INFLUENCE OF HEATING RATE ON INFLAMMATION TEMPERATURE OF MUTLILAYER Ti/Al FOIL

D.N. KUZMENKO, A.I. USTINOV, S.G. KOSINTSEV and **L.V. PETRUSHINETS**
E.O. Paton Electric Welding Institute, NASU
11 Bozhenko Str., 03680, Kiev, Ukraine. E-mail: office@paton.kiev.ua

Self-sustaining exothermal reaction of synthesis in multilayer foil consisting of intermetallic forming elements may proceed by means of self-propagation of high-temperature synthesis reaction front through foil (self-propagating high-temperature synthesis (SHS) or as a result of synthesis reaction running through the entire volume (autoinflammation (AI)). The latter is realized under the condition of foil heating up to a certain critical temperature, at which the synthesis reaction runs in the entire volume without external heat supply. In the work influence of foil heating rate on AI temperature was studied in the case of Ti/Al multilayer foil. It is shown that there exists a certain critical heating rate, below which foil AI is not observed, and at heating rates above the critical rate AI temperature decreases with increase of heating rate. Dependence of AI temperature on heating rate is nonmonotonic: at low heating rates AI temperature abruptly decreases, and at further increase of heating rate AI temperature remains practically unchanged. Such nonmonotonic dependence of foil AI temperature on heating rate is associated with running of the process of thermally activated solid phase reactions in it, which are accompanied by formation of intermetallic interlayers on the boundary between titanium and aluminium layers, preventing diffusion mixing of elements. With increase of heating rate, interlayer thickness decreases, promoting AI temperature lowering. 11 Ref., 4 Figures.

It is known that consolidated systems, based on elements capable of entering into synthesis reaction, have become widely applied, primarily due to the possibility of synthesizing refractory compounds, intermetallics and ceramics in the reaction process, as well as depositing coatings on their base, and producing permanent joints [1, 2]. The latter is due, mainly, to the fact that the synthesis process in such systems is accompanied by intensive heat evolution, which is sufficient for realization of welding or brazing process with limited use of external energy sources [3–5]. In the case of local heating of the joint zone through reaction of self-propagating high-temperature synthesis (SHS), heat removal is an essential factor, limiting its application [6]. Conditions for initiation of autoinflammation (AI) in multilayer foil were studied only on powder materials. Therefore, practical implementation of this approach in welding requires determination of the conditions for AI initiation in the multilayer system.

It is known that the nature of heat evolution depends on the method of solid-phase reaction initiation in the system [7]. If system preheating is performed locally, solid-phase reaction can be initiated in the heating area, which will be capable of propagation through the system without external heat supply (SHS-reaction). Here, heat evolution will be localized, chiefly, on the reaction front [7, 8]. When the entire system volume is uniformly heated up to the temperature of synthesis reaction initiation in it (AI temperature), heat evolution proceeds in the entire volume. This allows achieving the maximum intensity of its evolution (thermal explosion) [2].

It is believed that to ensure the conditions of SHS process realization in a reaction system it is necessary to apply a heat pulse, the power of which is commensurate with the heat of intermetallic formation, and for AI the system must be heated to a certain critical temperature, at which the synthesis reaction will run without additional heat supply [2, 8].

First experimental studies of AI conditions were conducted on systems, produced by consolidation of powders of pure elements [1, 2]. In the case of systems with high heat of intermetallic formation, such as Ni/Al, Ti/Al, etc., it was shown that for AI initiation the system had to be heated up to aluminium melting temperature. The latter is due to the fact that in powder materials individual particles are covered by oxide film, and its breaking up is the necessary condi-

tion of the start of reaction between them. Aluminium oxide film is the most stable (aluminium oxide melting temperature is 2040 °C), so that its removal from aluminium particle surface at low temperatures is impossible. It turned out, however, that it is enough to break up the oxide film integrity to start diffusion interaction between the elements. This can be achieved, for instance, at aluminium melting. Owing to bulk effect at its melting, the oxide shell on aluminium particles cracks and aluminium, flowing out of the particle, enters into a reaction with another element [2].

In multilayer systems, produced in the process of layer-by-layer vacuum deposition of intermetallic-forming elements, the situation is different. In this case there is no barrier in the form of oxide film between element layers, hampering their diffusion interaction. Therefore, already at slight heating of such a multilayer structure, element diffusion reaction can run in it [2]. It is clear that such a reaction system structure will have an essential influence on the conditions of synthesis reaction initiation in it. So, for instance, according to results of [7], AI of Ti/Al foil was observed at its heating up to the temperature of about 350 °C.

