Thermodynamical Prediction of In-Situ Formed Al_3Zr and Al_3Ti Aluminides During Friction Stir Processing based on Effective Gibbs Free Energy Change of Formation (ΔG_i^e) Model

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1. Introduction

Particles reinforced aluminum matrix composites are gaining enormous importance due to their improved mechanical properties compared to the unreinforced matrices. Particles reinforced surface composites fabricated by friction stir processing (FSP) fall in this category where either ex-situ added or in-situ forming reinforcing particles are incorporated into the surface. Meanwhile, the preplaced reinforcing particles on the surface of the work piece and the pre-existing intermetallic particles are fragmented and distributed more uniformly throughout the stir zone (SZ). Severe plastic deformation and the high temperature generated during FSP accelerate the formation of in-situ intermetallic compounds by the chemical reactions at the interface between the matrix and the particles. The in-situ Al_3Zr and Al_3Ti aluminide formation via FSP has not been reported in earlier studies. In this study, an AA3003/ Al_3Zr and Al_3Ti in-situ formed surface composites were synthesized by preplacing Zr and Ti elemental powders into the surface groove of an AA3003-H14 alloy matrix by employing FSP technique. The aluminide phases were predicted by ΔG^e concept and confirmed by the experimental observations.

2. Materials and Methods

A rolled plate of 9 mm thickness of Al3003-H14 alloy was used as a base metal. A longitudinal groove with 1.4 mm width, 4 mm depth, and 160 mm length was machined on the surface of the plates and filled with the Zr and Ti powders before applying FSP. The Zr and Ti powders have an average particle cluster diameter of 20 μm, and a purity of 99.99 %. All samples were subjected to six passes of FSP. The passes were performed at a rotational speed of 1000 rpm and traveling speed of 56 mm min^{-1}. The FSP tool was made of H13 hot working tool steel which had been heat treated to a surface hardness of 52 HRC. The threaded cylindrical pin had length and diameter of 5 and 6 mm, respectively. The temperature was measured using a K type thermocouple at the center of the nugget. The microstructure was observed using an SEM equipped EDS, and X-ray diffraction was used for phase identification. The effective Gibbs free energy change of formation (ΔG_i^e) concept was used to predict the first phase formation at the interfaces in the Al-Zr and Al-Ti systems. The (ΔG_i^e) for the i phase formation can be written as:

$$\Delta G_i^e = \Delta G_i \times \frac{C_e}{C_i}$$

where ΔG_i is the Gibbs free energy change of formation for the i formation phase, C_e is the effective concentration of the limiting element at the interface and C_i is the concentration of the limiting element in the compound.

3. Results and discussion

The focus was the formation of in-situ Al_3Zr and Al_3Ti aluminide particles during FSP at the interface between Zr and Ti particles, and the aluminum matrix through SEM and EDS analysis (Figures 1 and 2, respectively) and, it was further verified by XRD (Figure 3) and, also by the (ΔG^e) concept. The micrograph in Figure 1a reveals that white Zr particles were surrounded by a light gray envelope, which is identified as Zr-rich aluminide by the EDS analysis shown in Figure 1b. Similarly, in Figure 2 formation of Al_3Ti is shown and identified with EDX analysis.

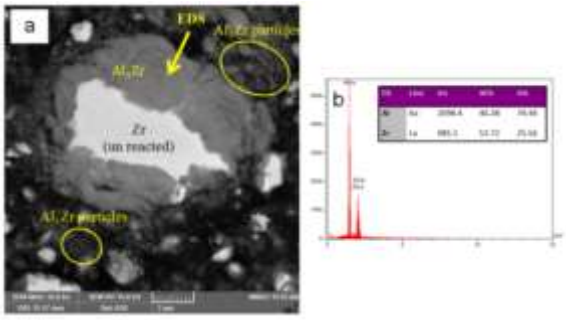

Figure 1. a) SEM Micrograph of the composite reinforced with Zr particles, and b) the corresponding EDS analysis of aluminides

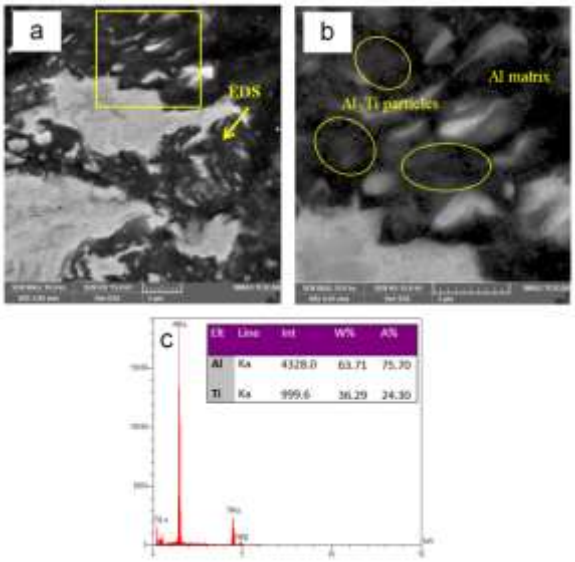

Figure 2. a) SEM Micrograph of the composite reinforced with Ti particles, b) higher magnification of the location marked by a rectangle in image (a), and c) the corresponding EDS analysis of fragmented aluminides

