

Composite Zones Produced In Situ in the Ni₃Al Phase

E. Olejnik^{a,*}, A. Janas^a, G. Sikora^a, T. Tokarski^b, J. Nowak^a

AGH University of Science and Technology,

^aFaculty of Foundry Engineering, Reymonta St. 23

^bFaculty of Non-Ferrous Metals, Mickiewicza Av. 30
30-059 Krakow, Poland

* Corresponding author. E-mail address: eolejnik@agh.edu.pl

Received 25.07.2012; accepted in revised form 04.09.2012

Abstract

The study presents the results of research on the development of composite zones in castings based on the intermetallic phase of Ni₃Al. Composite zones were obtained by placing packets with substrates for the reaction of titanium carbide in a foundry mould. To provide a variable carbides content in the composite zone, two compositions of the packets were prepared. The first packet contained only substrates for the reaction of TiC synthesis; the second one also contained a filler. The resulting composite zones in castings were examined for the filler effect on changes in the volume fraction, size and morphology of carbides in the zone. In addition, the effect of filler on the mechanical properties of the zone was verified, observing changes of Vickers hardness in this area. It was found that the presence of filler in the composition of the packet for synthesis reduced the content of carbides, as well as their size and morphology. Lower surface content of carbides reduced hardness of the zone, which enabled smooth control of the mechanical properties. At the same time, the use of the selected filler did not disturb the course of the TiC carbide synthesis.

Keywords: Composite layer, Ni₃Al, Cast intermetallic, In situ, Synthesis TiC carbides

1. Introduction

One of the basic characteristics of intermetallic phases is their high melting point, other features include relatively low density, high strength parameters and resistance to corrosion and oxidation at elevated temperatures. All these advantages allow the intermetallics to be used for structures operating in aggressive corrosive environments and at high temperatures. A major limitation to their use at ambient temperatures is brittleness and low ductility [1].

A good example of the phase with very interesting strength parameters is the Ni₃Al intermetallic compound. It is characterised by an anomalous tendency to increase the strength parameters in function of temperature [2], and owing to this

precisely characteristic is considered a very promising structural material. Moreover, in the Ni - Al system, it forms a eutectic with nickel solution (γ - γ'), which enables producing alloys with a wide range of properties. This mainly concerns the ductility, which increases in the presence of an (Ni) solution. The improved ductility promotes the use of this eutectic in nickel-based superalloys to obtain optimum strength properties at high temperatures and dynamic load carrying capacity. Of course, the discussed system does not include the effect of alloying elements, which cause a number of positive changes in properties of these alloys [3].

The mechanical properties of the Ni₃Al phase can be improved by the introduction of hard and creep-resistant ceramic phases of the carbide or boride type. One of the ways to carry out this process is by the SHSB (Self Propagating High-Temperature

Synthesis in Bath) method [4-6]. Its essence consists in introducing into the liquid alloy compressed packets containing a stoichiometric mixture of metal - non-metal powders, inducing the SHS reaction in selected compound. The method enables the fabrication of bulk composites. This means the mechanical properties, mainly the compressive strength and hardness, improved within the entire casting volume. Yet, this feature is not always the desired one, since it is associated with a deterioration of, even normally inferior, ductility of the Ni₃Al phase.

Local improvement of mechanical properties, and of the hardness of the above mentioned phase – in particular, is possible through the application of local hardening with the ceramic particles. One of the methods to achieve this effect is by the in-situ synthesis of ceramic phases. It enables producing in a selected fragment of the casting a composite area reinforced with e.g. carbides, while properties of the casting core remain unchanged [7].

This study presents the results of research related with the generation of composite zones reinforced with TiC carbides in the Ni₃Al intermetallic phases. The methodology used to make these zones and their general metallographic and mechanical characteristics have been presented.

2. Experimental

A mixture of substrates necessary for the synthesis of titanium carbide was prepared in an atomic ratio of 1:1. For this purpose, commercial products, such as powders of titanium (99.98%, 44 µm) and graphite (99.99%, 30 µm) were used. The prepared powders were mixed without the access of air for 24 h, to make next two compositions of substrates for the synthesis of composite zones. The first composition contained only a stoichiometric mixture of titanium and carbon, while the second composition additionally contained a filler in the form of nickel powder (99.4%, 44 µm). Both materials were pressed under a pressure of 500 MPa, yielding packets of 30 grams each. The dimensions of the packets were 15 × 10 × 55 mm for the packets without filler, and 11 × 10 × 55 mm for the packets with 50% filler content.

