Conference Paper

Using of Technogenic Raw Materials Based on Titanium-containing Slag and Aluminum Bronze for the Development of Composite Material

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Abstract

In this study, the possibility of using of the following technogenic raw materials to obtain a composite material was considered: titanium-containing slag, with the addition of aluminum bronze grade PG-19M-01 (TU 48-4206-156-82) and aluminum powder grade PA-4 (GOST 6058-73). The percentage of components in the mixture were as follows (wt. %): slag - 40, PG-19M-01 - 30, PA-4 - 30. A thermodynamic simulation of the selected system was preliminarily carried out using TERRA program in the temperature range 273 - 4273 K. The chemical and granulometric composition of the initial powders was investigated. From the powder mixture there were compressed the tablets and then they were sintered in an inert atmosphere. Micro-X-ray analysis of sintered samples showed that they consist of large particles of various shapes, most likely containing titanium and iron aluminides, their compounds between themselves and with copper.

Keywords: titanium-containing slag, composite material, thermodynamic modeling, intermetallic compounds, pressing, powder materials.

1. Introduction

This work is devoted to investigation of the possibility of using of technogenic raw materials - titanium-containing slag, with the addition of aluminum bronze grade PG-19M-01 (TU 48-4206-156-82) and aluminum powder grade PA-4 (GOST 6058-73), to obtain a composite material. It was supposed to produce a composite material consisting of particles of intermetallic compounds based on titanium, iron and aluminum, located in a soft, plastic matrix, providing the subsequent molding of the composite in the form of a wire. This wire can be used to obtain a powder material or plasma spraying of coatings hardened by intermetallic particles and not requiring the application of an additional sublayer.

Bronze powder was added to the composition of the mixture to obtain a composite to improve and intensify the thermal conductivity in the bulk, reduce porosity, remove

non-metallic inclusions and gas bubbles to the periphery, and also for better formation of the sample during compression of the mixture. Aluminum powder was introduced into the mixture for the reduction of oxides of iron, titanium and other valuable metals, despite the fact that its solubility in bronze is limited.

The composition, structure and content of the components, and, consequently, the integral physicochemical properties of the new materials, depend on the initial ratio of the elements, parameters and the degree of disequilibrium of the system under study (heating, cooling, temperature gradients and other technological factors). When implementing a sustainable controlled process, it is often necessary to vary the input parameters: initial composition, temperature, pressure, etc. The selection of these parameters can be largely carried out using thermodynamic calculations, which can significantly reduce the amount of experimental research and, thereby, reduce the time and material costs for testing the process.

The necessary step in the study for equilibrium (quasi-equilibrium) processes is the implementation of thermodynamic calculations. In the case of nonequilibrium processes, thermodynamic calculations allow us to estimate the limiting values of various process parameters.

In this work, the study was carried out using the TERRA software package [1] and the thermodynamic modeling methodology [2–4]. The reliability and effectiveness of the results of thermodynamic modeling is largely determined by the availability of reliable data on the thermochemical properties of substances and their mutual consistency. In order to form a database for modeling, a search was made of experimental and theoretical results on the thermodynamic properties of the compounds that make up the system under study [5–17]. However, it should be noted that in the available literature, information on the thermodynamic properties of a number of binary compounds in the condensed state (solid and liquid) are absent, and sometimes contradictory. Therefore, the thermodynamic properties (standard enthalpies and entropies of formation, temperature dependences of heat capacities, enthalpy increment $H_{298}^0 - H_0^0$) were calculated using various methods, [see, for example, [18–21]).

2. Thermodynamic Modeling of the System ``Slag - Bronze - Aluminum''

The simulation was executed in the temperature range of 273–4273 K in a helium atmosphere (1 wt.%) at a total pressure of P = 5.10^4 Pa (0.05 MPa). The compositions of slag and bronze were determined according to the results of chemical analysis. The following 17 elements were included in the composition of the modeling system:

Al, Ca, Cl, Cr, Cu, Fe, Mg, Mn, Mo, Ni, O, Si, Ti, V, Zn, F, He. When modeling, the thermochemical properties of the above elements, as well as binary, ternary and more complex compounds in condensed (solid and liquid) and gaseous states that can be formed in this system, were taken into account.

