Liquid metal dealloying combined with polymer impregnation as novel promising technology for bioHEA-based implant manufacturing

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Abstract. The paper provides a short review of liquid metal dealloying (LMD) combined with subsequent polymer impregnation as promising technology to synthesize low modulus metal-polymer composites for biomedical applications. The introduction presents the key problems and relevance of the development and synthesis of such materials. The "Theoretical basis" chapter defines the LMD method and the main steps required to activate this process. The fundamental principles of thermodynamics, kinetics and morphology evolution of LMD process are presented here. Due to their favorable mechanical characteristics in the context of biomedical applications, the so-called biocompatible high-entropy alloys (bioHEAs) are proposed as promising candidates for LMD treatment combined with polymer impregnation and, accordingly, the synthesis of novel metal-polymer bioHEA materials.

1 Introduction

Traditional medical alloys used in endoprosthetics such as stainless steels, CoCrMo and Ti-based (TiNi, Ti-6Al-4V, Ti-6Al-7Nb, etc.) alloys have a number of significant disadvantages [1]. The main ones are the release of metal ions (Ni, Co, Cr and Al) and a high Young's modulus significantly exceeding the value of human cortical bone. In the first case, the release of ions can provoke various allergic reactions and the weak interfacial bond between the alloy and the bone which negatively affects the osseointegration. Another indicated disadvantage of these alloys is the mismatch of their stiffness with human bone which results stress shielding effect causing bone resorption and eventually the separation of the metal implant. Thus, the design and synthesis of new functional materials for biomedical applications, in particular, for implant manufacturing, is still an urgent and important fundamental task requiring the complex multidisciplinary approach based on physics, chemistry, materials science, biology and engineering sciences.

The important place in the class of polyfunctional biomedical materials is occupied by high-entropy alloys (HEAs) possessing a set of favorable mechanical characteristics: high

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strength and ductility, high corrosion and wear resistance, low Young's modulus in comparison with the traditional medical alloys and others. However, the value of Young's modulus of these HEA materials is still significantly higher than the value for the cortical bone (3–40 GPa) [2, 3].

Effective way to reduce the stiffness of the above materials is the formation of homogeneously distributed porosity in them according to novel technology invented in the group of prof. H. Kato – liquid metal dealloying [4]. Materials for LMD treatment are selected based on the mixing enthalpy. One important condition must be met to activate the LMD process – the value of the mixing enthalpy between the melt (for example, Mg, Ni, etc.) and the main chemical element of the future implant must be positive, and between the melt and the component for the formation of the future porous microstructure – negative. More detailed information about LMD method is described in the chapter "Theoretical basis".

Over the past 10 years, the colossal work has been carried out to design and synthesis micronanoporous Ti-based materials [4–9]. However, the development of porous bioHEA materials by LMD method is in its infancy and requires detailed research. Thus, the selection of existing bioHEAs with a number of favorable mechanical characteristics and the formation of porosity in them by LMD to reduce Young's modulus while maintaining high strength and ductility is an urgent task in the context of biomedical applications, in particular, for the synthesis of a new class of implant materials.

The paper goal is to present a brief review of the unique combined technology of LMD process with subsequent polymer impregnation to synthesize of novel low modulus metal-polymer composites based on bioHEA materials.

2 Theoretical basis

2.1 Liquid metal dealloying

LMD is a metallurgical process based on selective corrosion in a liquid metal for synthesis of porous materials. This method can be used to obtain less noble porous metals, such as Ti, Zr, Nb, Hf and etc. It uses the diffusion of a liquid metal into a precursor material accompanied by selective dissolution of one or more components. The rest part of the precursor material doesn’t mix with the liquid metal and is rebuilt into bicontinuous scaffold consisting of interconnected pores and ligaments. The size (average thickness) of the ligaments of porous materials obtained by dealloying method can be effectively tuned in the range from micro- to nanometers by controlling the processing conditions [5–9].

