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Evaluation of the thermodynamic possibility of *in-situ* composites fabrication in aluminum-metal and aluminum-metal oxide systems through friction stir processing

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Thermodynamic evaluations of the possibility of the interaction reaction of aluminum with powders of Ti, Ni, Fe, TiO_2, NiO and Fe_2O_3 leading to the formation of intermetallics and aluminum oxide Al_2O_3 during friction stir processing (FSP) were carried out. The Gibbs energy was considered as a determining parameter since its change resulted from chemical transformations makes it possible to establish the fundamental possibility of a chemical reaction proceeding under certain conditions. The change in the Gibbs free energy with temperature was calculated, and the Ellingham diagrams were plotted for the reactions observed experimentally during FSP in the systems Al+Ti, Al+TiO_2, Al+Ni, Al+NiO, Al+Fe and Al+Fe_2O_3. The evaluations were performed for 1 mole of aluminum. The selected temperature range was 620 – 720 K because during FSP of aluminum and its alloys the peak temperatures usually fall into this temperature range. It was shown that all considered reactions of aluminum interaction with both pure metals (Ti, Ni, Fe) and oxides (TiO_2, NiO, Fe_2O_3) were thermodynamically possible. However, chemical reactions involving aluminum interaction with TiO_2, NiO and Fe_2O_3 gave higher absolute values of ΔG than those with Ti, Ni, and Fe. In the systems Al+NiO and Al+Fe_2O_3 in reactions involving the formation of intermetallics of $MeAl_3$ type and oxide Al_2O_3 the absolute values of ΔG were approximately the same and in two times higher than that for the system Al+TiO_2. It was concluded that for manufacturing of the *in-situ* Al-based composites by FSP the use of nickel and iron oxides (NiO and Fe_2O_3) is preferable to the pure metals (Ti, Ni, Fe) and the titanium oxide (TiO_2).

Keywords: friction stir processing (FSP), metal matrix composites (MMC), intermetallic compounds, Gibbs energy.

1. Introduction

Due to their high strength-to-weight ratio and corrosion resistance, aluminum alloys are widely used in the aerospace, automotive, and shipbuilding industries. However, aluminum alloys are characterized by low wear resistance. The properties of aluminum alloys can be improved by adding reinforcing particles to the matrix material, producing the so-called metal matrix composites (MMCs). Recently, the use of MMCs has expanded due to the enhancement of mechanical properties and wear resistance [1, 2]. The MMCs are conventionally fabricated using an *ex-situ* approach, in which pre-prepared reinforcing particles are introduced into the matrix material by metallurgical methods such as casting, electromagnetic stirring casting, injection molding. These methods require thorough mixing of the melt due to the poor wettability of the reinforcing particles and their agglomeration [3 – 5]. Another problem is that the reinforcing particles have a tendency to react with the matrix material or can degrade at elevated temperatures, and undesirable compounds can arise that decrease the mechanical properties of the MMCs.

In-situ composite technologies based on the synthesis of strengthening particles directly in the process of composite component mixing are lately becoming more and more widespread [6]. Such technologies provide a tighter contact and good adhesion between the matrix and reinforcing particles, reduce contamination with foreign oxides, adsorbed gases, and moisture. One of the *in-situ* technologies is friction stir processing (FSP). FSP is promising for the fabrication of composites with a metal matrix due to the simplicity of the fabrication process and the reliability of products, in comparison with MMCs obtained by casting and powder metallurgy. FSP is carried out in a solid-phase state without melting the matrix material, which contributes to the refinement of the microstructure and improvement of mechanical properties. FSP requires no additional thermal energy, is environmentally friendly, and does not produce harmful gases [7 – 11].

An approach based on FSP is known to introduce transition metal powders such as Ti [12,13], Ni [14,15], Fe [16], Cu [17], Mo [18] into an aluminum alloy substrate. The reaction between Al and transition metals is exothermic, so the heat released during its course accelerates the reaction. However, it requires a sufficiently high temperature for its initiation, which can be achieved by FSP processing. Multi-pass FSP grinds and mixes metal particles and heats the workpiece. This promotes formation of reinforcing nanoscale intermetallic compounds and, as a result, the high-strength composite material.

Another approach to fabrication of *in-situ* composites is associated with introducing metal oxides instead of pure metals into the aluminum matrix. The MMCs obtained

through FSP of Al-metal oxide compositions have been recently extensively studied [19 – 23]. When aluminum interacts with oxides such as TiO_2 [19,20], NiO [21], Fe_2O_3 [22], and CuO [23], an aluminothermic reaction occurs leading to formation of particles of aluminum-rich intermetallic compounds and Al_2O_3.