Figure 1 shows the temperature dependences of the content of the components of the condensed phase formed upon equilibrium heating of the simulated system. As can be seen from the Figure 1, the main components of the condensed phase are $FeAl_3$, TiAl, TiO, Cu_2Al, Al_2O_3, $MgAl_2O_4$. The content of the remaining components is significantly lower (less than 1 wt.%).

Thermodynamic calculations of the possible production of reaction products showed that at all selected sintering temperatures the same compounds are formed ($FeAl_3$, TiAl, TiO, Cu_2Al, Al_2O_3, $MgAl_2O_4$, etc.), but their ratio changes at 1100°C.

a)   b)
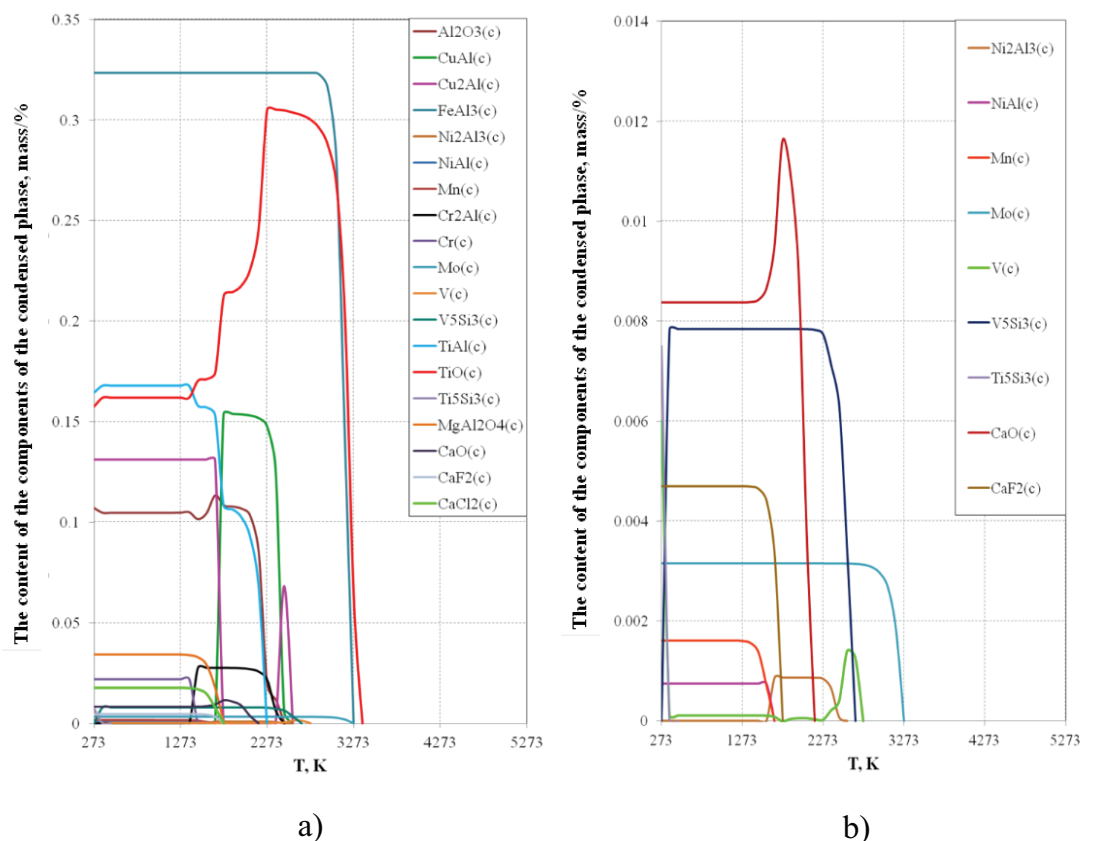
Figure 1: The content of the components of the condensed phase according to the results of modeling: a – basic components; b – components with a content of less than 1 wt.%.