At the same time, it is known that solid-phase reactions in Ti/Al foil run intensively already at temperatures of about 300 °C, that is accompanied by formation of intermetallic phase interlayers on layer boundaries. The formed intermetallic layers can be barriers for diffusion mixing of elements. It was theoretically shown earlier that presence of such an interlayer has an essential influence on propagation velocity of SHS reaction front [9]. It can be assumed that depending on the rate, at which the foil is heated, the interlayer thickness will change, that should influence its AI temperature.

In this work dependence of foil AI temperature on heating rate was studied in the case of Ti/Al multilayer foil.

Experimental procedure. Multilayer Ti/Al foils, consisting of alternating layers of titanium and aluminium, were produced by the method of layer-by-layer electron beam deposition of elements on horizontally rotating substrate, fixed on a vertical shaft, by the procedure described in [10]. Microstructural analysis of foil cross-section (Figure 1) showed that layer alternation period (i.e. thickness of Ti + Al multilayer) was equal to 68 nm at total thickness of mutlilayer film of 26 μm.

Schematic of the setup for AI temperature measurement is shown in Figure 2. Features of
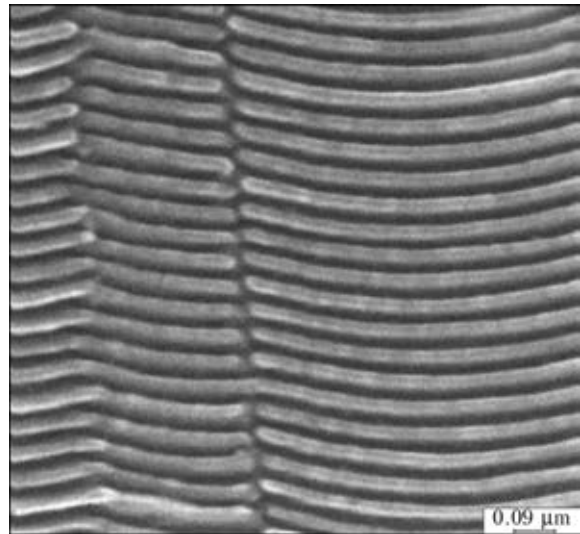

Figure 1. Cross-sectional microstructure of foil obtained by SEM (light strips correspond to titanium layers, dark strips are aluminium layers)

the procedure are due to small weight (of about 50 mg) and small thickness (26 μm) of samples. To reduce the influence of external factors and lower heat losses in the sample, the measuring block, in which the multilayer foil was placed, was shielded by aluminium foil.

AI process was studied with application of mechanically cut out strips of multilayer foil 1.5 cm wide and 2.5–3.0 cm long. The studied strip was fastened by its ends in a holder of nichrome filaments. Foil was heated by infrared radiation from a flat heater made from nichrome wire, which was located under the foil at a fixed distance. Heater power and radiation heating intensity, accordingly, were selected so as to ensure the specified foil heating rate, close to a linear one, right up to AI temperature. Sample temperature was taken by two chromel-alumel ther-
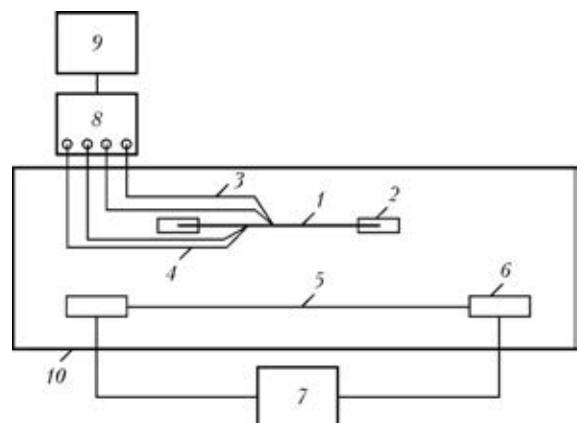

Figure 2. Schematic of experimental set up: *1* — sample; *2* — holder; *3*, *4* — upper and lower thermocouple, respectively; *5* — nichrome holder; *6* — copper contacts; *7* — laboratory autotransformer; *8* — ADC; *9* — computer; *10* — aluminium shield
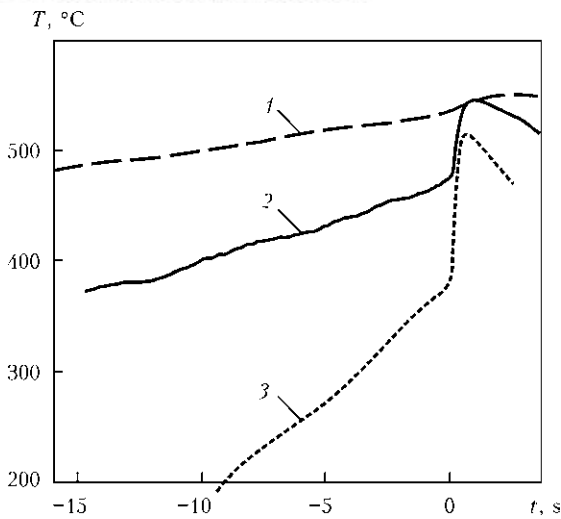
Figure 3. Dependence of temperature on time at constant heating with rates of 2.5 (*1*), 4.6 (*2*) and 21.2 (*3*) °C/s