Typically, the *in-situ* chemical reaction between reinforcing particles and aluminum matrix can not be completed in a single tool pass, so multi-pass FSP is used. A groove with a width approximately equal to the diameter of the tool shoulder remains on the workpiece surface after the tool passes through. Multi-pass FSP results in an increase in the depth of this groove. The surface of the workpiece must be machined to remove a groove after FSP. The more the number of passes, the more machining is required. The number of tool passes, in turn, depends on the rate of chemical interaction of the reinforcing particles with the aluminum matrix. The faster the reinforcing particles interact with the aluminum matrix, the fewer passes are required to obtain a high concentration of nanosized particles of intermetallic compounds and aluminum oxide. From a practical point of view, it is important that the *in-situ* reaction takes place in fewer tool passes. Therefore, the choice of such a reinforcing additive is relevant, which will allow obtaining a high concentration of reinforcing particles in a minimum number of tool passes during FSP.

Despite a large number of experiments on the *in-situ* formation of the Al-based composites, no comparative assessment of their efficiency has been carried out in terms of the rate of interaction with an aluminum matrix. The purpose of this work was to carry out thermodynamic evaluations of possibility of the reaction of aluminum interaction with powders of Ti, Ni, Fe, TiO_2, NiO and Fe_2O_3 leading to formation of intermetallics and aluminum oxide Al_2O_3 at FSP. The Gibbs energy changes were calculated that allowed us to establish the fundamental possibility of chemical reactions between the aluminum matrix and the mentioned powders under certain conditions.

2. Evaluation method

The temperature dependences of the Gibbs free energy (Ellingham diagrams) were plotted for the reactions observed experimentally during FSP in the Al+Ti, Al+TiO_2, Al+Ni, Al+NiO, Al+Fe and Al+Fe_2O_3 systems. The calculations were performed for 1 mole of aluminum. The temperature range of 620 – 720 K was chosen because the majority of the peak temperatures during FSP of aluminum and its alloys fall into this temperature range [24].

3. Results and discussion

Based on the values of the enthalpy of compound formation, in particular intermetallics, one can assess the possibility of their formation and stability. Pretorius et al. [25,26] proposed the concept of effective heat of formation based on which it is possible to predict the sequence of formation of different intermetallic compounds in binary metal-metal systems depending on concentration of the initial components. Based on this concept and experimental data, we assumed that under conditions of a significant excess of the aluminum concentration over the metal concentration of the hardening phase, only intermetallic compounds of the $MeAl_3$ type will form. Table 1 shows the formation values of enthalpy and entropy of the considered intermetallic compounds $TiAl_3$, $NiAl_3$ and $FeAl_3$.

Al+Ti and Al+TiO_2 systems. According to the experimental data [12,13], the reaction

$$Ti + 3Al = TiAl_3 \quad (1)$$

occurs in the case of FSP of titanium powder in an aluminum matrix. In the Al+TiO_2 system, without taking into account intermediate reactions, the reaction

$$3TiO_2 + 13Al = 3TiAl_3 + 2Al_2O_3 \quad (2)$$

proceeds during FSP [19]. Ellingham diagrams for reactions (1) and (2) are shown in Fig. 1. It is seen that in the investigated temperature range for reaction (1) the $\Delta G(T)$ value is varied in the range of −43…−42 kJ/mol, while for reaction (2) the $\Delta G(T)$ value is varied from −66 to −65 kJ/mol.

Al+Ni and Al+NiO systems. During FSP of the Al+Ni system the intermetallic compound $NiAl_3$ is formed according to the reaction [15]

$$Ni + 3Al = NiAl_3. \quad (3)$$

According to [21], during FSP in the Al+NiO system the reaction

$$3NiO + 11Al = 3NiAl_3 + Al_2O_3 \quad (4)$$

occurs. Fig. 1 shows the dependences $\Delta G(T)$ for reactions (3) and (4) for which the values of $\Delta G(T)$ are varied in the range of −48…−47 kJ/mol and −116…−113 kJ/mol, respectively.

Al+Fe and Al+Fe_2O_3 systems. Under FSP of the Al+Fe system the formation of Fe_4Al_{13} particles was observed [16]. Under FSP of the Al+Fe_2O_3 system as a result of the Al+Fe_2O_3 reaction the particles of metastable phases Fe_4Al_{13} and Al_2O_3 are formed [22,23]. The Fe_4Al_{13} phase is close in composition to $FeAl_3$, and, therefore, in our thermodynamic evaluations we assumed that the reaction

$$Fe + 3Al = FeAl_3 \quad (5)$$

took place in the Ai+Fe system, and in the case of the Al+Fe_2O_3 system, the $FeAl_3$ and Al_2O_3 compounds were formed via the reaction

$$Fe_2O_3 + 8Al = 2FeAl_3 + Al_2O_3. \quad (6)$$

According to the Ellingham diagram for reaction (5), the $\Delta G(T)$ is varied in the range of −21…−19 kJ/mol, while according to reaction (6), the value of $\Delta G(T)$ is varied in the range of −119…−117 kJ/mol (Fig. 1).

