G Model
JMST-1017; No. of Pages 5

ARTICLE IN PRESS

Journal of Materials Science & Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

A promising new class of plasticine: Metallic plasticine

Yiping Lu [a,b,1], Zhongyi Tang [a,1], Bin Wen [b,1], Gang Wang [c,1], Shiwei Wu [c], Tongmin Wang [a,*], Yubo Zhang [a], Zongning Chen [a], Zhiqiang Cao [a], Tingju Li [a,d,**]

[a] *Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China*
[b] *State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China*
[c] *Laboratory for Microstructures, Institute of Materials, Shanghai University, Shanghai 200444, China*
[d] *Key Laboratory of Materials Modification by Laser, Ion, and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China*

ARTICLE INFO

Article history:
Received 1 May 2017
Received in revised form 24 May 2017
Accepted 23 June 2017
Available online xxx

Keywords:
Metallic plasticine
Alloy design
Conductivity
Microstructure design
Microstructure

ABSTRACT

Soft, malleable, and non-dry on exposure in air are the typical features for plain plasticine, which lead plasticine to be widely used in many industrial fields and our daily life. As a kind of clay, poorly electric conductivity and thermal conductivity of plain plasticine seriously limit its applications. Therefore, synthesizing a kind of plasticine having metallic bond is of importance for extending its applications in some special cases, such as thermal-cooling medium, anti-static electricity, electromagnetic shielding, etc. Here, we report a novel $GaInSnCdZn_2$ alloy, which exhibits similar behavior as compared to those of plasticine at near room temperature (30–40 °C), and a good electrical conductivity due to its nature of metal. This new $GaInSnCdZn_2$ alloy can be called as metallic plasticine that contains the near-eutectic structure with low melting point and the other relatively high melting point phases. In this metallic plasticine, the near-eutectic structure with low melting point plays the same role as the oily ingredient in plain plasticine, dominating the plastic deformation, while the other relatively high melting point phases act as the stuffing like the CaCO3 in plain plasticine. The creation of metallic plasticine offers a general strategy for designing/preparing a new class of plasticine which possesses both the nature of metal and plasticine.

1. Introduction

Plasticine has made a big progress in its composition and performance since it was invented in 1897 [1–7]. The excellent malleable ability and non-dry feature make plasticine to be formed in diverse shapes isotopically. Therefore, the plasticine was widely used in many industrial fields, such as modeling materials, raw material for clay animation in the film industry, props for teaching art in school, die material for casting plaster and plastics, and analogue materials for experimental deformation [1–6]. Moreover, it also can be used as sealing materials to keep sealing during the accidental failure and protective agent to avoid scratching when assembling precision instruments for its large compactness and softness. The properties of plasticine are dominated by its special structure that is composed of oily ingredient and $CaCO_3$ etc. The oily ingredient acts as a lubricant to deliver the plastic strain between the stuffing of $CaCO_3$.

However, the weakness of plasticine is also self-evident, which is substantially derived from its composition. Due to the insulativity of the organic and the inorganic substance, the mixture of both makes the plasticine nonconductive (part of plasticine with salt water has a weak conductivity, but the conductivity will be lost when it dries completely.). Yet, some special industrial applications field, for instance, electronic industry, need plasticine possess good conductivity/thermal/magnetic conductivity.

Motivated by the structure in plasticine, we conjecture that if a "lubricant" can be introduced into alloy matrix to lubricate the grains, a metallic plasticine possibly can be fabricated by using metallic elements. Accordingly, we designed a novel plasticine based on high entropy alloys (HEAs) concept, which consists of low melting point metal elements (such as, Bi, Cd, Ga, In, Pb, Sb, Sn, Zn elements etc.) [8] HEAs or multi-component alloys (MCAs) is a new

* Corresponding author.
** Corresponding author at: Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China.
E-mail addresses: tmwang@dlut.edu.cn (T. Wang), tjuli@dlut.edu.cn (T. Li).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jmst.2017.06.022
1005-0302/

Fig. 1. Dalian University of Technology emblems formed by hand stamping on (a) plain plasticine and (b) metallic plasticine ($GaInSnCdZn_2$ alloy) at 30–40 °C, respectively.

alloy category [9,10], which was proposed by Yeh et al. and Cantor et al., and composed of at least five principle components [11–22].

Although many kinds of low melting alloys have been developed, such as the tin-base alloy, bismuth-base alloy, lead-base alloy etc. [8,23,24], none of these alloys can be deformed like the plasticine at room temperature owing to their relatively high hardness and melting point, except for the Ga-In and Ga-In-Sn (Zn) eutectic alloys etc., because they are already liquid at room temperature [8,25,26].