The wide range of porous materials including Ti [4], Zr [5], Fe [10], Cr [10], Nb [7], Ta [11], TiNb [5, 12], TiFe [12], TiZr [5, 13], TiHf [14], hierarchically structured Fe-based alloy [15] and HEA TaMoNbVNi [16] were developed by LMD. Moreover, LMD method is effective for biomedical surface modification applications, in particular, for structuring adaptable nanotopographies [17] and selective removal of toxic elements [18]. Metal-polymer composites, obtained by polymer impregnation of LMD-processed titanium alloys, offer new possibilities for their application as load-bearing elements [19] and promising implant materials [5, 14].

2.1.1 Thermodynamics of the dealloying process

The key principle for activating LMD process is the compliance with certain ratios of the mixing enthalpy. When two elements are mixed, the free energy change is described by the formula:
\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}
\]

where \(\Delta H_{\text{mix}}\) – mixing heat, \(\Delta S_{\text{mix}}\) – mixing entropy and \(T\) – absolute temperature. Usually, the entropy value increases after mixing. According to the thermodynamic point of view, if \(\Delta H_{\text{mix}} < 0\) then \(\Delta G_{\text{mix}} < 0\), and the mixing reaction can occur spontaneously. On the other hand, if \(\Delta H_{\text{mix}} > 0\) then the sign (positive or negative) of \(\Delta G_{\text{mix}}\) depends on temperature. If the corresponding temperature value is controlled so that the enthalpy term larger than the entropy term, then \(\Delta G_{\text{mix}} > 0\) and mixing of two elements can be avoided. When using LMD method, the binary precursor A–B alloy is immersed into C melt. If the mixing heat between B and C elements – negative, i.e. \(\Delta H_{\text{mix}, B-C} < 0\), and between A and C elements – positive, i.e. \(\Delta H_{\text{mix}, A-C} > 0\), then by temperature control, only B elements dissolve out of the precursor A–B alloy into C melt. Therefore, A elements are removed out of C melt and self-organizes into a porous structure due to surface diffusion as for electrochemical dealloying method [20]. The LMD scheme with triangle relationship of the mixing enthalpies among A, B, and C elements is schematically shown in Figure 1. The compliance with all the above conditions is necessary to activate the LMD process which includes the selective dissolution of B atoms (orange) into C melt (pink) and surface diffusion of the remaining A atoms (green) [21].

![Fig. 1. Synthesis scheme of porous materials by LMD method](image-url)
4. Removal of C element by chemical etching with an acid or alkaline solution (the remaining A component must be inert in the solution).

It is important to note that in order to activate LMD process, it is necessary to calculate the exact value of the mixing heat taking into account the temperature and chemical composition. The mixing heats between transition metals and, transition metals and metalloids can be obtained from the Boyer and Perrifor table [22], the values of which are approximately calculated according to the Miedema model, and for other metals from the table developed by Takeshi et al. [23]. Figure 2 shows the values of $\Delta H_{AB}^{\text{mix}}$ (kJ/mol) calculated by Miedema’s model for atomic pairs between Mg and elements indicated in the plot.

![Fig. 2. The values of $\Delta H_{AB}^{\text{mix}}$ (kJ/mol) calculated by Miedema’s model for atomic pairs between Mg and elements indicated in the plot [23]](image)

As shown in Figure 3, the polymer impregnation of LMD-based porous materials is used for synthesis of metal-polymer composites with higher strength while maintaining a low Young’s modulus.

![Fig. 3. Synthesis scheme of metal-polymer composites](image)
2.1.2 Kinetics of the dealloying process

The activation energy of porous layers formed in the synthesized materials during the LMD process is considered as the main mechanism activating the reaction. This energy can be expressed using an Arrhenius-type equation [9]:

\[ k = k_0 \exp(-E/RT) \]  

(2)

where \( k_0 \) – pre-exponential factor, \( E \) – activation energy and \( R \) – gas constant. Kirkendall-type mass flow typically results in a porous morphology of the reaction layers in the solid diffusion couple. A large difference between the intrinsic diffusivities of the couple components introduces atomic vacancies, which will eventually cluster to form voids in one of the layers.

