MECHANISTIC STUDIES OF COMBUSTION AND STRUCTURE FORMATION DURING COMBUSTION SYNTHESIS OF ADVANCED MATERIALS: PHASE SEPARATION MECHANISM FOR BIO-ALLOYS

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INTRODUCTION. Among all implant materials, Co-Cr-Mo alloys demonstrate perhaps the most useful balance of resistance to corrosion, fatigue and wear, along with strength and biocompatibility [1]. Currently, these widely used alloys are produced by conventional furnace technology. Owing to high melting points of the main alloy elements (e.g. $T_{m.p.}$(Co) ~1768 K), high-temperature furnaces and long process times (several hours) are required. Therefore, attempts to develop more efficient and flexible methods for production of such alloys with superior properties are of great interest.

The synthesis of materials using combustion phenomena is an advanced approach in powder metallurgy [2]. The process is characterized by unique conditions involving extremely fast heating rates (up to 10^6 K/s), high temperatures (up to 3500 K), and short reaction times (on the order of seconds). As a result, combustion synthesis (CS) offers several attractive advantages over conventional metallurgical processing and alloy development technologies. The foremost is that solely the heat of chemical reaction (instead of an external source) supplies the energy for the synthesis. Also, simple equipment, rather than energy-intensive high-temperature furnaces, is sufficient.

This work was devoted to experiments on CS of Co-based alloys by utilizing thermite (metal oxide-reducing metal) reactions, where phase separation subsequently produces materials with tailored compositions and properties. Owing to high reaction exothermicity, the CS process results in a significant increase of temperature (up to 3000 °C), which is higher than melting points of all products. Since the products differ in density, phase separation may be a gravity-driven process: the heavy (metallic phase) settles while the light (slag) phase floats. The goal was to determine if buoyancy is indeed the major mechanism that controls phase segregation.

RESULTS AND DISCUSSION. Fundamental studies of phase separation during CS of Co-based alloys were carried out in both terrestrial and microgravity conditions. The details of the experimental set-up, as well as used procedure, are described elsewhere [cf. 3,4]. Briefly, the samples were placed in the reaction chamber, which was evacuated (approximately 10^3 Pa) and then filled with high-purity argon to 10^5 Pa. An electrically heated tungsten coil was used to initiate the combustion reaction, typically from top of the sample. The combustion front propagation was recorded through a quartz window by using a video camera. The velocity of wave propagation was determined by statistical analysis of the obtained video images (30 frames/s). The temperature-time history of the process was measured by thermocouples (Type C, diameter 0.508 mm, Omega Eng.). Finally, quenching, which involves rapid cooling of the combustion front in massive copper cone-shaped block, was utilized to investigate the mechanisms of microstructural transformation taking place during CS.

While the Co-based alloy used in orthopaedic implants contains other metals such as Cr and Mo [1], for a fundamental study of phase separation, the simpler Co_3O_4-Al system was used in the present work. The following overall reaction occurs in the combustion wave front:

$$3Co_3O_4 + 8Al + xCo + yAl_2O_3 \Rightarrow (4+y)Al_2O_3 + (9+x)Co \qquad (1)$$
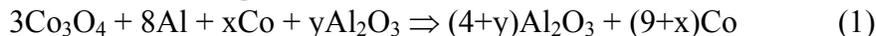
where x and y are coefficients that can be varied to obtain the desired product composition and combustion temperature. Since the metal fraction in melt may be a controlling factor of phase separation process, systems with different ratio of metal and slag were investigated (Table I).

Table I. Characteristics of reaction compositions investigated.

Composition	T_{ad}, K	$T_{m.p.}$, K Al_2O_3	$T_{m.p.}$, K MeO	$T_{m.p.}$, K Me	$T_{m.p.}$, K Al	Metal vol. %
$3Co_3O_4 + 12Co + 8Al \Rightarrow 21Co + 4Al_2O_3$	2690	2327	2123	1768	933	49
$3Co_3O_4 + 8.5Co + 8Al \Rightarrow 17.5Co + 4Al_2O_3$	2966	2327	2123	1768	933	44
$3Co_3O_4 + 3.2Al_2O_3 + 8Al \Rightarrow 9Co + 7.2Al_2O_3$	2677	2327	2123	1768	933	19

Phase Separation. It was shown that the yield, ψ (defined as ratio of the metal product mass to the theoretical metal mass formed from reaction), reaches high values under μg conditions and increases only slightly with gravity (see Table II and also ref. 3). These results suggest that some non-gravity driven phase separation mechanism plays an important role in the CS process of Co-based alloy.