Thus, the Ellingham diagrams show that for all considered reactions of the interaction of aluminum with both pure metals (Ti, Ni, Fe) and oxides (TiO_2, NiO, Fe_2O_3) the values of ΔG are less than zero, so they are thermodynamically possible.

Table 1. Enthalpy and entropy of formation of $TiAl_3$, $NiAl_3$ and $FeAl_3$ intermetallic compounds.

	Compound	ΔH^0_{298} kJ/mol	ΔS_{298}, kJ/mol·K
1	$TiAl_3$	−146.44	0.092
2	$NiAl_3$	−150.62	0.110
3	$FeAl_3$	−89.785	0.092

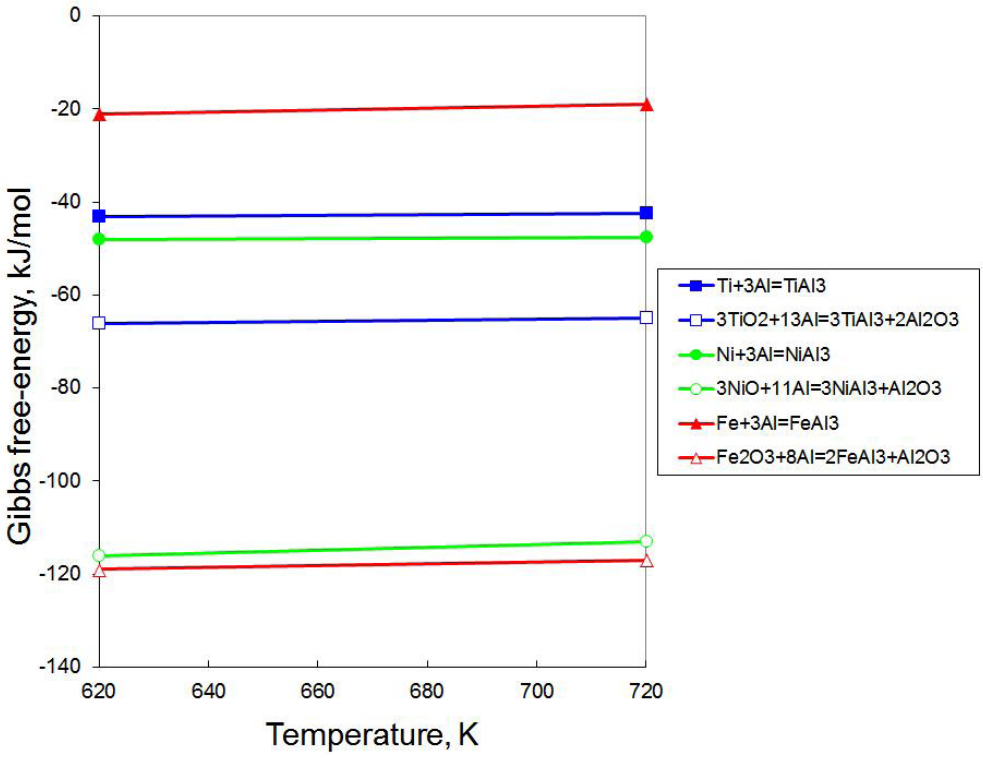

Fig. 1. (Color online) Temperature dependences of the Gibbs energy (Ellingham diagrams) calculated for the interaction of aluminum with Ti, TiO_2, Ni, NiO, Fe and Fe_2O_3.

However, for the *in-situ* formation through FSP of aluminum-based composites, metal oxides TiO_2, NiO and Fe_2O_3 are more preferable as compared to pure metals Ti, Ni and Fe because chemical reactions involving oxides have higher absolute ΔG values. In the systems Al+NiO and Al+Fe_2O_3 in reactions with the formation of intermetallics $MeAl_3$ and aluminum oxide Al_2O_3 the absolute values of ΔG are approximately the same and in two times higher than in the system Al+TiO_2. It can be assumed that the *in-situ* composites in the systems Al+NiO and Al+Fe_2O_3 will be formed faster than in the Al+TiO_2 system under the same FSP conditions.

The experimental data presented in the literature, which could be used to evaluate the rate of formation of intermetallics $MeAl_3$ and Al_2O_3 in aluminum-metal and aluminum-metal oxide systems at FSP, were obtained under different conditions, which does not allow us to compare them with each other. To verify the thermodynamic evaluations presented in this work, in particular for aluminum systems with the titanium, nickel, and iron oxides, comparative experiments should be performed under the same conditions to study the effect of the number of passes at FSP on the volume fraction of formed intermetallic compounds and aluminum oxide, provided that the powders of initial oxides of the same granularity are used.

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