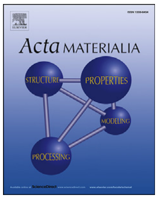
Acta Materialia 125 (2017) 327–339

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat



Full length article

Deposition mechanisms of metallic glass particles by Cold Gas Spraying

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ARTICLE INFO

Article history:
Received 4 August 2016
Received in revised form
27 November 2016
Accepted 5 December 2016

Keywords:
Metallic glasses
Reynolds number
Homogeneous flow
Shear thinning
Cold Gas Spray

ABSTRACT

The deposition mechanisms of metallic glass particles impacting a substrate at high velocity (385–485 m/s) and temperatures near and above the glass transition are studied using finite element modeling. The deformation mechanisms of the metallic glass particles in these conditions are extremely dependent on their Reynolds number only leading to deposition and bonding at high Reynolds number. Unlike early works, this study includes the homogenous flow deformation under Newtonian and non-Newtonian regime modeled using the constitutive equations of the free-volume model. The computed results are compared against experimental data of metallic glass coatings build-up by Cold Gas Spray. A critical value of the Reynolds number is found by both experiments and simulation, showing that it is a useful parameter to control the activation of viscoplastic deformation and bonding of metallic glass particles. Interestingly, this work demonstrates that deposition of metallic glass particles is governed by a cooperative movement of the liquid instead of a simple shear instability effect at the particle-substrate interface unlike polycrystalline metals.

1. Introduction

Thick metallic glass (MGs) coatings offer interesting physical and chemical properties to be applied at industrial level [1–4]. Despite the interest for this type of coatings, they are not fully developed because the deposition techniques able to produce them lead to undesired coating defects, i.e. porosity, oxidation and crystallization [5–8]. Cold Gas Spray (CGS) is a deposition technique consisting in the impact of accelerated and heated particles onto a substrate. The formation of coatings by CGS is characterized for being a solid-state process avoiding many detrimental effects of conventional thermal spray techniques such as oxidation and undesired phase transformations [9–11]. In the case of MGs, early works [12–15] found useful to preheat the MG particles within the supercooled liquid region prior to impact, i.e. at temperatures above the glass transition (T_g) and below the crystallization temperature (T_x), where MG particles experience softening and improved deposition efficiency with respect to the non-preheated MG particles. The coatings were successfully built-up but the deformation mechanisms needed for deposition and bonding were not fully described. The lack of information about the mechanisms of deformation of MG particles acting at impact is associated to the difficulty of measuring many important quantities experimentally such as strain and stress. The short time of impact hinders as well any other study from direct experimental observation about the response of the MG particle during impact [16]. As a result, manufacturing MG coatings by CGS with a good quality is still a challenge.

For crystalline materials, the deformation mechanisms of particles impacting a metallic surface at high velocity and moderate temperatures, i.e. sprayed by CGS, are well-studied and fairly well understood. The work of Assadi et al. [9] was the first to point out that successful bonding of an impacting particle requires localized deformation and adiabatic shear instabilities at the particle-substrate interface both occurring at sufficiently high impact velocities, above the so-called critical velocity. This work allowed subsequent studies to develop a general formulation, incorporating material properties and particle size, to compute the critical velocity in crystalline materials. The generalized approach supplied the tools needed to predict optimum spray conditions for successful

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http://dx.doi.org/10.1016/j.actamat.2016.12.007
1359-6454/

cold spraying of various crystalline materials and establishing a window of deposition depending on the mechanical and thermal properties of the sprayed material.

The first attempts to calculate the window of deposition of Fe-based MG deposited by CGS [15] used the model for crystalline alloys. However the calculations did not include considerations about the properties and deformation mechanisms of MGs in the supercooled liquid region. The MG deformation behavior was accounted as a simple crystalline alloy with an arbitrarily chosen softening temperature. As a result, the window of deposition could not be generalized to other MGs. A recent work has shown that the deposition efficiency of MGs is not well-correlated to the velocity at impact unlike crystalline materials. Instead, a model based on the impact of a liquid droplet onto a surface has been used to correlate the experimental deposition efficiency with the Reynolds number (*Re*) of the MG particle before impact [17]. The *Re* is defined by the ratio between the inertial and viscous forces of MGs at impact, and is useful from the engineering point of view with the aim to predict the window of deposition of MGs from the velocity and viscosity of the particles at impact. The use of *Re* to predict the conditions for coating build-up suggests that the deposition of MG particles is mainly activated by their temperature, i.e. low viscosities, and the inertial forces which promote the activation of viscous flow. This marked dependency on the temperature is contrasted to crystalline materials, therefore it is necessary to note that while the yield stress of a majority of crystalline materials may change by a maximum of 2 orders of magnitude from room temperature to the typical impacting temperatures, a metallic glass in its supercooled liquid state can change its viscosity by 8–10 orders of magnitude from its glass transition to typical impacting temperature. In our previous work, a critical *Re* (Re_{critical}) was found to reach significant deposition efficiencies. The Re_{critical} is then defined as the point at which inertial forces are able to activate viscous flow inside the MG particle and hence, the MG particle sufficiently deforms to produce a typical CGS coating. Although the model successfully describes the deposition of MGs and allows the possibility to compute a window of deposition for different MGs, the deformation mechanisms of the MG particles at impact are not yet fully understood.