Table II. Average yield (%) of the alloy in different experimental conditions.

Systems	Normal Gravity, 1 g		Microgravity, 10^{-2} g	
	Propagation Direction		Propagation Direction	
	Downward	Upward	Downward	Upward
Co (8.5)	83	96	73	86
Co (12)	90	98	73	88

It was also observed that under both gravity and microgravity conditions, after reaction and separation, thin alumina tube formed on the container wall (see Fig.1 for schematic representation). It was also seen that the height of this tube decreases with increase of gravity condition. In fact, under overload conditions (1.7 g), instead of tube an alumina cap forms on top of metal ingot. By making experiments using different container materials, it was shown that alumina tube formed in all cases and that the container material, did not influence the phase separation process (i.e. yield). The following picture of phase separation in the system was thus suggested. The reaction starts at about melting point of Al ($T_{m. p.}$ = 933 K), which coats solid metal oxide (Co_3O_4) particles, leading to their dissolution (see next section for details). Further, after reaction when temperature is above melting point of all products, two immiscible liquid phases (Co and Al_2O_3) form (Fig. 2b). In cooling stage, when temperature decreases, Al_2O_3 ($T_{m. p.}$ = 2327 K) crystallizes first, while Co ($T_{m. p.}$ = 1768 K) remains in liquid form (Fig. 2c). Since at this point, the only solid phase for Al_2O_3 to wet is the container it spreads along its wall (Fig. 2d). From these considerations, it can be concluded that the formation of oxide tube is primarily a characteristic of the system and does not depend strongly on wettability of the container.
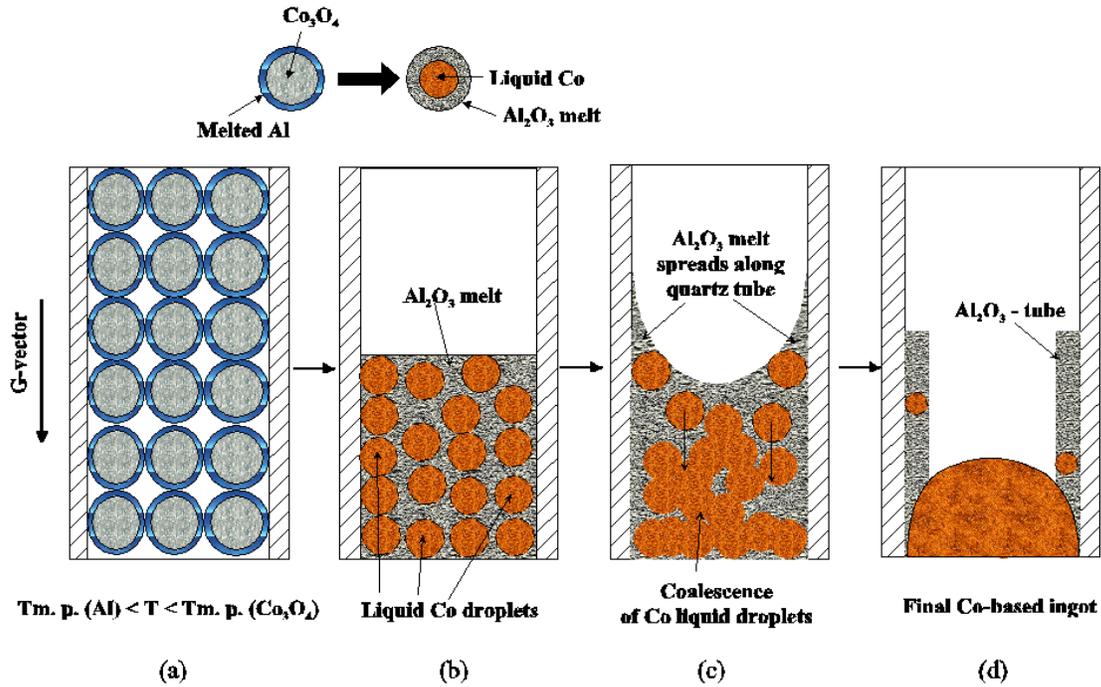
Fig. 1 Schematic representation of structural transformations during combustion in Co-based system.