The chemical composition of the base alloy used for all the conducted melts was consistent with the Ni₃Al phase stoichiometry. The charge for an Exo-Mel™ synthesis [8] of the Ni₃Al phase was prepared preserving the nominal atomic ratio (Ni/Al = 3:1). For this purpose, nickel and aluminium of a 99.98% and 99.7% purity, respectively, were used.

Moulds were made of molochite and sodium silicate in a ratio of 20 : 3, conducting next the hardening operation by blowing with CO₂. The choice of the moulding material was dictated by the high temperature of alloy pouring. The ready packets were placed at the bottom of each mould. A 3D mould cross-section and packets for the synthesis are shown in Figure 1.

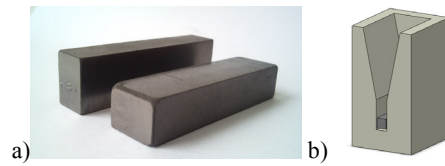


Fig. 1. Packets for the carbide synthesis (a) and 3D drawing of the mould cross-section with packet placed at the bottom (b)

Moulds before pouring were dried at 523 K for 10 minutes and were successively placed in the chamber of a Balzers vacuum furnace. Melting was conducted under the conditions of an initial vacuum of 6.7×10^{-5} MPa, followed by pouring under the atmosphere of argon (99.98%) at a pressure of 5×10^{-2} MPa. The weight of the base alloy charge was 0.4 kg.

The resulting Y-shaped ingots were cut, ground and polished for metallographic examinations and mechanical testing.

Table 1 gives numbers of individual melts with the corresponding weight fraction of the filler in packets.

Table 1. Melt numbers with the corresponding weight fraction of the filler introduced to individual packets

| Melt No. | Weight fraction of filler [wt. %] | Weight fraction of substrates for TiC synthesis [wt. %] |
|----------|-----------------------------------|---|
| M0 | 0 | 100 |
| M50 | 50 | 50 |

Metallographic examinations and chemical analysis in microregions were performed by the X-ray microanalysis (EDX) with scanning electron microscopy (SEM), using a Hitachi SU-70 microscope. The average diameter of carbides and their surface fraction were determined by an ImageJ software. Hardness HV of the castings was measured using a HPO 250 hardness tester under the load of 294.2 N and with the time of load application equal to 15 seconds.

3. Results

Figure 2 shows macrostructures of composite zones produced in the two studied alloys designated as M0 and M50, without the filler (Fig. 2a) and with the filler (Fig. 2b), respectively. The composite zones obtained in both alloys had similar thicknesses, i.e. ~ 15 mm, corresponding to the dimensions of packets for the synthesis placed in moulds.

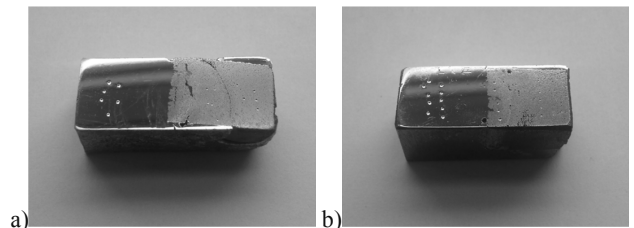


Fig. 2. Macrostructures produced in M0 and M50 alloys using packets for the carbide synthesis without and with the filler, respectively

Figure 3 shows the BSE image of a microstructure of the composite zone in M0 alloy. The precipitates of titanium carbides (dark colour) visible in Figure 3 are located in the matrix area (bright colour). The majority of carbides present in the composite zone are non-faceted crystals. The average diameter of carbides is 3 μm , and their surface fraction is $\sim 46\%$.

