Structural Transformations of a Gas-atomized Al_{62.5}Cu_{25}Fe_{12.5} Alloy during Detonation Spraying, Spark Plasma Sintering and Hot Pressing

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Abstract:

In this work, we traced structural transformations of an Al_{62.5}Cu_{25}Fe_{12.5} alloy, in which a quasicrystalline icosahedral phase (i-phase) can be formed, upon spraying onto a substrate and consolidation from the powder into the bulk state. The Al_{62.5}Cu_{25}Fe_{12.5} powder was obtained by gas atomization and consisted of i-phase and τ-phase AlCuFe. The powder was detonation sprayed (DS) and consolidated by spark plasma sintering (SPS)/hot pressing (HP). During DS, the particles experienced partial or complete melting and rapid solidification, which resulted in the formation of coatings of a complex structure. The composite regions containing i-phase were inherited from the powder alloy. The fraction of the material that experienced melting solidified as β-phase AlFe(Cu) in the coating. It was suggested that the difficulty of obtaining i-phase upon post-spray annealing is related to aluminum depletion of the alloy during DS. During SPS and HP, the elemental composition of the alloy was preserved, while the exposure to an elevated temperature led to phase homogenization. SPS and HP conducted at 700 °C resulted in full densification and the formation of a single-phase quasicrystalline alloy. The sintered single-phase alloy showed a higher microhardness in comparison with the DS coatings.

Keywords: Quasicrystalline alloy; Detonation spraying; Spark plasma sintering; Microstructure.

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1. Introduction

Attractive properties of quasicrystalline alloys – high hardness, low electrical and thermal conductivity, low coefficient of friction, high oxidation resistance and biocompatibility – have stimulated interest to materials capable of forming the quasicrystalline phases [1]. The formation of these phases in metallic systems is known to be very sensitive to the processing conditions and elemental composition of the alloy [1-5]. In the Al-Cu-Fe alloys, the quasicrystalline phase can be formed either by rapid cooling of the melt (the cooling rate should be of the order of $10^6$ K s$^{-1}$) or via a series of peritectic reactions [1].

The phase homogenization of the alloy upon consolidation of a powder or upon deposition on a substrate is an important issue in fabricating bulk materials and coatings from the Al-Cu-Fe powders. It was shown that composite coatings containing a quasicrystalline Al-Cu-Fe (i-phase) could be formed by thermal spraying, e. g., by the high-velocity oxy-fuel process [6].

Modern detonation spraying (DS) facilities allow controlling the spraying conditions in a very flexible manner and yield reproducible results [7]. To our best knowledge, the DS behavior of Al-Cu-Fe alloys has not been reported in the literature. In the present work, structural transformations of an Al-Cu-Fe alloy containing a quasicrystalline (icosahedral) phase during DS were investigated. For comparative purposes, spark plasma sintering (SPS) and hot pressing (HP) were used to consolidate the powder into bulk alloys.

2. Materials and Experimental Procedures

The Al$_{62.5}$Cu$_{25}$Fe$_{12.5}$ alloy powder was obtained by nitrogen gas atomization using a HERMIGA 75/5VI gas atomizer (Phoenix Scientific Industries Ltd., UK). DS was conducted on a computer-controlled detonation spraying (CCDS2000) facility [7]. An oxygen-acetylene mixture with an $O_2/C_2H_2$ molar ratio of 1.1 was used. The powder was deposited on steel substrates. The volume of the explosive mixture used for each shot of the gun was 50-70% of the barrel volume. Annealing of the detonation coating samples was conducted in an atmosphere of argon (ambient pressure).

Sintering of the powders was carried out using a SPS Labox 1575 apparatus (SINTER LAND Inc., Japan) at a uniaxial pressure of 40 MPa in forevacuum. HP was conducted on a custom-made facility (developed at the Institute of Automation and Electrometry SB RAS) in an atmosphere of argon at a uniaxial pressure of 40 MPa.

The morphology of the powder and microstructure of the alloy was studied by scanning electron microscopy (SEM) using a Hitachi TM-1000 Tabletop microscope and a Hitachi S-3400N microscope (Japan). Secondary electron (SE) and back-scattered electron (BSE) images were recorded. Energy-dispersive spectroscopy (EDS) was conducted using a NORAN Spectral System 7 (Thermo Fisher Scientific Inc., USA) attached to the Hitachi S-3400N. The X-ray diffraction (XRD) patterns were recorded using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu K$\alpha$ radiation. Vickers microhardness of the alloys obtained by SPS was measured using a DuraScan 50 hardness tester (EMCO-TEST, Austria) at a load of 100 g.