3. Experiment

As experimental equipment IV-micro vibration eraser, X-ray fluorescence spectrometer S8 Explorer, Camsizer XT Particle Analyzer, MS-500 press, laboratory vacuum furnace, scanning electron microscope Quanta 200 Pegasus were used.

For experiments, a powder material was obtained from titanium-containing slag by crushing and subsequent abrasion in a vibration eraser. Particles are not spherical, but close to symmetrical (the average coefficient of symmetry of particles was 0.870, sphericity - 0.616). The chemical composition of the slag was following (mass. %): Ti - 52.01; O - 21.00; Fe - 14.85; Ca - 3.34; Cl - 2.55; Al - 2.21; V - 1.35; Mg - 1.05; others are 1.64.

The elemental analysis and particle shape parameters of the PG-19M-01 bronze powder were determined in the same way as for slag powder. The particles are fragmentation, not symmetrical (the average coefficient of symmetry of the particles was 0.758, sphericity - 0.451). The chemical composition of the bronze powder, wt. %: Cu - 48.98; Fe - 30.11; Cr 9.61; O - 6.90; Al - 1.40; Mn — 0.54; Si 0.38; others 2.08.

The parameters and particle shape of the aluminum powder were also determined on a Camsizer XT instrument. Particles are not spherical, fragmentation, slightly symmetrical (the average coefficient of symmetry of particles was 0.777, sphericity - 0.540).

All components were taken with a fineness of (-100) microns. To obtain a composite material, the following composition was selected (wt. %): slag - 40, bronze - 30, aluminum - 30. Dose by weigh (4 g each) were taken from the mixture of components, from which tablets were pressed in a collapsible mold at a pressure of 350 kN/m^2 (1981.6 MPa). The obtained tablets were sintered in a laboratory vacuum furnace in helium at an excess pressure of 5.10^4 Pa (with preliminary evacuation) at temperatures of 1173, 1273 and 1373 K. The heating rate was taken equal to 6 K/min, the exposure time at maximum temperature was 1 hour and cooling with the furnace.

X-ray analysis showed that as a result of sintering in the samples (Figure 2), large particles of various shapes (both geometric and shapeless) with a low copper content and a high content of titanium, iron and aluminum (average: 11% Al, 37% Ti, 22% Fe, 26% Cu).

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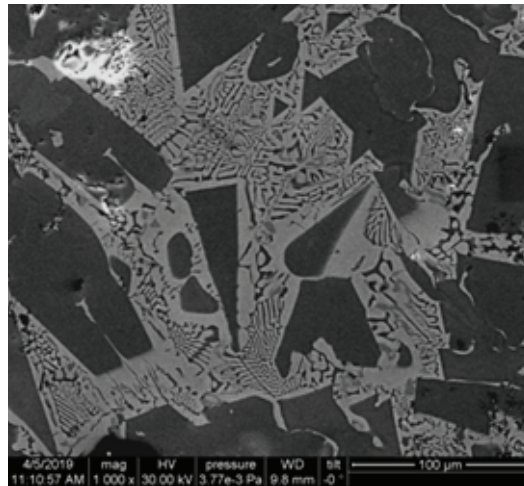
Figure 2: A microsection of a sample sintered at 1273K, × 1000

to the large particles. The distribution of chromium in the sample is uniform. Pores and inclusions are found mainly in the matrix. In the large particles, they are single.

4. Conclusions

Thermodynamic modeling of the system "slag - bronze - aluminum" was carried out in the temperature range 273–4273 K in a helium atmosphere at a total pressure of P = 5.10^4 Pa. Peculiarities of behavior and temperature intervals of the existence of the main components of the condensed and gas phases formed during equilibrium heating are revealed. Thermodynamic data give an idea only about the equilibrium states of complex systems, while the real states of systems are often nonequilibrium. It explains some possible discrepancy in experimental and theoretical results.

The samples obtained in this work consist of large particles of various shapes, most likely containing titanium and iron aluminides, their compounds with each other and with copper, and a matrix solid solution based on copper, from which small particles of similar composition are released to large ones. To obtain a composite material from the mixture considered in this work, a sintering temperature of at least 1273 K is necessary. In the future, it is planned to evaluate the effect of temperature on the structure and properties of the obtained material.

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