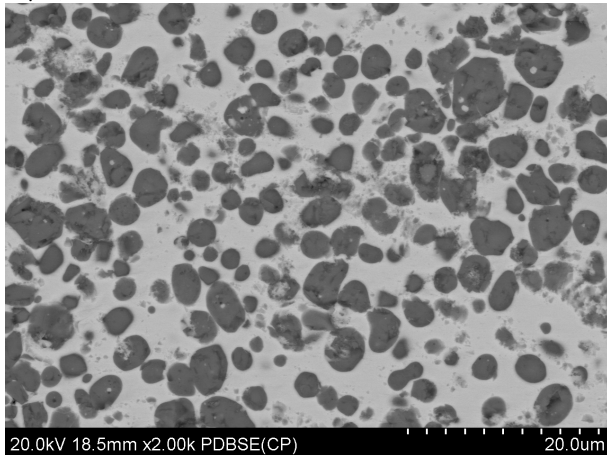


Fig. 3. BSE image of the composite zone in M0 alloy

Figure 4 shows the resulting composite zone obtained in M0 alloy without the addition of filler. The precipitates of non-faceted titanium carbides are visible against the partially etched matrix of the Ni_3Al phase.

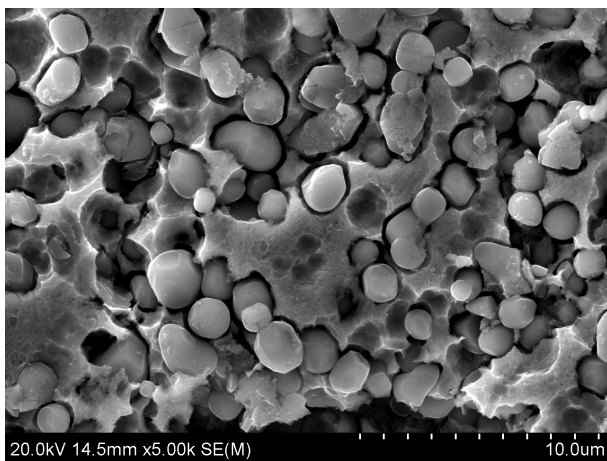


Fig. 4. Composite zone produced in M0 alloy. Deep-etched microstructure

Figure 5 shows the BSE image of a microstructure of the composite zone in M0 alloy with points marking the X-ray microanalysis. The results of the microanalysis of the composite zone in M0 alloy are summarised in Table 2. At points 1 and 2, carbon and titanium were mainly identified. On the other hand, at points 3 and 4, aluminium and nickel in an atomic ratio of 1:3 were present, suggesting the occurrence of phases from the Ni-Al system, probably Ni_3Al .

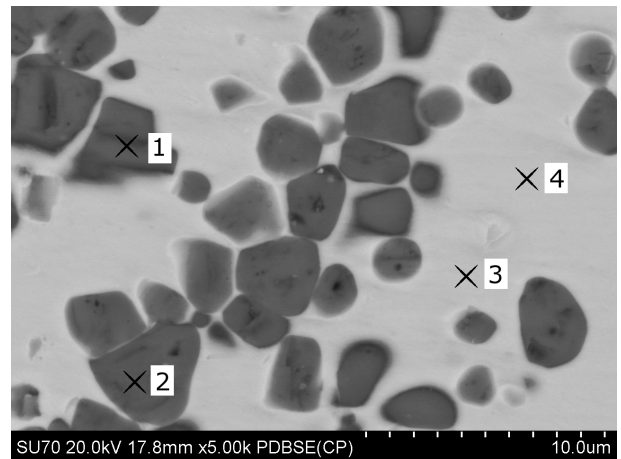


Fig. 5. BSE image of the composite zone in M0 alloy with points marking the X-ray microanalysis

Table 2. Chemical composition at points marking the X-ray microanalysis in Figure 5

| Point No. | Chemical composition [at. %] | | | |
|-----------|------------------------------|------|------|------|
| | C | Al | Ti | Ni |
| 1 | 35 | 0.5 | 61.5 | 3 |
| 2 | 41.1 | 0.5 | 56.6 | 1.8 |
| 3 | 10.2 | 21.7 | 1.1 | 66.9 |
| 4 | 10.2 | 21.6 | 1.1 | 67.2 |

Figure 6 shows the BSE image of a microstructure of the composite zone obtained for a composition containing 50 wt.% of filler in the form of Ni powder (M50 alloy). The majority of carbides present in the composite zone are faceted crystals. The average diameter of the TiC carbide precipitates present in the composite zone is 1.35 μm , and their surface fraction is $\sim 28.5\%$.

