



Experimental investigation of high temperature oxidation during self-propagating reaction in Zr/Al reactive multilayer films

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ABSTRACT

High temperature oxidation behavior during a fast self-propagating reaction is reported in binary 1Zr/1Al reactive multilayer films. Magnetron sputtered deposited freestanding Zr/Al films with different bilayer thicknesses were investigated experimentally to characterize the oxidation behavior during a self-propagating reaction, ignited by an electrical arc. X-ray diffraction (XRD) analysis of reacted film, ignited in air indicates the formation of oxides of both Zr and Al besides intermetallic compounds. In argon 4.6 atmosphere, oxidation has been reduced, but it is also evident that a very small amount of only ZrO₂ forms. The temperature profiles measured by a high-speed two-color pyrometer exhibit the temperature plateau after reaching the maximum temperature. The static temperatures in plateau vary from 1475 °C to 1588 °C depending on bilayer thicknesses. This temperature plateau becomes more pronounced with increasing bilayer thickness. However, an extended time duration at high temperature plateau characterizes the significant oxidation in air during a self-propagating reaction, which can influence reaction properties and thus broaden the scope of applications.

1. Introduction

As a new class of energetic materials, layer by layer deposited multilayer films can act as reactants and release their stored chemical energy. Generally, the nanoscale alternating reactant layers in multilayer film react in a self-sustained way and release a large amount of heat within milliseconds [1,2]. This self-propagating reaction can be stimulated by an external source of electrical, mechanical or thermal ignition [1,2]. When the reaction starts, fast atomic mixing in multilayers generates heat quickly due to the formation of intermetallic compounds [1–3]. Usually, reactive multilayer films react with a propagation velocity of 0.05 to 80 m/s and heat release varies from 25 to 105 kJ/mol [1–4]. Therefore, the self-propagating reaction offers an exciting opportunity to use such type of films as an external heat source in joining applications [4,5], igniters [6] or airbag initiators [7].

Self-propagating reactions primarily involve the internal mixing of the alternating reactant layers. Usually, two different reactant layers form a bilayer (λ). Many studies reported the self-propagating reaction in Ni/Ti, Co/Al, Ti/Al, Al/Ni and Pt/Al multilayer films, where the film composition and morphology control the reaction heat and propagation [8–12]. During this type of reaction, a reaction front propagates through the films, reacts exothermically by fast atomic mixing and releases heat due to formation of mainly intermetallic compounds. The unreacted

zone ahead of the front is heated by the reaction heat and then continues the reaction itself [13,14]. However, the secondary oxidation reaction was early observed in Sc/Cu multilayers besides intermetallic formation during a self-propagating reaction in air [15]. Then, the recent study characterized the oxidation effect by an extended plateau in the temperature profile in 1Zr/1Al multilayer film ignited in air, compared to that film of Al-rich compositions [16]. The available studies [17] demonstrate the composition dependent reaction velocity and reaction heat in Zr/Al reactive films, which are listed in Table 1. Furthermore, the self-propagating reaction properties of such multilayers namely reaction heat, propagation velocity and temperature profile can also be influenced by the secondary oxidation process. In that event, it is especially important to characterize oxidation behavior in Zr/Al multilayer film during a self-propagating reaction in order to extend their uses.

In this work, the high temperature oxidation behavior has been investigated during the self-propagating reaction in 1Zr/1Al reactive films ignited in air. The goal of this research is to investigate the oxidation effects on self-propagating reaction properties in 1Zr/1Al reactive films for different bilayer thicknesses. We pursue to understand, how additional oxidation reaction influences on self-propagating reaction properties. Consequently, effects of oxidation were characterized comprehensively in terms of temperature evaluation, microstructural

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Table 1

Parameters of film morphology and self-propagating reaction heat and reaction front velocity in Zr/Al multilayer films found in literature.

Composition	Total thickness [μm]	Bilayer thickness [nm]	Reaction heat [kJ/mol]	Reaction front velocity [m/s]	[Ref.]
1Zr/1Al	40	90	–	1.6	[17]
1Zr/2Al	16–50	10–50	-51 ± 4	1.5–11.5	[14]
1Zr/3Al	16–50	10–50, 18–90	-46 ± 3	4–12	[14]

features and reaction products. We also attempt to understand the role of surrounding environment of air and argon for the formation of oxides, which are expected to influence the reaction heat evolution. Moreover, an extended temperature plateau in T-t profile characterizes the significant oxidation in air, which influences the reaction propagation. The experimental results in this work provide the useful information about the oxidation behavior of 1Zr/1Al multilayer films for different bilayer thicknesses of 20–55 nm. In the presence of air, films with comparatively thicker bilayer thicknesses oxidize preferably during a fast self-propagating reaction. In order to utilize their reaction properties, the oxidation characteristics could be beneficial to design such films for extending applications. For example, it can be applied for defeating biocidal chemical compounds or joining applications, where heat release for a longer period is desired. In addition, the formation of ceramic oxide layers on the intermetallic compounds could also allow us to use these systems as protective coatings.

