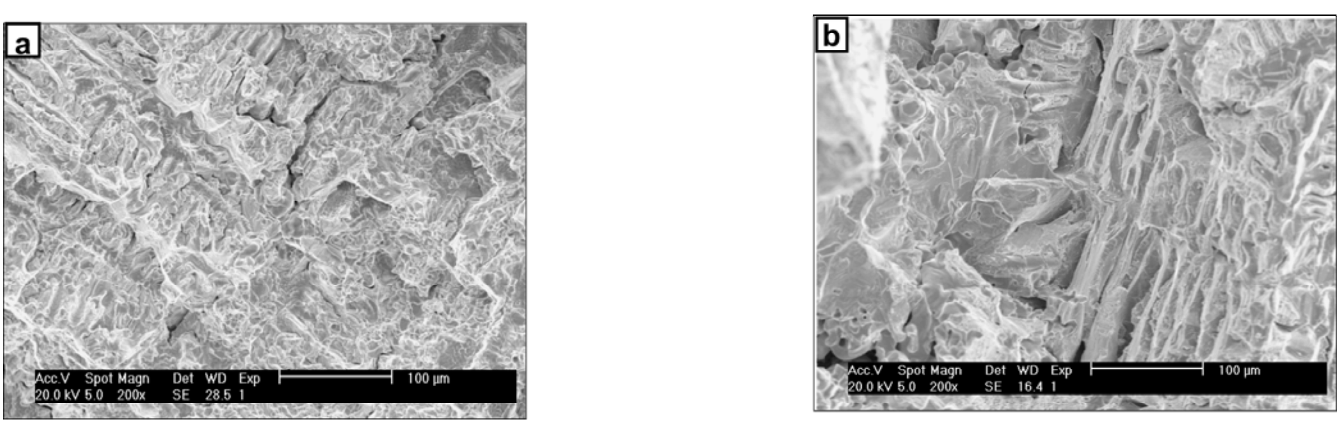

Fig. 4. The structure of fractures obtained in the static tensile tests for Ni_3Al (Cr, Zr, B) alloy at room temperature in air: a) as-cast condition, and b) after homogenization 1200°C/10h/argon

TABLE 1
Comparison of tensile properties of coarse-grained Ni_3Al alloys (room temperature tests, in air atmosphere – mean value from five tests)

Materials conditions		UTS [MPa]	TYS [MPa]	Elongation [%]	KV300/5 [J/cm^2]
Ni_3Al (Zr, B) alloy	as cast	540±40	340±21	7±2	105±3
	after homogenization 1200°C/100h/air	–	–	–	130±10
	after homogenization 1200°C/100h/argon	760±35	300±30	16±3	145±4
Ni_3Al (Cr, Zr, B) alloy	as cast	600±50	515±42	1±0,5	9,5±1
	after homogenization 900°C/100h/air	590±35	400±40	2±0,2	3,5±0,5
	after homogenization 1200°C/10h/argon	660±25	380±22	5±1	–

UTS – ultimate tensile strength, TYS – tensile yield strength

Impact bending test (at room temperature, in air atmosphere)

In order to find an determine the influence of heat treatment on the dynamic behaviour of the investigated alloys, evaluation of energy absorption capability in an impact test for limiting material conditions was attempted. The test parameters included:

- **Ni_3Al (Zr, B) alloy** – an as-cast sample is annealed for 100 hours at a temperature of 1200°C in an argon or air atmosphere,
- **Ni_3Al (Cr, Zr, B) alloy** – an as-cast sample is annealed for 100 hours at a temperature of 1200°C in an argon atmosphere