mocouples of 0.7 mm thickness, which were in contact with the sample from two sides.

Thermocouple readings were recorded by an analog-digital converter (ADC) with data entering into a computer. Difference of thermocouple readings on foil opposite surfaces was within 30—50 °C in the entire studied temperature range. Mean temperature by two thermocouple readings was taken as sample temperature.

Results and their discussion. Figure 3 shows thermograms of heating of Ti/Al foil at different rates. Moment of the start of an abrupt jump of foil temperature (multilayer foil AI) is taken as process count time. Mean heating rate was determined by the slope of straight line section, approximately 200 °C before AI, which describes dependence of temperature on time in the best way. It is seen that foil temperature rises uniformly at the specified rate up to achievement of
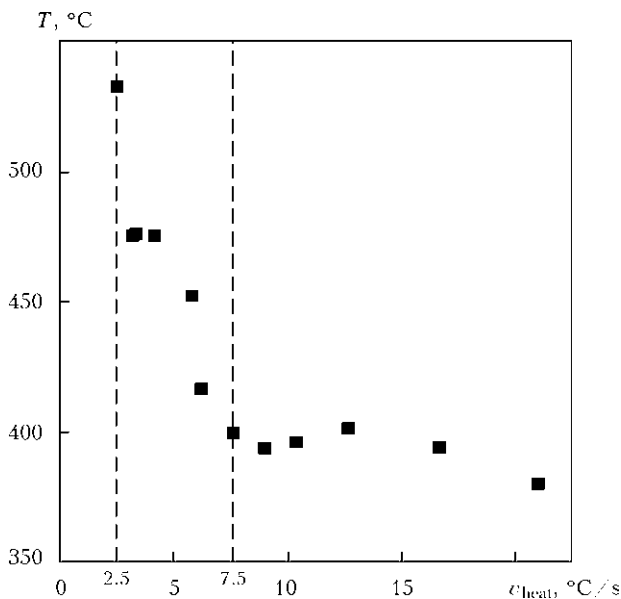

Figure 4. Dependence of multilayer foil inflammation temperature on its heating rate

a certain critical value, at which its abrupt rise (jump) takes place. Such abrupt temperature rise is accompanied by bright glowing through the entire foil volume, that is indicative of intensive heat evolution as a result of running of solid phase reaction (AI).

Presented thermograms show that with lowering of heating rate foil temperature at the moment of AI rises, and at rates below 2.5 °C/s (critical rate) no AI of foil is observed. Note that foil inflammation temperature, obtained for different heating rates, is in the range of 350—500 °C that is by 200—300 °C lower than the temperature of inflammation of powder samples of a similar composition (Ti + Al) [1, 2].

As is seen from the thermograms, presented in Figure 3, foil AI takes place at different temperatures of the sample. AI temperature changes markedly, depending on foil heating rate. For instance, for heating rate of 21.2 °C/s (*3*) it is 380 °C, while for 4.6 °C/s (*2*) it is 475 °C.

Moreover, note the fact that at heating rate lowering, magnitude of sample temperature jump at AI decreases right to its complete disappearance at foil heating at rates below the critical one. As sample temperature is determined mainly by the quantity of elements, entering into the reaction at the moment of AI, from thermogram analysis it can be assumed that with lowering of foil heating rate the volume fraction of elements, which have not reacted before the start of AI process, becomes smaller.

Measurements were the basis for plotting the dependence of AI temperature on heating rate, shown in Figure 4. Obtained data show that foil AI is realized for heating rate higher than a certain critical value v_{cr} ~ 2.5 °C/s. For the case of heating rates below 2.5 °C/s no AI indications were observed, that corresponds to quasistationary running of intermetallic forming reaction. At heating rates higher than the critical value, AI temperature changes. Its dependence on heating rate can be conditionally divided into two ranges: in the first range (2.5—7.5 °C/s) AI temperature decreases markedly with increase of heating rate, and in the second one (at rates higher than 7.5 °C/s) AI temperature is weakly dependent on heating rate.