Fracture toughness of the alloys was determined from the Palmquist equation [8]:

$$K_{IC} = 0.0319 \frac{P}{(a l_a^{1/2})},$$

where $P$ is the load, $a$ is half-diagonal of the indent and $l_a$ is the length of a crack emanating from the corner of the indent.
3. Results and Discussion

The gas-atomized alloy powder consisted of i-phase and τ-phase AlCu(Fe) (Fig. 1a–d). The two-phase structure of the alloy was characterized by EDS. The dark areas marked (1) in Fig. 1c correspond to i-phase, which is richer in Al than the bright phase (τ-phase). These phases can be distinguished in the XRD pattern of the powder alloy (Fig. 1d). The composition of the characteristic regions of the microstructure of the powder is given in Table I.

![Image of the Al62.5Cu25Fe12.5 particles, SE image (a), microstructure of an alloy particle, BSE image (b), a higher magnification image of the alloy microstructure showing two phases differing in composition, BSE image (c). XRD pattern of the Al62.5Cu25Fe12.5 powder (d).](image)

During DS, a charge of 50 % (cold mode) created conditions under which only a small fraction of the particles melted, so the integrity of the coating was poor, the coating had numerous cracks and was not uniform in thickness. When the explosive charge was increased to 60 % (normal mode), a coating of uniform thickness was formed (Fig. 2 a,b). The coating shows regions that did not experience melting (two-phase regions) as well as regions of a re-solidified material. The coating consisted of i-phase and Al-Cu-Fe intermetallics inherited from the powder or formed by crystallization of the melt (Fig. 3).
Fig. 2. General view (a, c) and microstructure (b, d) of detonation coatings obtained under normal (a, b) and hot (c, d) modes, BSE images.

Fig. 3. XRD patterns of the coatings obtained by DS and annealing.
As is seen in Table I, certain losses of Al occurred during spraying. At an explosive charge of 70% (hot mode), most of the particles melted (Fig. 2 c,d), so the content of i-phase in the coating was low. More significant compositional changes occurred in the hot mode (Table I). Annealing of the coating at 700 °C in an atmosphere of argon did not change its phase composition (Fig. 4a). Annealing of the deposited material not in contact with the substrate (flakes intentionally separated from the substrate) was also conducted but produced the same results (Fig. 4b). During DS, evaporation of aluminum from the molten alloy changed the coating composition relative to the gas-atomized powder, even in the normal spraying mode (Table I). Indeed, shifts in the alloy composition are known to complicate the formation of i-phase. For example, enrichment of the alloy with iron due to iron contamination during ball milling of the powder was suggested as a reason for the formation of β-phase instead of i-phase in an Al-Cu-Fe alloy [9]. The Al impoverishment in the DS coatings shifted the alloy’s composition towards the region of stability of the β-phase [1].

**Tab. I** Energy-dispersive spectroscopy of the gas-atomized powder, sintered alloy and detonation coatings (point and area analyses).

| Sample                                                      | Concentration of elements, at.% |
|-------------------------------------------------------------|---------------------------------|
| Gas atomized powder, cross-section                         |                                 |
| From the two-phase region, 30 μm*40 μm                      | Al: 63.7, Cu: 24.3, Fe: 12.0    |
| Dark phase (marked 1 in Fig. 1c)                           |                                  |
| Bright phase (marked 2 in Fig. 1c)                         |                                  |
| Surface of the detonation coating, normal mode, from area 75 μm*100 μm | 59.6, 26.8, 13.6               |
| Cross-section of the detonation coating, normal mode, from area 75 μm*100 μm | 59.2, 26.7, 14.1               |
| Surface of the detonation coating, hot mode, from area 75 μm*100 μm | 53.6, 29.2, 17.2               |
| Cross-section of the SPS-consolidated material, 700 °C, 5 min, from area 75 μm*100 μm | 61.4, 26.2, 12.4               |

**Fig. 4.** XRD patterns of the coating detonation sprayed in the normal mode and annealed at 700 °C for 30 min in an argon atmosphere, annealing in the presence of the steel substrate (a) and without the substrate (b).
A single-phase quasicrystalline Al-Cu-Fe alloy was obtained by SPS of the gas-atomized powder in ref. [10]. To verify the ability of the powder obtained in the present work to transform into the single-phase quasicrystalline alloy, we consolidated it by SPS and HP. During SPS and HP, the exposure of the alloy to an elevated temperature allowed phase homogenization to take place along with densification. Fig. 5 shows a cross-section of the alloy obtained by SPS at 700 ºC. EDS taken from the bulk alloy obtained by SPS indicates that the composition of the alloy is very close to that of the gas-atomized powder (Table I). Both SPS and HP at 700 ºC resulted in the formation of bulk single-phase quasicrystalline alloys (Fig. 6).