Different LMD process conditions, time and temperature, affect the kinetics of ligament coarsening. The ligament coarsening occurs with increasing immersion time and temperature during LMD reaction. It can be expressed by exponential function similar to the behavior of the grain growth in polycrystalline solids [9]:

\[ d^m = ktD_s \]

(3)

where \( d \) – ligament size, \( m \) – coarsening component, \( k \) – constant, \( t \) – immersion time and \( D_s \) – surface diffusivity. Provided that the \( d^m \) logarithm together with the reciprocal of the LMD temperature \( T \) have direct relationship, \( d^m \) can be expressed as function of \( T \) using an Arrhenius-type equation [9]:

\[ D_s = D_0 \exp(-E/RT) \]

(4)

Combining the last two equations, the temperature dependence of the ligament size can be expressed as follows [9]:

\[ d^m = ktD_0 \exp(-E/RT) \]

(5)

2.2 BioHEA materials

High-entropy alloys (HEAs) are materials formed by mixing equal or relatively large proportions with an atomic ratio ranging from 5 to 35 at. % of five or more elements [24, 25]. The basic idea is to utilize high mixing entropy and lattice disorder to enhance formation of solid solution phases instead of forming intermetallic compounds or segregated states. This provides HEAs with unique microstructural features and improved mechanical properties over conventional commercial alloys. The key mechanical characteristics of HEAs include high strength and ductility, high corrosion and wear resistance. The Young’s modulus of HEAs can be more easily adjusted than conventional alloys due to the large compositional variation providing great possibility to design low-modulus metallic biomaterials [26].

The relationship between phase composition and microstructure as well as the physical and mechanical characteristics of HEAs is explained by four main effects: high-entropy effect, sluggish diffusion, severe lattice distortion and cocktail effect [27]. The mixing enthalpy and entropy, melting points, atomic size difference and valence electron concentration are used as phase formation rules for HEAs. These principles allow to predesign HEAs with characteristics that are best suited to the context of the intended application. Table 1 presents the mechanical characteristics of literary known biocompatible high-entropy alloys (bioHEAs) [26, 28–30].
### Table 1. Mechanical characteristics of literary known bioHEAs

<table>
<thead>
<tr>
<th>BioHEAs</th>
<th>Young's modulus, $E$ (GPa)</th>
<th>Yield strength, $\sigma_y$ (GPa)</th>
<th>Plastic strain, $\varepsilon_p$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Zr-Nb-Ta</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ta$_x$HfZrTi</td>
<td>57–135</td>
<td>0.23–1.37</td>
<td>0.73–32.5</td>
<td>[26]</td>
</tr>
<tr>
<td>Nb$_x$HfZrTi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta$_x$Nb$_x$HfZrTi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equiatomic TiZrNbTaMo</td>
<td>153–164</td>
<td>1.39</td>
<td>~ 6</td>
<td>[28, 29]</td>
</tr>
<tr>
<td>Ti$<em>x$(NbTaZr)$</em>{90-x}$Mo$_{10}$</td>
<td>40–154</td>
<td>1.13–1.36</td>
<td>23–33</td>
<td>[30]</td>
</tr>
</tbody>
</table>

According to Table 1, the bioHEAs have the most suitable mechanical properties in the context of biomedical applications compared to traditional commercial alloys. Thus, bioHEAs are promising candidates for LMD treatment combined with polymer impregnation and, accordingly, the synthesis of metal-polymer bioHEA materials.

### Conclusion

The review paper describes the unique combined technology of LMD process with subsequent polymer impregnation to synthesize low modulus metal-polymer composites for biomedical applications. The fundamental principles of thermodynamics, kinetics and morphology evolution of the LMD process are presented here. Due to their favorable mechanical characteristics in the context of biomedical applications, the bioHEAs are proposed as promising candidates for LMD treatment combined with polymer impregnation and, accordingly, the synthesis of novel metal-polymer bioHEA materials.

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### References