After homogenisation, an improvement in ductility of greater than 40% was observed for the **Ni_3Al (Zr, B)** alloy (Table 1). A high impact strength KV300/5 in a range of 105 to 145 J/cm^2, as well as a very good repeatability of test results for individual fractured samples, for the coarse-grained cast material was obtained. Typical, representative graphs for the force and breaking energy courses versus hammer point path, starting from the contact with a fractured sample surface, were obtained and are presented in Fig. 5 for the two investigated **Ni_3Al (Zr, B)** alloys. The shape of the force change shows that, for the as-cast sample, the increment and next drop (from the maximum) of the force necessary to fracture the sample were more dynamic than for samples after homogenisation (Fig.5a i 5c). The investigated alloy, even in the as-cast condition, presents high deformability during dynamic bending, which is clearly seen even at macroscopic observation of fractures obtained during the impact test (Fig. 5b). The fracture microstructure is weakly related to the dendritic composition. This is probably due to a large fraction of diphase (γ + γ') zones in the interdendritic regions for the as-cast condition. These regions shorten the path for easy growth of cracks and cause the development of numerous, multi-system slip bands presented in the fracture. Plastic strain of the fracture zones was increased for samples after homogenisation (Fig. 5d). The fracture surface is more developed since a decrease in the fraction of diphase (γ + γ') zones increases homogeneity, and a tendency to transcrystalline cracking of post-dendritic areas. Simultaneously, this drop in the fraction of diphase zones increases material deformability. Fractures that developed exhibited a significant fraction of high plastic strain regions for applied dynamic bending.

