Journal of Alloys and Compounds 738 (2018) 10–15

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Pressure controlled micro-viscous deformation assisted spark plasma sintering of Fe-based bulk amorphous alloy

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ARTICLE INFO

Article history:
Received 30 August 2017
Received in revised form
12 December 2017
Accepted 14 December 2017
Available online 16 December 2017

Keywords:
Bulk amorphous alloy
Spark plasma sintering
Contact pressure
Viscous flow deformation

ABSTRACT

In this paper, the theoretical framework of viscous flow deformation is presented as a model to investigate the inherent role of applied pressure in the densification of Fe-based amorphous alloy powder during spark plasma sintering. The proposed model revealed that the evolution of the structural geometry of the powder compact resulted in an amplification of the applied pressure to a larger contact pressure. The resulting pressure controlled compressive viscous flow deformation of the particles exhibited the contribution of increased applied pressure towards enhancement of densification and thus confirmed the validity of the present model for analyzing pressure-assisted sintering of amorphous alloy powder. The application of this theoretical model correctly predicted the trend of increasing final density of the compacts with pressure while further improvement on its accuracy can be attained upon establishment of the relative contribution of mass flow and deformation of powder particles towards their consolidation.

1. Introduction

The perpetual quest to circumvent limitations of high cooling rates during solidification processing of bulk amorphous alloys has paved the way to net-shape manufacturing of these materials under pressure at temperatures considerably lower than their melting point [1]. For example, solid state powder consolidation techniques such as hot pressing (HP) and spark plasma sintering (SPS) are being increasingly investigated in order to fabricate these alloys in bulk sizes such that their attractive high strength, elastic limit and corrosion resistance can be utilized for structural applications [2]. SPS is particularly alluring with attributes such as high heating rates and short sintering cycles [3] and is thus being increasingly utilized for the pressure-assisted processing of a wide range of bulk amorphous alloys. Among the numerous parameters employed, applied pressure is of critical importance for the successful accomplishment of an SPS cycle as it affects not only densification of the powder [4] but also retention of the amorphous phase [5]. Numerous studies, thus focused on the determination of the role of applied pressure during SPS of amorphous alloy powders, have thus revealed an increase in packing density, mechanical locking [6] and bonding between the particles [7] with increased pressure. High pressure has also been reported to lower activation energy for mass transfer resulting in an overall increment in density [8].

Investigations on the effect of pressure have been largely limited to the supercooled liquid region (SLR) of these amorphous alloys in order to utilize the drastic reduction in viscosity of these materials therein [9,10]. Nevertheless, processing even below the crystallization temperature, T_x, in the SLR introduces metastable microcrystalline phases in the amorphous matrix [11]. For example the amorphous alloy, $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$, used in the present work, has been reported to not only undergo devitrification to yield Y-Mo rich islands and nanocrystalline carbides [12] but also lead to the formation of medium-range-ordering colonies [13] upon heating below T_x. Such partial crystallization can lead to drastic embrittlement [14] and has been widely observed in a number of transition metal-metalloid amorphous alloys [15]. Thus it is imperative to restrict the same in order to avoid catastrophic failure that may severely limit their application. On the other hand, processing just below the glass transition temperature, T_g, considerably reduces the possibility of crystallization, thereby facilitating net-shape manufacturing [1]. Comparatively higher viscosities at these temperatures than in the SLR also mandates application of higher pressures that are likely to result in a pronounced manifestation of

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https://doi.org/10.1016/j.jallcom.2017.12.147
0925-8388/

their effects, in addition to an increase in density. For example, during pressure-assisted SPS of Zr-based bulk amorphous alloys [16], deformation of the powder particles was observed without the occurrence of crystallization. This resulted in the pores being polyhedral in shape with their walls oriented in various directions giving rise to a triaxial state of stress and generation of multiple shear bands leading to plastic ductility. This was further confirmed by the deformation of particles at the bonding necks during SPS of Fe-based bulk amorphous alloys [17]. Increased pressure was also observed to effectively breakdown oxide layers at the surface of Al-based amorphous alloy powders [18]. This eliminated excessive localized heating preserving the amorphous structure and resulting viscous flow at the particle interfaces enabled complete densification of the bulk amorphous alloy compacts. The highlights of these conclusions are summarized in Table 1.

In spite of these extensive experimental studies, considerable differences between the pressure employed and the one conveyed at the interparticle contacts [19,20] render it difficult to draw inferences on the inherent role of pressure on the SPS of bulk amorphous alloys. Hence it is necessary to analyze the densification of these alloys during SPS within an appropriate theoretical framework that incorporates the relationship between applied and contact pressures in order to establish a cogent understanding of the contribution of pressure to sintering. This paper, therefore, investigates the pressure-assisted SPS of Fe-based bulk amorphous alloy powder entirely below its T_g. The effect of systematic increments in applied pressure on its densification is presented followed by a discussion on the evolution of the structure of the compact and interparticle contact pressure during sintering. These results are analyzed under the theoretical framework of compressive viscous flow deformation of particles in order to establish the inherent role of pressure during SPS of bulk amorphous alloys.