**Fig. 5.** A cross-sectional view of the bulk Al\(_{62.5}\)Cu\(_{25}\)Fe\(_{12.5}\) alloy obtained by SPS, 700 ºC, 5 min, BSE image.

![Cross-sectional view of the bulk Al\(_{62.5}\)Cu\(_{25}\)Fe\(_{12.5}\) alloy](image)

**Fig. 6.** XRD patterns of the sintered and hot pressed alloy.

The bulk quasicrystals obtained by SPS showed a hardness of 860 ± 20 HV and fracture toughness of 1.3-1.4 MPa m\(^{1/2}\) (Table II), which agrees well with the results of ref. [10]. The DS coatings showed a lower microhardness, which can be explained by a reduced content of the i-phase. The fracture toughness of the coatings was not measured, as the pre-existing cracks complicated the interpretation of the indentation results.
The powder metallurgy approach remains attractive for obtaining metallic alloys of different compositions [11, 12]. The starting materials for these alloys are powder mixtures. A promising development of the present work is the fabrication of composites containing Al-Cu-Fe alloys by sintering of an aluminum powder mixed with an Al-Cu-Fe powder. The powder of the Al_{62.5}Cu_{25}Fe_{12.5} alloy can serve directly as reinforcement or act as a precursor to form a reinforcing phase via the interaction with the added aluminum.

| Sample | Microhardness, HV₀·₁ | Fracture toughness, MPa m^{1/2} |
|--------|-----------------------|---------------------------------|
| SPS, 700 °C, 5 min | 860 ± 20 | 1.4±0.2 |
| SPS, 700 °C, 15 min | 860 ± 20 | 1.3±0.1 |
| DS, normal mode | 610 ± 80 | - |
| DS, hot mode | 680 ± 70 | - |

4. Conclusion

Structural transformations of the Al_{62.5}Cu_{25}Fe_{12.5} alloy consisting of i-phase and τ-phase AlCu(Fe) upon DS and consolidation by SPS and HP were studied. During DS, the alloy experienced partial or complete melting, depending on the spraying conditions, and rapid solidification. DS can be conducted in such a manner that coatings partially inherit the composite structure of the powder alloy. Melting and solidification resulted in the formation of AlFe(Cu) β-phase in the coatings. The difficulty of obtaining i-phase during the post-spray annealing is a partial loss of aluminum during DS, shifting the composition of the alloy. Both SPS and HP conducted at 700 °C resulted in the formation of bulk single-phase quasicrystalline alloys. The sintered single-phase alloy showed a higher microhardness in comparison with the DS coatings.

Acknowledgments

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Сажетак: У овом раду смо пратили структурне трансформације легуре $Al_{62.5}Cu_{25}Fe_{12.5}$, у којој је могуће формирање квазикристалне икосаедралне фазе ($\textit{i}$-фазе), када се нанесе на супстрат и консолидује из праха у чврсто стање. Прах $Al_{62.5}Cu_{25}Fe_{12.5}$ је добијен гасном атомизацијом и састојао се из $\textit{i}$-фазе и $\textit{t}$-фазе $AlCu(Fe)$. Прах је прскан детонацијом и консолидован синтеровањем у плазми и топлим пресовањем. Током прскања, честице праха су делимично истопљене и брзо очврснуте, што је резултирало формирањем превлаке комплексне структуре. Композитни делови који садрже $\textit{i}$-фазу потичу од праха легуре. Фракција материјала која је прошла топљење очврснула је као β-фаза $AlFe(Cu)$ у превлаци. Претпоставља се да је тешкоћа добијања $\textit{i}$-фазе повезана са процесом осиромашивања легуре алуминијумом током прскања. Током синтеровања у плазми и топлом пресовања основни састав легуре је очувањ, док је приликом излагања високим температурама дошло до хомогенизације фаза. Синтеровање у плазми и топло пресовање на $700$ °C резултују једнофазне квазикристалне легуре. Синтерована једнофазна легура је показала вишу микрошвидћу у поређењу са прсканом превлаком.

Кључне речи: квазикристална легура, прскање детонацијом, синтеровање у плазми, микроструктура.

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