ABSTRACT

To thesis research on **«MULTILAYER STRUCTURE OF ALUMINIDE INTERMETALLIC COMPOUNDS OF COBALT, NICKEL, AND TITANIUM»,** Submitted for the Degree of Doctor of Philosophy PhD Majoring in Materials Science and Technology of New Materials- 6D071000

IBRAEVA GULZIRA MURATBEKOVNA

Evaluation of status on scientific problem to be solved. Nowadays among the major tasks of materials science, there is one on development of materials having special properties. In this regard to solve this type of tasks the permanent interest is to be manifested to intermetallics. They provide the higher strength for dispersion hardening alloys based on Al, Cu, and Fe, encountering in compositions of high-tensile structural materials. They also are used for strengthening successfully in form of second phase on regular alloys at high temperatures. Step-by-step the intermetallics have come to be recognized as promising high temperature structural materials due to their high hardness and stability. In 1950s, numerous studies have started to determine the potential of intermetallic structures. Their different properties were determined; among them, the brittleness has been considered as formidable obstacle preventing to their implementation. Nonetheless, there are attempts to pass over this problem by means of some processes, where the key task is related to microstructure modification. Other tasks on improvement of their mechanical properties are formulated too including the strengthening and cracking reduction.

Structural and microstructural studies play a certain role in development and modification of aluminide intermetallics. Basic data on phase composition, boundaries between phases, properties and distribution of elements and peculiarities of microstructure makes a critical contribution not only in modification area, but also in understanding of details in behaviour of intermetallic systems under operation conditions. Availability of multiphase volume permits to formulate tasks to compare phase interaction, stability, and compatibility. It is especially effective in case of application of diffusion couples method in cross section. Since order of appearance of phase transformations in general coincides with behaviour of equilibrium diagram the unique opportunity appears to study intermetallic phases using the different research methods.

Whereas the aluminide intermetallic compounds of practical interest are pricy materials, they are considered as the primary candidates to be applied in additive technologies. Therefore, the issue on comparability of microstructures resulted in case of diffusion couples method with phase formation pattern in case on additive technologies application becomes more and more actualized one.

Background and initial data for theme formulation. For studies of multilayer structures of diffusion zone and reaction zone, there were selected the binary systems Co-Al, Ni-Al, and Ti-Al where a number of intermetallic compounds is formed. Alloys on the base of ordered intermetallic compounds of these systems are considered as important class of structural materials with unique set of physical

and mechanical properties. Higher heat resistance, low density, high modulus of elasticity, and satisfactory oxidation resistance in temperature interval 550...850° C make them promising heat-resistant materials in applications in aerospace and energy production areas. Equilibrium diagrams of binary systems, structure and phase composition of the corresponding alloys have been studied due to practical interest to these alloys. However, there is still insufficient microstructure data on above-mentioned systems.

Justification of implementation of this scientific research. In binary systems, where intermetallic compounds formation take place, the regularities of diffusion zone and reaction zone formation are still unclear; it is true not only at temperatures above melting point of one component of system, but also at temperatures where solubility discontinuity occurs and formation of transitional phases. Differences in properties of these systems assist to disclose a number of peculiarities of diffusion zone and reaction zone formation in systems having unlimited solubility; it provides the corresponding structural database for intermetallic compounds.

The further development of intermetallics of these systems calls the comparative studies of structures formed by means of diffusion couples and additive technologies methods. It is expected that efficacy of such comparative studies gets higher in case of their microstructural similarity.

Rationale. It is justified by the necessity of experimental study on intermetallic compounds, which formation pieces together the consecutive and consolidated system. It is related to expansion of intermetallic application in additive technologies. Scientific results to be obtained in this work permit to control the structure and properties of intermetallic compounds from selected systems.

The goal of dissertation is to study the peculiarities of structure formation of diffusion zone and reaction zone in binary systems Al-Co, Al-Ni, and Al-Ti and to detect the aluminide intermetallic compounds by means of structural studies.

The basic tasks:

1. Verification of efficacy of diffusion couples method applied to selected systems;
2. Evaluation of treatment temperature-time effects on the intermetallic compound formation in diffusion zone and reaction zone;
3. Comparative study of the microstructure peculiarities of diffusion zone and reaction zone in selected systems;
4. Detection and comparison of similar microstructures formed by means of methods of additive technologies and diffusion couples.