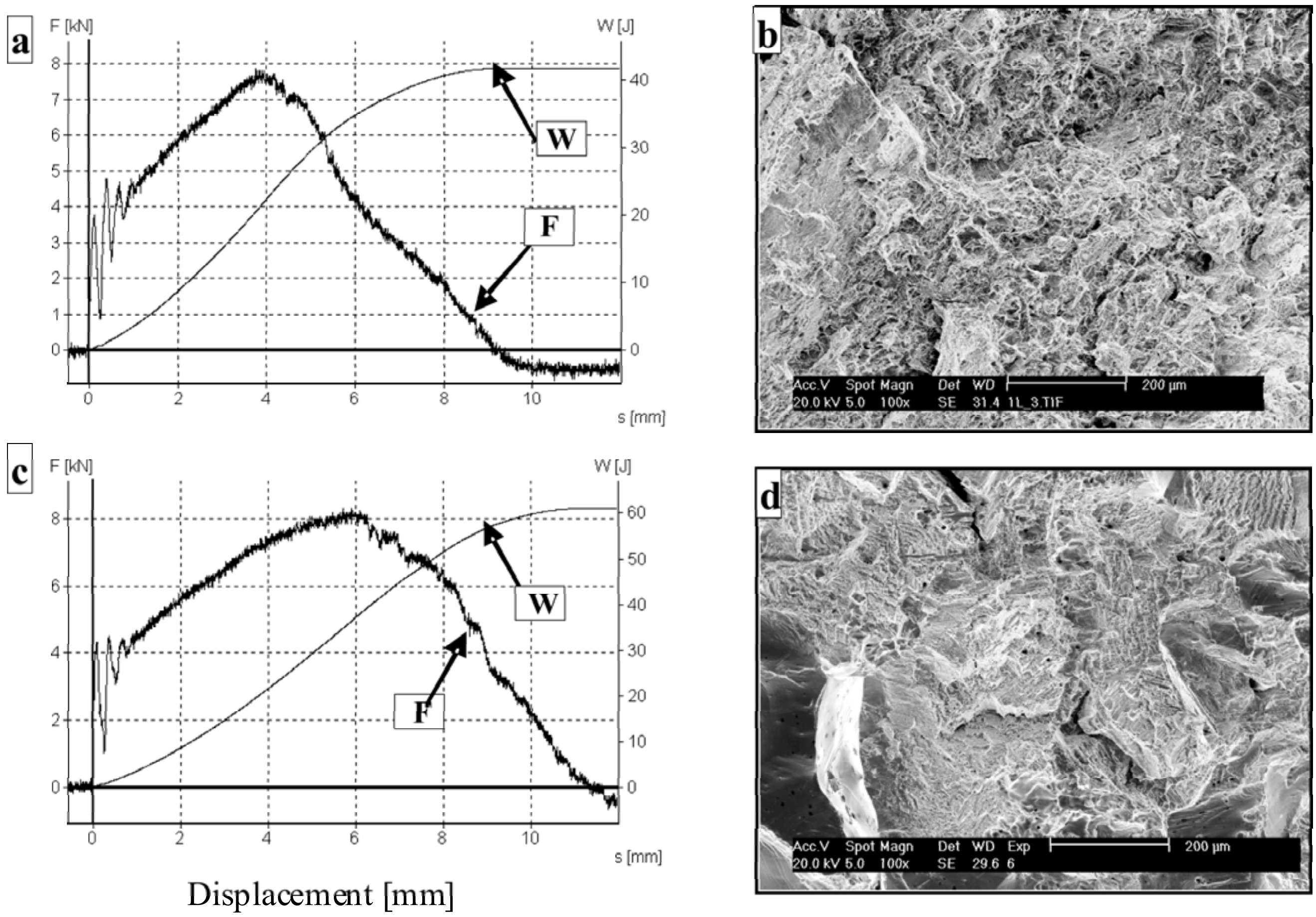

Fig. 5. Typical graphs for the cracking process and fracture surfaces obtained in dynamic bending of the Ni$_3$Al (Zr, B) alloy: a), b) as-cast condition, c), d) after homogenisation 1200°C/100h/argon; F – force, W – energy of breaking

For the **Ni$_3$Al (Cr, Zr, B)** alloy, low values of measured impact strength were found (Table 1). This points to a decrease of material ductility as a result of the homogenisation treatment. Such effects can be related to the unknown role of atmosphere, during homogenisation, on the retardation of morphology changes in diphase (γ' + β) regions. It is likely that an increase in (γ' + β) region hardness appeared after homogenisation in air. Characteristic courses of the force, F, at the impact pendulum tip, as well as a resulting breaking energy, W, accompanied by breaking of the Ni$_3$Al (Cr, Zr, B) alloy samples are presented in Fig. 6a i 6c. A non-monotonic course for the changes in breaking force shows the discontinuous growth of a fracture, meeting a very diversified resistance of individual phases of the structure along the direction of cracking. Brittleness of the investigated alloy is confirmed by the macrostructure of the obtained fractures. Plastic strain of the lateral section of the broken sample was not observed for any tested material condition. On the surface of the as-cast fracture sample, a primary, dendritic structure was revealed, dominated by interdendritic cracking (Fig. 6b). Deep discontinuities resulted from cleavage cracking of crystallites oriented, in this case, at large angles with respect to the fracture plane. On the fracture surfaces of samples after homogenisation (Fig. 6d), even greater brittleness is confirmed. This was observed while confirming lower impact resistance. Cracking is dominated by a transcrystalline cleavage along individual crystallites. For the alloy with chromium, an increased tendency to cleavage cracking, as a result of annealing, in a crystallite volume is not sufficiently compensated, as it is for the Ni$_3$Al (Zr, B) alloy, by improvement in the deformability of the zones of the boundaries. This property, accompanied by an additional increase of microhardness in the (γ' + β regions, is related to oxidation along grain boundaries. This phenomenon gives rise to a very low impact strength for this alloy. Similar influences of oxygen from air were observed by the authors of the papers [5-7].