2. Experimental details

The 1Zr/1Al reactive multilayer films were deposited on a cooled copper substrate by DC powered Magnetron Sputter Ion Plating method (MSIP-CemeCon CC 800/8). The individual Zr and Al layers were produced by arranging four targets of Zr and Al (99.99% pure) in an alternating manner. The coating and base pressure were kept at 0.53 Pa and at 9 mPa, respectively. Before the coating process, argon ion etching process was used to clean oxides from the substrate surface. The chemical composition of 1Zr/1Al reactive film was controlled by the relative thickness and atomic density of layers as demonstrated [14]. Here, the relative thickness of Zr and Al layers was controlled to achieve an equiatomic stoichiometry. In this work, 1Zr/1Al multilayer composition was selected due to their propensity to oxidize in ambient air as mentioned [13]. Different bilayer thicknesses of 20–55 nm were produced by adjusting the target powers by keeping constant gas flow rate of 230 mln (milliliter normal per minute) and rotation of 1.2 rpm. The overall deposition conditions are listed in Table 2. In general, the number of bilayer was fixed in all films. Film thicknesses are in the range of 8–15 μm, which differ only within a narrow range. All films are of the similar chemical compositions and bilayer density, the difference is mainly in the bilayer thicknesses. Here, we attempt to understand the effects of bilayer thicknesses on oxidation reactions during a high temperature self-propagating reaction in air. No bias voltage was

Table 2

Deposition conditions and film morphology of 1Zr/1Al reactive multilayer films.

Conditions	Parameters
Reactant combinations	1Zr/1Al
Deposition pressure [Pa]	0.53
Target to substrate distance [cm]	12
Zr target power [kW]	0.65–3.10
Al target power [kW]	0.80–3.30
No. of bilayers	300 ± 20
Bilayer thickness, λ [nm]	20–55

introduced. The as-deposited reactive films have the layer sequences of substrate/Zr/Al/Zr/.../Al. Then the chemical etching of the Cu substrate was performed to make reactive films freestanding as mentioned [18].

Microstructural features of the as-deposited and reacted films were investigated by using Transmission Electron Microscope, TEM (Philips TECNAI) and Scanning Electron Microscope, SEM (Zeiss DSM 982) with an energy dispersive spectrometer (EDX). The quantitative image analysis was conducted by using oxford instruments microanalysis with Aztec materials characterization system. The standard enthalpy of formation (reaction heat) of Zr–Al system was simulated at standard conditions of 298 K and 1 bar pressure by using CALPHAD (CALCulation of PHase Diagrams) based Thermo-Calc 3.1 simulation.

Freestanding 1Zr/1Al foils were placed on a ceramic plate and ignited locally using a 9 V electrical arc in air. The reaction temperature was measured by using a high speed two-color pyrometer (Metis HQ22) at short infrared wavelengths within the spectral range of 1.45–1.8 μm. The spot size of approx. 2 mm was maintained on the plan view of the film during the measurement. The reaction propagation was recorded by using a high speed camera (Keyence VW 9000 high speed microscope) up to 2000 frames per second. Then the reaction front velocity was measured from the captured time variant successive images in the plan view. For every bilayer thickness, reaction velocities of at least seven specimens were measured. Generally, ambient air corresponds the real condition of practical applications. However, the surrounding environment significantly influences the oxidation behavior during a self-propagating reaction. Therefore, the freestanding 1Zr/1Al foils were also ignited by 9 V arc in argon 4.6 atmosphere and investigated, whether oxides formed.

The reaction products were then analyzed after a fast self-propagating reaction in both environments. The reacted Zr/Al films ignited in air were characterized by XRD (Diffractometer Bruker D 5000) using Cu K_α (λ = 0.15406 nm) radiation. The phase analysis was carried out by using crystallography database [19]. The reacted films ignited in argon, were characterized by using X-ray diffractometer (STOE-STADI MP) vertical system working in transmission mode equipped with a linear PSD detector using Mo K_α (λ = 0.70930 nm) radiation.

3. Results and discussions

3.1. Details of as-deposited and reacted 1Zr/1Al films

As-deposited 1Zr/1Al reactive films have the bilayer thicknesses in the range of 20 nm and 55 nm. A cross-section of the freestanding as-deposited 1Zr/1Al film presented in Fig. 1(a), exhibits the fine columnar microstructure. Fig. 1(b) shows the alternating multilayers, which are arranged in a coherent way in the columnar microstructure. This cross-sectional TEM image exhibits also the regularity of deposited Zr and Al multilayers with a controlled thickness. During the deposition process, the premixing layer ('w' shown in Fig. 1b) forms between reactants. The thickness of 1–3 nm can be estimated for the premixing layer. However, all as-deposited films have similar chemical compositions and film morphology of columnar microstructure. EDX analysis shows the presence of 54 ± 2 at. % Zr and 46 ± 2 at. % Al in all 1Zr/1Al reactive films for the bilayers of 20–55 nm. Fig. 1(c) exhibits the cross-sectional SEM image of the reacted film with the reaction products. During an exothermic reaction, the alternating multilayers of Zr and Al react together and form the reaction products of intermetallic at the cross-section. Then the phase formation in all reacted films was investigated by XRD analysis. The reacted freestanding films were ground into smaller pieces as flakes in order to identify the reaction products.

Fig. 2 exhibits XRD diffractograms of Zr/Al films for different bilayer thicknesses after a fast self-propagating reaction in air. This reaction environment corresponds the real conditions for phase formation in practical applications. The results indicate the formation of major intermetallic compounds of tetragonal Al₃Zr (COD #2100751,

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