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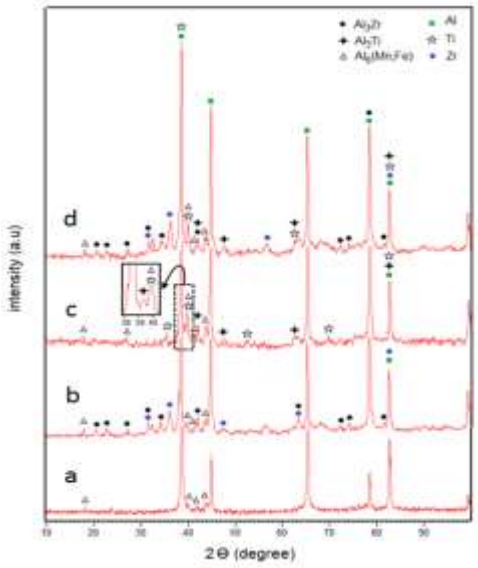

Figure 3. XRD patterns for the a) base metal, b) composite reinforced with Zr particles, c) composite reinforced with Ti particles, and d) hybrid composite

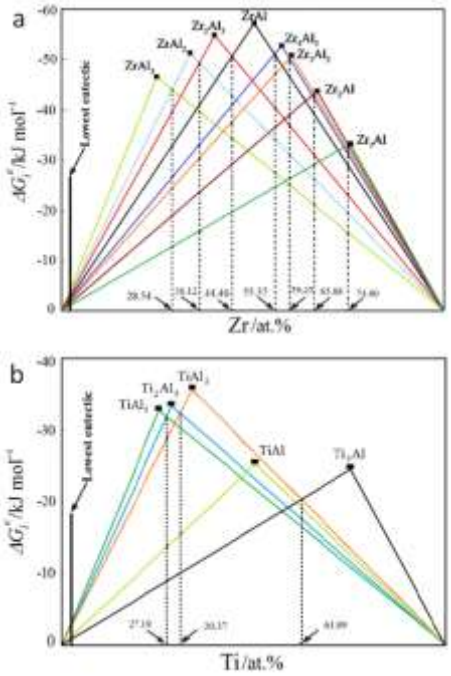

Figure 4. The effective Gibbs free energy change of formation (ΔG_i^e) diagrams for the binary systems of a) Al–Zr, and b) Al-Ti

3.1. Thermodynamic and kinetic assessment of aluminides formation. In this study, the maximum temperature of 410 °C was recorded in the SZ. According to the binary phase diagrams of Al-Zr, and Al-Ti, many intermetallic compounds are expected to form. These are equilibrium phases and the one with the most negative free energy of formation is expected to form first at interface. So, in this temperature range, for the Al-Zr and the Al-Ti systems, Al_3Zr and Al_3Ti intermetallic phases are expected to form first since have lowest free energy change, compared to the other intermetallics in the concerned systems. For convenience, the calculations of the effective free energy change for the Al-Zr and Al-Ti systems can be performed graphically as is shown in Figures 4a and 4b, respectively. As can be noticed, based on (ΔG_i^e), in the Zr composition range of 0-28.54%, 28.54-36.12%, 36.12-44.4%, and 44.4-55.37%, the compounds of Al_3Zr, Al_2Zr, Al_3Zr_2 and AlZr are expected to be formed, respectively. In this study, the effective concentrations at the Al-Zr interface system, are taken as 2 at.% Zr, and 98 at.% Al, (concentration at lowest liquidus temperature). Based on this presumption, and according to Figure 4a, this concentration lies in the concentration range of 0-28.54% , where Al_3Zr possesses the most negative effective free energy change of formation ($\Delta G^e_{Al_3Zr}$= -3.733 kj mol^{-1}), and its formation is thermodynamically feasible. Similarly, for the Al-Ti system, it can be shown that Al_3Ti aluminide is formed first with the lowest free energy ($\Delta G^e_{Al_3Ti}$ = -2.661 Kj/mol).

4. Conclusion

The formation of in-situ Al_3Zr and Al_3Ti aluminides during the FSP were identified at the interface between the powders and the aluminum matrix and confirmed by the analyses. The effective Gibbs free energy change of formation (ΔG_i^e) concept predicted the first phase formed at the interface of the interacting phases, and matched well with the experimental observations.