Object of study is diffusion zone and reaction zone formed between elements of systems Al-Co, Al-Ni, and Al-Ti in conditions of high-temperature treatment.

Subject of study is a structure of multilayer diffusion zone and reaction zone of systems Al-Co, Al-Ni, and Al-Ti.

Methodological base of studies. The main studies and analyzes used in the performance of the thesis are:

– Thermodynamic computations using the Thermo-Calc software (TTAl7 base);

– Microstructural studies of multilayer diffusion zone and reaction zone using the scanning electron microscopy studies and electron probe microanalysis (SEM-EPMA) on JXA-8230 (JEOL);
– Microhardness measurements for intermetallic compounds in multilayer diffusion zone and reaction zone using the devices PMT-3 and DuraScan G5;
– Qualitative and quantitative determination of phase composition for intermetallic compounds in multilayer diffusion zone and reaction zone using X-rays diffractometry (Bruker D8 Advance).

Above-mentioned instruments comply with requirements of Governmental Metrological Checking (Accreditation certificate #KZ-I.02.1138 of February 23, 2016).

Scientific novelty.

– There was implemented the integrated study of microstructure of multilayer diffusion zone and zone reaction in Al-Co, Al-Ni, and Al-Ti systems, which were obtained by means of diffusion couples method;

– For the first time there were revealed new stoichiometric relationships between components of phases CoAl and NiAl in metastable conditions of high-temperature treatment;

– There were revealed the temperature shifts of existence of the aluminide intermetallic compounds in Al-Co, Al-Ni, and Al-Ti systems to higher temperature regions by 163-446 ºC compared to the corresponding equilibrium diagrams.

– Originally disclosed that formation of peculiarities in globular intermetallic particles in Al-Ti system obtained by means of diffusion couples method at 1150ºC is structurally similar to intermetallics obtained by means of additive technology method at 1000ºC;

– There was developed the technique for linear wave-dispersive microanalysis of profiles of intermetallic compounds components.

Practical significance is that structures obtained by means of diffusion couples and additive technologies methods have the qualitative and quantitative similarity. Therefore, data on multilayer intermetallic structures obtained for conditions of diffusion couples method should be taken into account in the additive technologies research areas for multiphase items. Practical significance is confirmed by the corresponding Act for Implementation in research methodical operations in Laboratory for Physical Research Methods of Joint Stock Company "Institute for Metallurgy and Ores Beneficiation". Due to standardized measurement of aluminide intermetallic compounds, the time to be consumed for measurement condition settings for WDS profiles at the instrument JXA-8230 becomes in 10-15 times shorter.

Scientific statements to be put forward for defence of the thesis

1. The phase composition, which has been revealed by means of methods of Electron Probe Microanalysis, of diffusion zone and zone reaction in systems of Al-Co, Al-Ni, and Al-Ti, consisting from intermetallic compounds of aluminides forming in temperature range from 700 to 1375°C;

2. Detected regions of existence of intermetallic compounds of aluminides in systems of Al-Co, Al-Ni, and Al-Ti, obtained by means of method of diffusion

couples, demonstrating the temperature shift to 163-446°C compared to their existing equilibrium diagrams;

3. Intermetallic compounds of aluminides, which were detected by means of methods of energy-dispersive and wave-dispersive spectrometry, in systems of Al-Co, Al-Ni, and Al-Ti, having new stoichiometric relationships and representing the Berthollides $Co_{79}Al_{21}$, $Co_{56}Al_{44}$, $Co_{80}Al_{20}$, $Ni_{49}Al_{51}$, etc.;

4. Data on elements of control on structure-phase status of diffusion zone and reaction zone in selected systems, including the layer widths, sequence of phase location, and layer structure as well.

Basic scientific-practical results:

1. By means of Thermo-Calc (TTAl7 base) there were calculated and built the fragments of equilibrium diagrams for Al-Co, Al-Ni, and Al-Ti in area of concentrations 0-100% Co, 0-100% Ni, and 0-100% Ti. During the crystallization and subsequent cooling processes in selected solid-state systems the besides solid solution the well-known phases are formed correspondingly:

in Al-Co system: Co_2Al_9, Co_4Al_{13}, $CoAl_3$, Co_2Al_5, CoAl;

in Al-Ni system: $NiAl_3$, Ni_2Al_3, Ni_3Al_4, NiAl (β), Ni_5Al_3, Ni_3Al (γ');

in Al-Ti system: Ti_3Al, TiAl, Ti_5Al_3, $TiAl_2$, Ti_5Al_{11} и Ti_9Al_{23}.