In this work, GaInSn-base alloy was developed by adding various low melting point elements on the basis of binary phase diagram and HEAs design theory. A $GaInSnCdZn_2$ (mole ratio) HEA was successfully synthesized, which possesses similar deformation properties with that of the plain plasticine at near room temperature.

2. Materials and methods

The selected elements Ga, In, Sn, Cd and Zn with purity better than 99.99 wt% were used as the raw materials, and some corresponding properties were listed in Extended Data Table S3. Small laboratory ingots of 20 g were prepared by induction melting a mixture of high-purity metals under a high-purity argon atmosphere in a silica crucible (with inner diameter of 14.72 mm and height of 70.90 mm). The Cd and Zn element was put on the bottom of the silica crucible which was designed to form a cylindrical shape to avoid the mass loss of the volatile elements. The crucible was placed in the middle of the high frequency induction coil located in a vacuum chamber. The vacuum chamber was evacuated to 5×10^{-3} Pa and then backfilled to 0.05 Pa with high-purity argon gas. By imputing current in high frequency induction coil, the sample was melted and then cooled to room temperature in the furnace. Finally, a $GaInSnCdZn_2$ alloy was obtained, and the dimension of the obtained cylindrical rod is about $\Phi 15 \times 50$ mm.

The phase constituent analysis was characterized by the X-ray diffractometer (XRD, EMPYREAN with Cu $K\alpha$ radiation) with the angle of 2θ scanning from 20 to 100 deg. The analysis of microstructure was investigated by scanning electron microscopy (SEM, Zeiss supra 55) equipped with the energy dispersive spectrometry (EDS) system. The differential scanning calorimetry (DSC, Netzsch 214 Polyma) curve was performed under a protecting argon atmosphere with a heating and cooling rate of 10 K/min. In order to prevent the volatilization of elements in the process of DSC experiment, samples of 10–15 mg were put into pure Al sample pans, then covered by pure Al lids and compacted by the tablet press. In this work, the electrical conductivity measurement experiments were

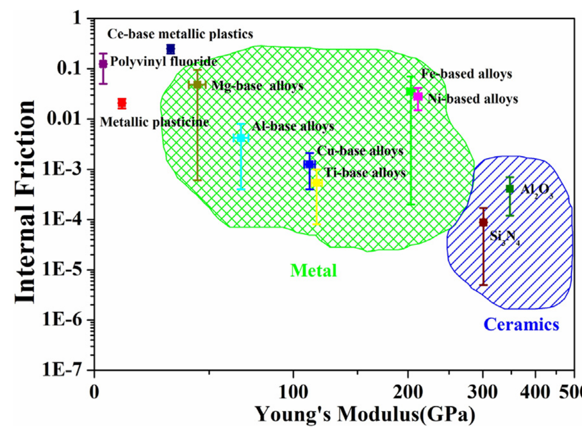

Fig. 2. Measured Young's modulus and internal friction for the metallic plasticine at room temperature, compared to experimental Young's modulus and internal friction for Ce-based amorphous metallic plastic, polyvinyl fluoride plastics, conventional crystalline alloys and ceramics.

carried out in DK60 eddy current conductivity tester, and the final electrical conductivity result was an averaged value for at least five times tests. The elastic modulus and internal friction of metallic plasticine were measured by EG-UHT Elastic Modulus Measurement System (NihonTechno-plus Co., Ltd), and the dimensions of the specimen were 1.3 mm × 10 mm × 50 mm. The elastic modulus and internal friction of Ce-based AMP were measured by TA Q800 dynamic mechanical analysis (DMA), and the dimensions of this specimen are 2 mm × 2 mm × 8 mm.

3. Results

As shown in Extended Data Fig. S1, the $GaInSnCdZn_2$ alloy can be plastically deformed by fingers like the plasticine at body temperature (~37 °C) (also see Supplementary Movie). Fig. 1a and b shows the Dalian University of Technology emblems were formed by hand stamping on plasticine, and the $GaInSnCdZn_2$ alloy at 30–40 °C, respectively. This good plastically forming ability of the $GaInSnCdZn_2$ alloy is as same as that of plasticine. Hence, we can name this new class of alloy as metallic plasticine.

To find the origin of good plastically forming ability of the metallic plasticine, Young's modulus and internal friction are measured, and plotted in Fig. 2 together with the values for the other alloys, conventional plastic and ceramic materials [27–30]. It can be seen that the metallic plasticine displays much lower Young's modulus (~10 GPa) as compared to those of alloys and ceramic materials,