2. Experimental procedure

Amorphous alloy powder with overall composition $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ (at.%) and mean size of particles about 40 μm was employed in this investigation. It exhibited a glass transition temperature, T_g of 575 °C measured at a heating rate of 20 °C min^{-1} [21]. Approximately 6 g of the powder was sintered in a commercial SPS unit (Thermal Technology, SPS 10-3) using a graphite die and a thermocouple for temperature measurement. The powder was first prepressed under the desired applied pressure of 20, 30, 50 and 70 MPa. This was followed by sintering from room temperature upto 560 °C at a constant heating rate of 25 °C min^{-1} while the pressure was kept constant in each case. These experiments yielded samples of diameter 15 mm and thickness of about 5 mm. Punch position was continuously recorded during each experiment and utilized for calculating the instantaneous fractional density of the sintered compacts. The morphology of the sintered powder particles was observed in a scanning electron microscope (FEI, Quanta 600).

Table 1
Summary of conclusions on pressure-assisted spark plasma sintering of different bulk amorphous alloys without crystallization.

Composition	Conclusion(s)	Ref.
$Zr_{55}Cu_{30}Al_{10}Ni_5$	Increased Young's modulus and reduced plastic ductility with increased pressure	[16]
$Al_{86}Ni_6Y_{4.5}Co_2La_{1.5}$	Breakdown of surface oxide layers with increased pressure	[18]
$((Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05})_{96}Nb_4$	Mechanism of compaction was deformation of individual particles due to viscous flow	[17]

3. Results and discussion

3.1. Densification

In order to understand the effect of applied pressure on the densification of Fe-based bulk amorphous alloy during spark plasma sintering, the increase in the fractional density, ρ, of the compacts with temperature under 20, 30, 50 and 70 MPa was investigated. This was accomplished by estimating ρ according to [22]:

$$\rho = \frac{L_o}{L}\rho_o \quad (1)$$

where ρ_o is the fractional green density and L_o (mm) and L (mm) are the thicknesses of the green and sintered compacts respectively. With an increase in the applied pressure the thickness of the green compacts decreased progressively and were measured to be 6.9, 6.6, 6.5, and 6.1 mm under 20, 30, 50, 70 and MPa, respectively. The corresponding values of ρ_o used for estimating ρ were 0.63, 0.65, 0.66, and 0.67. The estimated fractional densities are presented in Fig. 1 where it can be clearly observed that under all applied pressures they increased with temperature during sintering. In general, with an increase in the applied pressure from 20 to 70 MPa the fractional density attained higher values at the same temperature of sintering. Some aberrations from this general trend were observed around 540 °C for 30 and 50 MPa, possibly due to minute variations in the mass of powder that occurred during pouring into the die for sintering as well as the resolution in the measurement of punch displacement. However, the overall trend of an increase in fractional density with applied pressure was valid. Indeed, under the highest applied pressure of 70 MPa in this study, the compact underwent the largest densification attaining the highest fractional density of almost 0.98 at the end of the sintering cycle. On the other hand, the final fractional density attained by the compact sintered under an applied pressure of 20 MPa was, in contrast, only 0.80.

3.2. Contact pressure

The enhancement of densification with the increase in applied pressure was further investigated in order to identify its inherent effect. During pressure-assisted sintering there exists a

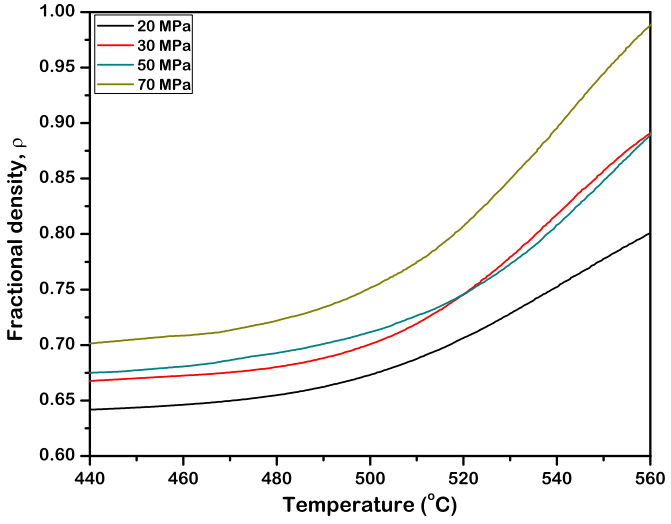

Fig. 1. Fractional density of Fe - based bulk amorphous alloy spark plasma sintered at different pressures.