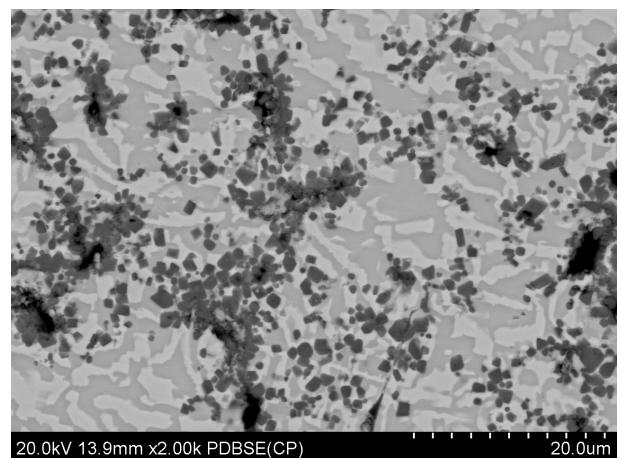


Fig. 6. BSE image of the composite zone in M50 alloy

Figure 7 shows the composite zone obtained in M50 alloy with filler in the form of Ni powder. The precipitates of fused

faceted titanium carbides are locally visible against the partially etched matrix of the Ni₃Al phase.

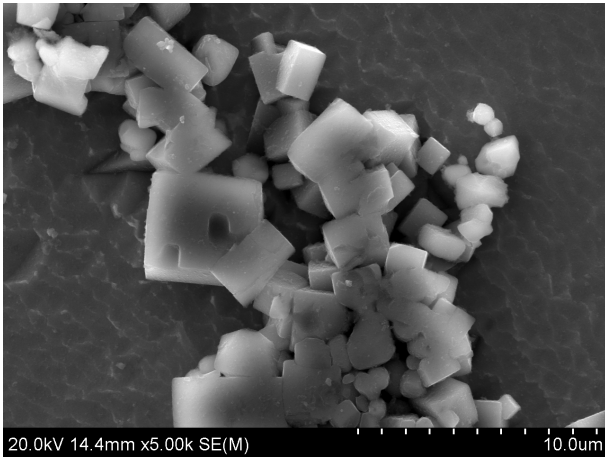


Fig. 7. Composite zone produced in M50 alloy with the visible precipitates of TiC carbides. Deep-etched microstructure

Figure 8 shows the BSE image of a microstructure of the composite zone in M50 alloy with points marking the X-ray microanalysis. The precipitates of titanium carbides (dark colour) visible in Figure 8 are located in the matrix area (bright colour).

The results of the microanalysis of the composite zone in M50 alloy are summarised in Table 3. At points 1 and 2, carbon and titanium in an atomic ratio of 1:1 were mainly identified, thus indicating the presence of phases from the Ti-C system, probably TiC. On the other hand, at points 3 and 4, aluminium and nickel in an atomic ratio of 1:3 were present, suggesting the occurrence of phases from the Ni-Al system, probably Ni₃Al.

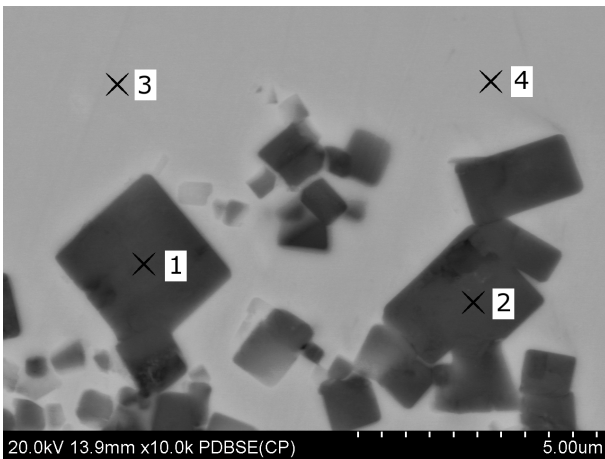


Fig. 8. BSE image of the composite zone in M50 alloy with points marking the X-ray microanalysis

Table 3. Chemical composition at points marking the X-ray microanalysis in Figure 8

| Point No. | Chemical analysis [at. %] | | | |
|-----------|---------------------------|------|------|------|
| | C | Al | Ti | Ni |
| 1 | 44.1 | 0.8 | 50.1 | 5 |
| 2 | 40 | 0.5 | 56.6 | 3.1 |
| 3 | 9.8 | 20.2 | 1.5 | 68.5 |
| 4 | 9.8 | 20.1 | 1.3 | 68.8 |

Figure 9 shows test indentations made in the M0 alloy casting core (a) and composite zone (b). There is a clear difference in the length of the diagonals of these indentations when made in the casting core (Fig. 9a) and in the composite zone (rys.9b). The difference is due to a large volume fraction of carbides in the composite zone.