As mentioned, MGs can be deposited by providing them a proper quantity of thermal energy since MGs deform homogenously at high temperatures, especially above T_g, where MGs become a supercooled liquid with low viscosity [18,19]. In this regime, the mechanisms of deformation allowing the deposition of the MG particles are associated to the liquid viscosity of the particle at impact and its evolution after impact. Zhou et al. [20] already simulated the impact of a MG particle onto a copper substrate using finite element analysis. In their study, the deformation of the MG particle by CGS was modeled as a viscoplastic material and its plasticity depended on the Newtonian viscosity of the liquid. The viscosity at any temperature was therefore modeled as that of a simple Newtonian liquid following the Vogel-Fulcher-Tamman (VFT) equation. Zhou et al. concluded that deposition is reached at high softening of the particles, i.e. low Newtonian viscosities at impact, such as it was predicted by Concustell et al. [17]. However, the model in Ref. [20] did not take into account the shear localization experienced by MGs at high strain rates and temperatures below T_g, leading to unrealistic results at low impacting temperatures. Furthermore, MGs exhibit a non-linear response to shear stress where viscosity is a shear rate dependent quantity, i.e. non-Newtonian behavior. According to well-known deformation maps of MGs, a transition from non-Newtonian to Newtonian regime is often characteristic of MGs undergoing homogenous flow [19,21]. At the extreme impact conditions involved in the CGS process, the transition from non-Newtonian to Newtonian flow must be taken into account since the high strain rates (around 10^6 - 10^7 s^{-1}) and thermal interaction at the interface affect directly the deformation behavior of the MG particle during impact. In fact, previous experimental observations suggest the necessity of shear thinning, i.e. non-Newtonian flow, for achieving the deposition of MG particles by CGS [22].

A detailed modeling study of the deformation of MG particles at different *Re* is carried out in this work. The viscoplastic behavior of MG particles at temperatures above T_g including the non-Newtonian and Newtonian behavior of the deforming MG undercooled liquid is considered. The constitutive equations to describe the viscous response of MGs are based on an earlier development using the free volume theory of MGs for temperatures in the range of the supercooled liquid region [23]. The finite element analysis software ABAQUS/Explicit has been used to recreate a single impact of a MG particle onto a metallic substrate and the outcomes of the simulations have been compared to experimental results obtained in this work. A set of *Re* has been employed based on experiments and previous works [17,22] and implemented into the simulations to generate plots of energy, stress, plastic strain, viscosity and temperature with the aims of comprehending the mechanisms of deposition of MGs by CGS and their dependence on the *Re* of the particles before impact.

2. Procedure

2.1. Experimental method

Fe-base MG coatings of composition $Fe_{72.8}Si_{11.5}Cr_{2.2}B_{10.7}C_{2.9}$ at% (Kuamet 62B, Epson Atmix Corp, Japan) were deposited onto carbon steel substrate AISI 4340 by CGS using a spherical feedstock powder with a particle size distribution ranging from 20 μm to 40 μm, with a $d_{\text{mean}} = 30$ μm. Substrate plates were prepared by grinding using 240 grit SiC paper prior to spraying. The CGS System Kinetics® 4000/17 kW (CGT, Ampfing, Germany) was employed to obtain the MG coatings using N_2 as carrier gas. The detailed process parameters used in this work for obtaining the Fe-base MG coatings are shown in Table 1. The different experimental conditions led to different particle velocities, V_{imp}, and temperatures, T_{imp}, at impact and are shown in Table 1. The experimental value of $Re = \rho \cdot d \cdot V_{imp}/\eta$ at impact (where: ρ = particle density; d = particle diameter; V_{imp} = particle impact velocity; $\eta_{Newtonian}$ = Newtonian viscosity of the glass at the impact temperature), hereafter designated as Re_{Exp}, was calculated from the impact velocity and the Newtonian viscosity according to the procedure described in Ref. [17].

The deposition efficiency (DE) was calculated by measuring the final coating mass after spraying and by dividing it over the total powder mass sprayed onto the sample without overspray. Microstructural investigations of the MG coatings were carried out by scanning electron microscopy (SEM) on the cross-section of the samples. The adhesive strength of the MG coatings to the substrate was determined following the ASTM C633-13 standard. The adhesion test was performed on 3 samples of each selected coating. A Servosis model ME-402/10 test apparatus was used at a velocity of 0.02 mm/s^{-1}.

2.2. Modeling: defining metallic glass behavior

2.2.1. Constitutive model based on the free volume mechanism

A number of constitutive models have been proposed in early works being able to capture the transition from non-Newtonian to Newtonian flow of MGs under various combinations of strain rates and temperatures [18,21,23–28]. Among classical models, the free volume model is likely the most widely used for explaining flow, diffusion, structural relaxation, glass transition, and mechanical properties of MGs. The free volume model is based on the concept