2. Microhardness values were measured for a number of aluminides including for thin layers about 10 microns. All microhardness numbers have reasonable matching with literature references. This manner the microhardness

in Al-Ti system was in the interval 3,998-8,334 MPA;

in Al-Ni system was in the interval 5,600-6,200 MPA;

in Al-Co system was in the interval 3,708-4,659 MPA;

3. The influence of treatment modes on the width of diffusion zone and reaction zone has been studied. The average width of diffusion zone and reaction zone for Al-Co system was 365,5±50 мкм;

for Al-Ni system was 370±10 мкм;

for Al-Ti system was 38,05мкм.

4. In Al-Ni and Al-Co systems there were revealed new stoichiometric relationships between components of phases CoAl and NiAl, which are compliant to compounds having the following compositions:

- For phase CoAl: $Co_{79}Al_{21}$ (78.02-78.72% Co), $Co_{56}Al_{44}$ (55.50-55.69% Co), $Co_{80}Al_{20}$ (79.39-79.55% Co) and $Co_{73}Al_{27}$ (72.70-73.29% Co); `
- For phase NiAl: $Ni_{49}Al_{51}$ (48.67-49.07% Ni), $Ni_{64}Al_{36}$ (63.80-64.06% Ni), $Ni_{70}Al_{30}$ (69.50-69.62% Ni) and $Ni_{68}Al_{32}$ (67.50-67.86% Ni).

5. There were revealed the temperature shifts of existence of aluminide intermetallic compounds to higher temperatures on 163-446 ºC compared to the corresponding equilibrium diagrams. In particular,

- in Al-Co system the temperature shift for intermetallic compound $CoAl_3$ was 165 ºC, and for Co_4Al_{13} it was about 207 ºC.
- in Al-Ni system the temperature shift for intermetallic compound $NiAl_3$ was 446 ºC, and for Ni_2Al_3 it was about 163 ºC.

- in Al-Ti system the temperature shift for intermetallic compound Ti_9Al_{23} at 1300 ºC was also revealed; according to equilibrium diagram this phase should be vanished beginning from 780°C.

6. There were determined the structural peculiarities general for diffusion zone and reaction zone in binary systems: multi-layers, areas with solid solution of one component in another component, porosity, cracks, and interface boundaries.

Relation of thesis with scientific research programmes. This work has been implemented in accordance to plan of Fundamental Studies Programme of the Institute of Metallurgy and Ores Beneficiation of KZ Ministry for Education and Science "Creation of fundamentals for industrial technology of high strength and heat-resistant intermetallic superalloys on the basis of aluminides by means of powder metallurgy method" Agreement 203/1. Grant funding of scientific researches on 2015-2017.

On quantity and types of publications, the dissertation meets the requirements of the Committee on Control in Area of Education and Science of KZ Ministry for Education and Science.

Personal contribution of author. The author has a major role in the formulation of research tasks and in the implementation of experimental work: sample preparation, observations and measurements, in data processing and generalization of the results obtained.

Practical evaluation of results. The basic provisions of thesis were reported and discussed at seminars of the Institute of Metallurgy and Ores Beneficiation.

The principal statements and results were reported on the International scientific conference "Resource-saving technologies in ores beneficiation and non-ferrous metallurgy" (Almaty, 2015), on the V International scholar scientific-practical conference "Engineering and Technology of Machine-Building" (Omsk, 2016), on the IX International scientific-practical "European scientific conference" (Penza, 2018), on the III International scientific conference "Innovations and development patterns in Technical and Natural Sciences (Berlin, 2018).

Publications. The basic provisions of dissertation were published in 9 scientific articles, 1 of them was published in journal indexed in Scopus database, 4 articles were published in journals recommended by the Committee on Control in Area of Education and Science of KZ Ministry for Education and Science; and 4 articles were published in proceedings of international conferences.

Volume and structure of thesis. Thesis consists of Content, List of Acronyms and Definitions, Introduction, six Chapters, Conclusion, and References containing 110 titles, printed on 82 pages, contains 28 Figures, 9 Tables, and 9 Attachments.