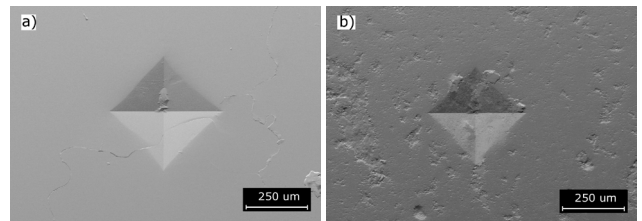


Fig. 9. BSE image of indentations made with a Vickers hardness tester in the M0 alloy casting core (a) and composite zone (b)

Figure 10 presents the results of hardness measurements taken in the M0 alloy casting core and composite zone. The average hardness values of the casting core and composite zone are ~ 272 HV and ~ 581 HV, respectively.

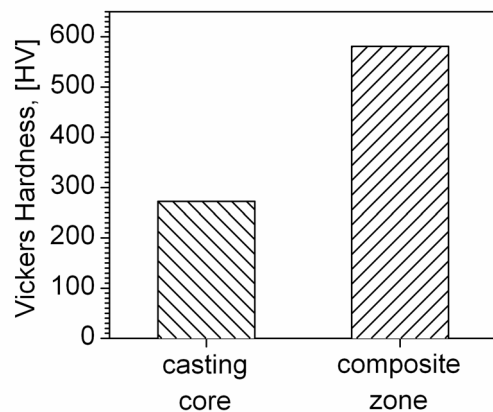


Fig. 10. The results of hardness measurements obtained for M0 alloy

Figure 11 shows selected indentations made in the M50 alloy casting core (a) and composite zone (b). For this alloy, the difference between the length of the diagonals of the indentations made in the casting core and composite zone is small, mainly due to a lower volume fraction of the TiC carbides.

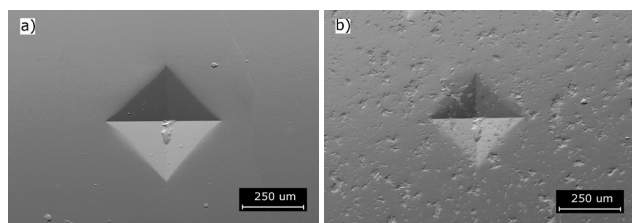


Fig. 11. BSE image of indentations made with a Vickers hardness tester in the M50 alloy casting core (a) and composite zone (b)

Figure 12 illustrates the hardness measurement results obtained for the M50 alloy casting core and composite zone. The average hardness values in the casting core and composite zone are ~ 256 HV and ~ 353 HV, respectively.

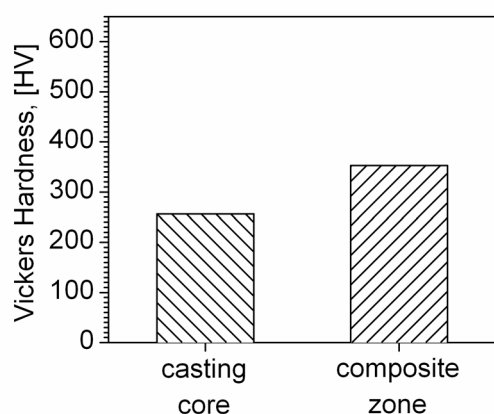


Fig. 12. The results of hardness measurements obtained for M50 alloy

4. Discussion

The introduction into foundry moulds of packets containing substrates for the TiC carbide synthesis enabled the formation of composite zones in castings based on the Ni_3Al intermetallic phase. The zones were characterised by compact structure, and their dimensions corresponded to the shape and dimensions of packets placed in the individual moulds. The thickness of the resulting composite zone was 15 mm and 16 mm for M0 and M50 alloys, respectively. This result promotes the use of materials with composite zones in structures exposed to heavy wear.