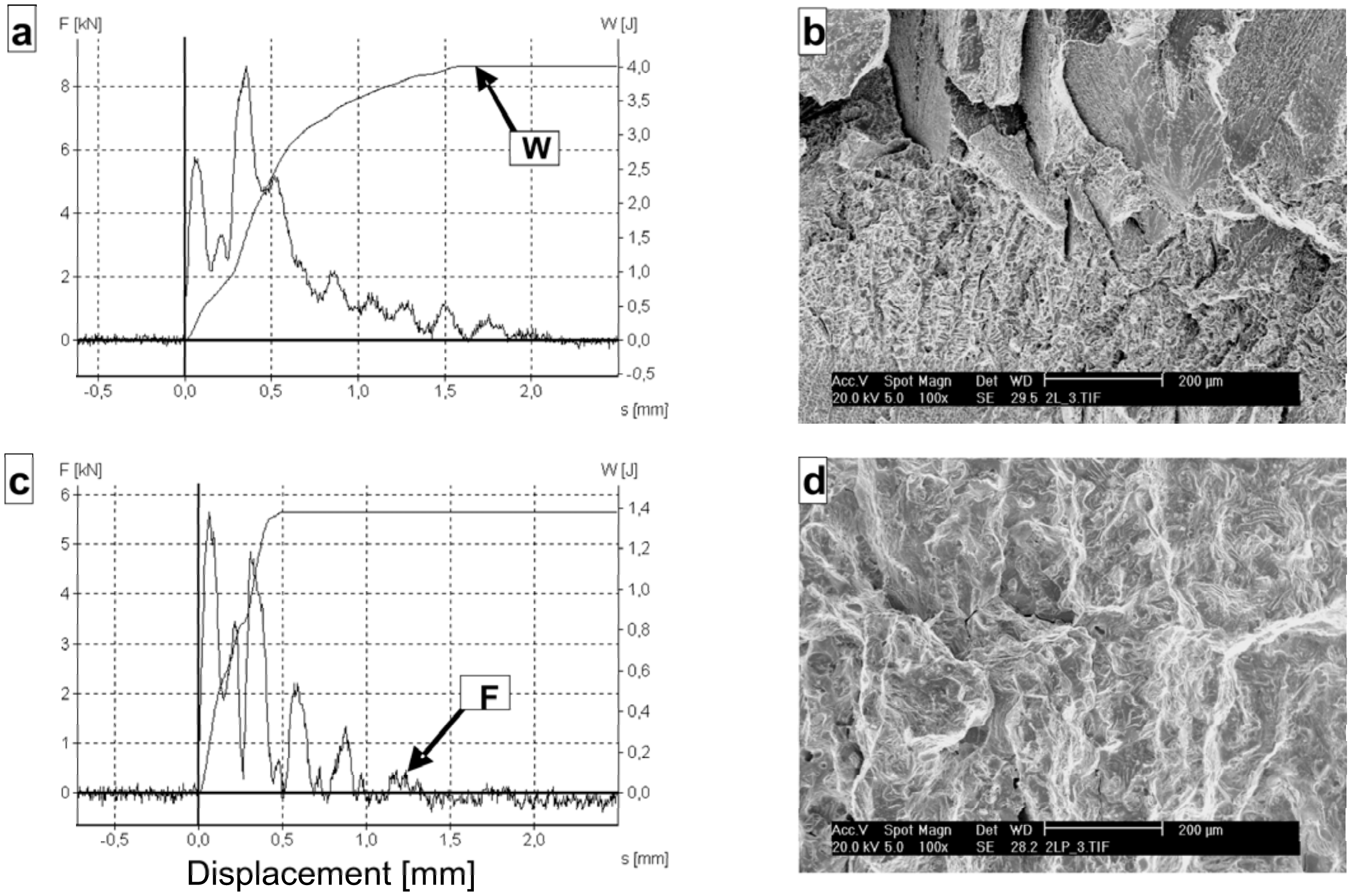

Fig. 6. Typical graphs of the cracking process and fracture surfaces for the Ni_3Al (Cr, Zr, B) alloy: a), b) as-cast condition; c), d) after homogenisation (1200°C/100h/air), F – force, W – energy of breaking

Heat treatment after additional cold working

Analysis of the possibility of improvement of mechanical properties (UTS, TYS) for the investigated alloys was obtained by shell casting without directional solidification. Alloy preparation included matrix structure refinement through cold working and recrystallisation. Complex tests were performed, including:

- selection of parameters for the individual deformation process, such as temperature, unit and total rolling reduction, and deformation velocity, and for plastic working, including rolling, open die forging or pressing.
- selection of the parameters of recrystallisation annealing, including temperature, time and annealing environment.