Mechanism of Reaction and Phase Separation. Investigations of quenched samples reveal that in general, one can identify three characteristic zones: (i) the most dynamic zone of initial products formation; (ii) post-reaction zone of cobalt coalescence; (iii) final product zone. The details of structural transformations in zone (i) are shown in Fig. 2.
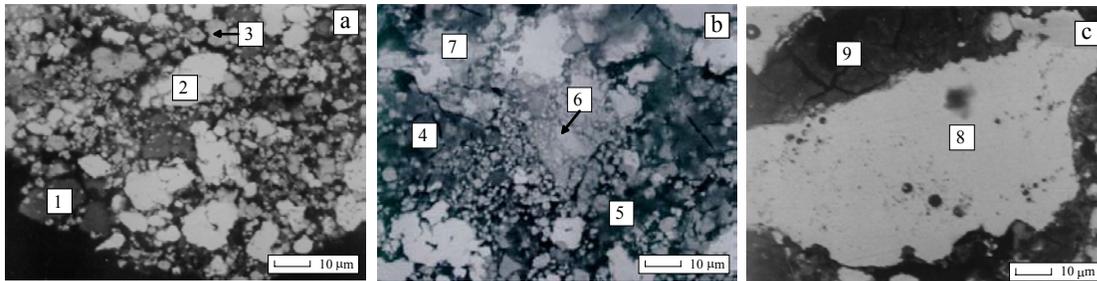
Fig.2 Back-scattered electron images of microstructural transformations in the initial product formation zone: (a) Precursor reactants; (b) Complex oxides and intermetallic compounds; (c) First stage of phase separation. The numbers refer to phases identified in Table III.

It can be seen (Fig. 2a) that initial medium remaining in the cone tip consists of relatively large (~ 20 μm) Al (phase 1) and Co (phase 2) particles, and finer (~ 5 μm) Co_3O_4 (phase 3) powder. This is followed by a relatively thin (~ 300 μm) reaction region, where complex oxides (4, 5) and intermetallic compounds (6, 7) are observed (Fig. 2b). At the end of this region, Co-rich (8) areas surrounded by alumina-rich phases (9) formed rapidly. These observations suggest that reduction of cobalt oxide, as well as metal-metal reactions in the system, occur in this stage due to dissolution of solid Co_3O_4 and Co in liquid aluminum, with formation of various complex phases.

More difficult to understand is the rapid formation of relatively large (~ 100 μm) Co-rich areas (8 in Fig. 2c) surrounded by Al_2O_3 layers (9 in Fig. 2c) at the end of this zone. The above results, along with effective phase separation in microgravity, suggest that the following non-

Table III. Relative intensity of elemental components in combustion zone.

Location	Relative Intensity (%)			Comment
	Al	Co	O	
1	Balance	Trace	Trace	Al
2	Trace	Balance	Trace	Co
3	7.5	72.9	19.6	Co_3O_4
4	23.5	62.1	14.4	Co_xAlO_y
5	14.2	73.7	12.1	Co_xAlO_y
6	44.0	51.2	4.8	$CoAl_x$
7	51.5	46.4	2.1	$CoAl_x$
8	Trace	Balance	Trace	Co
9	76.6	9.6	13.8	Al_2O_3

gravity driven mechanism may be responsible for the observed features. While complex oxides form due to dissolution of Co_3O_4 in liquid aluminum, the process accelerates dramatically at melting point of Co_3O_4 ($T_{m. p.} \sim 2100$ K), and at some point concentration of Co in the melt reaches a critical value above which only two immiscible liquids (Co and Al_2O_3) may exist. The latter leads to rapid formation of these liquid phases simultaneously with their separation at the microscopic level. Further segregation of immiscible liquid phases and coalescence of Co agglomerates occurs along an extended (~ 2 cm) post-reaction zone (ii) before reaching the final products region (iii), which involves large areas (~ 5 mm) of Co surrounded by layers of Al_2O_3.

SUMMARY. The obtained results lead to the following general conclusions: (i) non-gravity driven mechanisms play an important role in the phase separation process in such systems [see also 3]. Analysis of microstructural transformations in the quenched samples reveals the true reaction and phase separation mechanisms taking place in the combustion wave. The results show that the segregation process involves two stages: (1) separation of immiscible liquids in the reaction front, and (2) capillary coalescence of liquid metal droplets in solid oxide matrix in the post-reaction zone. These non-gravity driven processes explain the essentially complete phase separation achieved even in microgravity conditions [see also 4]. Based on the general understanding of phase separation mechanism in the investigated CS-systems, a novel technology for synthesis of Co-Mo-Cr bio-alloy has been developed [5].

Acknowledgements

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