Studies confirmed changes in the volume and surface content of carbides and in the hardness of the obtained composite zones. In castings containing packets with 100% mixture of substrates for the TiC synthesis, over twofold increase in the hardness of the composite zone was reported.

The addition of nickel in an amount of 50 wt.% reduced two times the average diameter of the carbide precipitates, i.e. from 3 μm to 1,35 μm . Such a change in the size of the carbide precipitates may be due to the carbide growth kinetics in liquid alloy. According to the data collected in [4], the critical growth-promoting factor is here the time of holding the carbide crystals in

liquid alloy after the synthesis. Moreover, the presence of filler reduces the surface content of titanium carbides. In M0 and M50 alloys it dropped to $\sim 46\%$, and $\sim 28.5\%$, respectively. Adding filler to the substrates of the reaction of synthesis in M50 alloy also caused a nearly twice decrease in the Vickers hardness of the composite zone, i.e. a drop from ~ 581 HV to ~ 353 HV.

In both the examined materials, a change was observed in the morphology of carbides obtained by synthesis. In the case of M0 alloy, the TiC carbides had a non-faceted shape, while in the M50 alloy, crystals of a faceted shape were produced. The changing morphology of TiC crystals may result from the kinetics of growth, dependent on the degree of undercooling of both alloys, on the cooling rate and on the content of surface carbides. According to the data collected in [9], an increase in the degree of undercooling favours the formation of non-faceted crystals observed in the M0 alloy without filler.

5. Conclusions

The study showed distinct changes in the size and surface content of TiC carbides in the two compared alloys, i.e. M0 and M50, without and with the filler, respectively.

The addition of filler affects the mechanical properties of the composite zone. It is possible to obtain a stepless change of the hardness values in this area, which is of utmost importance in designing the structural components resistant to abrasion. It allows smooth control of the plastic properties and impact resistance within the composite zone.

Acknowledgements

The results presented in this paper have been carried out within the framework of research grant No. N N507 311040 financed by the Polish Ministry of Science and Higher Education.

References

- [1] Deevi, S. C. & Sikka V. (1996). Nickel and iron aluminides: an overview on properties, processing and applications. *Intermetallics*. 4, 357-375.
- [2] Sikka, V. K., Santella, M. L. & Orth, J. E. (1997). Processing and operating experience of Ni_3Al -base intermetallic alloy IC-221M. *Materials Science and Engineering*. A 239-240 564-569.
- [3] Olejnik, E., Janas, A., Grabowska, B. & Kawalec, M. (2012). Effect of carbon addition on functional and mechanical properties of the Ni_3Al phase. *Metallurgija*. 51(4), 445-448.
- [4] Fraś, E., Janas, A., Kurtyka, P. & Wierzbński, S. (2003). Structure and properties of cast $\text{Ni}_3\text{Al}/\text{TiC}$ and $\text{Ni}_3\text{Al}/\text{TiB}$ composites. Pt. 1, SHSB method applied in fabrication of composites based on intermetallic phase Ni_3Al reinforced with particles of TiC and TiB. *Archives of Metallurgy and Materials*. 48(4), 383-408.

- [5] Fraś, E., Janas, A., Kolbus, A. & Olejnik, E. (2006). Matrix - particle interphase boundaries of the selected in situ and ex situ composites MMCs. *Archives of Foundry*. 18(6), 297-304 (in Polish).
- [6] Janas, A., Kolbus, A. & Olejnik, E. (2011). Synthesis of Ni₃Al composites reinforced by TiC, WC, ZrC, NbC, TaC – carbide particles. *Composites Theory and Practice*. 2, 114-119 (in Polish).
- [7] Olejnik, E., Janas, A., Kolbus, A. & Grabowska, B. (2011). Composite layers fabricated by in situ technique in iron castings. *Composites Theory and Practice*. 2, 120-124 (in Polish).
- [8] Deevi, S. C., Sikka, V. K. (1997). Exo-Melt™ Process for melting casting intermetallics. *Intermetallics*. 5, 17-27.
- [9] Karantzas, A. E., Lekatou, Georgatis, A., E., Arni, Z. & Dracopoulos, V. (2011). Solidification observations of vacuum arc melting processed Fe-Al-TiC composites: TiC precipitation mechanisms. *Materials Characterization*. 62, 1196-1204.