To obtain a fine-grained matrix structure, a process is applied, consisting of rolling for as much as 90% of the cold work and recrystallisation annealing at 1200 °C for 2 hours. This material, despite large differences in plastic deformability compared to the investigated alloys, has better mechanical properties than the material in as-cast condition. For the **Ni_3Al (Zr, B) alloy**, over 200% gain on UTS and 250% gain on TYS is seen compared to the as-cast condition. For the **Ni_3Al (Cr, Zr, B) alloy**, a 20% gain for UTS and 30% for TYS is seen compared to the as-cast condition. For both alloys, graphs of tension with clear yield point were obtained.

TABLE 2

Tensile properties of fine-grained Ni_3Al alloys, including room temperature test in an air atmosphere. Mean values from five tests are shown

Materials conditions		UTS [MPa]	TYS [MPa]	Elongation [%]
alloy No. 1	as cast + cold work + recrystalization	1760±30	1250±25	30±3
alloy No. 2	as cast + cold work + recrystalization	730±35	685±20	6±2

UTS – ultimate tensile strength, TYS – tensile yield strength

Based on the results obtained, an original, method of plastic working was developed in this study to make Ni_3Al strips with thickness less than 100 μm possible (Fig. 7). The method consists of cold rolling, with the controlled conditions of the process, such as cold rolling, rolling rate, etc. This method was described in more detail in a previous paper [11].

Fig. 7. Thin, high strength Ni_3Al (Zr, B) strip (0.08mm x 25mm x 2800mm) obtained by author's technology

4. Summary

Based on the investigations performed, heat treatment had a significant influence on **Ni_3Al (Zr, B) alloy** and a weak influence on **Ni_3Al (Cr, Zr, B) alloy**. The heat treatment mainly had an impact on the microstructure and mechanical properties.

A process of 100 hours of homogenisation at a temperature of 1200°C in an argon atmosphere causes an improvement in plasticity of the investigated **Ni_3Al (Zr, B) alloy**. Microfractographic analysis of the fractures in this alloy showed that they exhibit complex character and zones with intercrystalline and transcrystalline cracking. In many of the fragments, this takes place as cleavage cracking and is accompanied by a local zone of plastic strain, which is larger for the material after homogenisation.

Improvement in ductility for the **Ni_3Al (Zr, B) alloy** after homogenisation was proven as well in an impact bending test. Impact resistance tests correspond to the fractures obtained. It was found that fracture structure is weakly related to dendritic structure. Numerous multisystem slip bands were observed. Plastic deformations in the zones of sample breakage after homogenisation are much larger, and a fracture surface is more developed.

Annealing of the **Ni_3Al (Cr, Zr, B) alloy** carried out for 100 hours at a temperature of 1200 °C in air and argon atmospheres gives rise to a small change in morphology and the dimensions of diphase ($\gamma' + \beta$) regions.

A static tensile test of the investigated **Ni_3Al (Cr, Zr, B) alloy** at room temperature in an air atmosphere showed a change in tensile strength for the alloy, when annealed at 1200 °C/10 h/argon. In comparison to the as-cast condition, the yield point decreased by about 25%, and tensile strength value increased by about 10%. Microfractographic analysis revealed a greater fraction of intercrystalline cracking, which was observed on fracture surfaces for samples after homogenisation in air.

For the **Ni_3Al (Cr, Zr, B) alloy**, low values of measured impact strength were found. This points to a decrease in material ductility as a result of homogenisation treatment. Such an effect can be imputed to an increase in ($\gamma' + \beta$) region hardness, appearing after homogenisation in air. This is related to the phenomenon of oxidation along grain boundaries. Brittleness of the investigated alloy corresponds to the macrostructure of the fractures obtained. For all tested material conditions, plastic strain of the lateral section of the broken samples was not observed.

Additionally, through cold working by rolling and annealing, a fine-grained matrix structure of alloys in the form of thin strips with thickness less than 100 μm was obtained. This material possesses better mechanical properties than material in the as-cast condition.

Acknowledgements

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