Thus, three qualitatively different patterns of running of the reaction of intermetallic formation in multilayer foil can be in place, depending on its heating rate. In the case of heating rates below v_{cr}, solid phase reaction runs under the condition of continuous increase of foil temperature. As intensity of reaction running is determined by two factors, namely temperature, increase of

which enhances the diffusion mobility of atoms, and thickness of intermetallic interlayer between the reactive layers, increase of which prevents diffusion mixing of elements, it can be assumed that at heating rates below the critical one increase of interlayer thickness occurs faster that diffusion mobility is increased. It follows that at heating rates above the critical one, at achievement of AI temperature the intermediate interlayers formed at foil heating up to this temperature, did not prevent intensive diffusion mixing of elements.

It is clear that with increase of heating rate interlayer thickness will decrease that promotes AI temperature lowering. This accounts for lowering of AI temperature in the range of heating rates from v_{cr} to a certain transition rate v_{tr}, above which AI temperature practically does not change at further increase of heating rate. At such rates of heating above v_{tr}, intermetallic interlayer, apparently, does not have enough time to form up to the moment of reaction start and structure of multilayer foils heated at different rates practically does not differ from each other at the moment of AI.

Results of works [9, 11] can be proof of the fact that it is exactly intermetallic interlayer thickness dependent on heating rate that influences AI temperature in the long run. In these studies it was shown that velocity of SHS-reaction front propagation slows down with increase of interlayer thickness, and at a certain critical thickness SHS process can be inhibited.

Thus, in the case of Ti/Al multilayer foil it was shown that its AI temperature depends nonlinearly on heating rate. There exists a threshold rate of foil heating (in this case $v_{cr} \sim 2.5$ °C/s), at which its AI does not take place. At increase of heating rate above the critical one (in the range of 2.5−7.5 °C/s) an abrupt lowering of the temperature of AI is observed (from 530 °C at the rate of 2.5 °C/s to 400 °C for 7.5 °C/s), which slows down and becomes weakly dependent on heating rate, when its certain transition value has been reached (above $v_{tr} \sim 7.5$ °C/s). The established non-linear dependence of temperature of multilayer foil AI on its heating rate is associated with a change of its structure, as a result of formation of an intermediate interlayer on the interface of titanium and aluminium layers during heating up to temperatures, at which intensive diffusion mixing of elements can occur.

1. Merzhanov, A.G. (1983) *Self-propagating high-temperature synthesis*. Moscow: Khimiya.
2. Merzhanov, A.G. (2000) *Solid flame combustion*. Chernogolovka: ISMAN.
3. Ustinov, A.I., Falchenko, Yu.V., Ishchenko, A.Ya. et al. (2008) Diffusion welding of gamma-TiAl alloys through nanolayered foil of Ti/Al system. *Intermetallics*, **16**, 1043−1045.
4. Wang, J., Besnoin, E., Duckham, A. et al. (2003) Room temperature soldering with nanostructured foils. *Appl. Phys. Lett.*, **83**, 3987−3989.
5. Duckham, A., Spey, S.J., Wang, J. et al. (2004) Reactive nanostructured foil used as a heat source for joining titanium. *J. Appl. Phys.*, **96**, 2336−2342.
6. Zaporozhets, T.V., Gusak, A.M., Ustinov, A.I. (2011) Conditions of propagation of the SHS reaction front in nanolayered foils in contact with heat-conducting material. *The Paton Welding J.*, **8**, 37−41.
7. Rogachev, A.S., Grigoryan, A.E., Illarionova, E.V. et al. (2004) Gas-free combustion of multilayer bimetallic Ti/Al nanofoils. *Fizika Goren. i Vzryva*, **40**(**2**), 45−51.
8. (2003) *Concept of SHS development as a field of scientific-technical progress*, 7−12, 92−108. Chernogolovka: Territoriya.
9. Zaporozhets, T.V., Gusak, A.M., Korol, Ya.D. et al. (2013) Inverse problem for SHS in multilayer nanofoils: Prediction of process parameters for single-stage SHS reaction. *Int. J. SHS*, **22**(**4**), 217−226.
10. Ishchenko, A.Ya., Falchenko, Yu.V., Ustinov, A.I. et al. (2007) Diffusion welding of finely-dispersed AMg5/27 % Al$_2$O$_3$ composite with application of nanolayered Ni/Al foil. *The Paton Welding J.*, **7**, 2−5.
11. Trenkle, J.C., Koerner, L.J., Tate, M.W. et al. (2008) Phase transformations during rapid heating of Al/Ni multilayer foils. *Appl. Phys. Lett.*, **93**, 081903.