COLD-SPRAY TECHNIQUE AS EFFICIENT ALTERNATIVE PROCESS FOR CONSOLIDATION OF POWDERED Al-Fe-Cr ALLOYS REINFORCED BY NANOQUASICRYSTALLINE PARTICLES

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ABSTRACT

A brief outline of the processing parameters involved in the search for technique offering efficient consolidation of high-temperature strength Al-based powdered alloys reinforced by metastable nanoquasicrystalline particles is presented. Feedstock powder of $Al_{94}Fe_3Cr_3$ alloy was employed in experiments. Superior advantages of the cold-spraying as alternative solid-state process for consolidation and structural performance of quasicrystalline alloys by plastic deformation is discussed in comparison with that resulted from currently employed hot extrusion put into practice at the 623 K. As opposed to extrusion assisted by unidirectional deformation, adiabatic shear instability is primary responsible for creating the mostly effective intimate metallic bonding between the adjacent Al-powder particles under cold spraying when the temperature was even well below melting point, i.e. 473 K. The main benefit of cold-spraying is that the composite quasicrystalline structure in the interior of heavily deformed particles was believed to be actually the same as that of feedstock powder while warm extrusion results in the decrease by 23% fraction volume of metastable quasicrystalline particles, shifting their decomposition to the lower temperatures. Advantage of cold-sprayed $Al_{94}Fe_3Cr_3$ alloy concerns excellent balance between high ductility (plasticity characteristic $\delta_H \cong 0.9$) and high strength that superior roughly about 35% to that of as-extruded composite.

Key words: Cold spraying, Al-Fe-Cr alloy, nanoquasicrystalline particles, powder, consolidation, bonding, microstructure, mechanical properties

INTRODUCTION

High strength of Al-Fe-based nanoquasicrystalline alloys exebited attractive mechanical properties are presently of great attention for researches employed in scientific and engineering applications [1-4]. Some of them show increased structural stability and, therefore, are much promising for application under elevated temperature. Quasicrystalline Al-Fe-based alloys belong to the

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group of metal matrix nanoquasicomposite. Their microstructure typically consists of nanometer-sized icoshedral (i-phase) quasicrystalline particles embedded in an α-Al matrix [1]. Compared to commercial Al-based alloys recommended for service under elevated temperature, Al-based nanoquasicomposites show remarkable advantages in material mechanical performance because of excellent balance between high strength and sufficient ductility [2, 3]. Formation of quasicrustalline i-phase with long range orientation order and no translational symmetry in rapidly-cooled Al-alloys was originally discovered by Shehtman et al. in 1984 [5] and, then, promoted by additions of Mn, Fe, Cr, V, Ti, Zr, Nb and Ta [2-4, 6]. Since nanoquasicrystalline Al-based alloys are usually performed as semi-product in form of melt-spun ribbons/flakes, [6], and gas/water atomised powders [3, 4] their following consolidation is required for manufacturing the bulk-shaped material and, as consequence, further improvement of its microstructural stability is desirable to maximize elevated temperature. Superior advantages of cold-spraying as alternative solid-state process for consolidation and structural performance of nanoquasicrystalline Al-Fe-based alloys by plastic deformation is presented and discussed by comparison with currently employed warm powder extrusion under the temperature usually ranged from roughly about 673 to 723 K [3, 4].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Feedstock quasicrystalline powders of Al-alloy with nominal composition of $Al_{94}Fe_3Cr_3$ (oxygen content about 0.3%) was chosen for experimentations and fabricated by water-atomisation technique using inhibited high-pressure water with Ph 3.5 [8]. Fraction volume of quasicrystal particles contained by feedstock powder was not less than 35% [4]. After atomisation powder was sieved to less than 40 μm. Consolidation of powdered Al-based alloy was performed by two different techniques, i.e. by cold spraying and by powder extrusion process.

A commercial cold spray system (DYMET 403) was used in spraying experiments done under compressed air. Cold-sprayed principle and technical setup for cold spraying are described elsewhere [9]. Velocity of air/particle jet was roughly about 700 m/s whenever its temperature was not higher than 473 K [10-12].

Consolidation of pre-compacted feedstock powder via extrusion was done in hermetic capsule at the temperature of 653 K [4, 10]. Prior extrusion degassing the capsule of 25mm in diameter filled by powdered compact was implemented at the temperature of 623 K during 1 hour. Press of 2000 kg in power equipped by extrusion die with inner diameter of 9.3 mm and length for working part of 2 mm was used in extrusion process. Extrusion was fulfilled in the single pass with reduction coefficient, k_e, of 7.2. Extrusion velocity was as great as $V_e = 15 \times 10^{-3}$ m/s.

Scanning electron (SEM) microscope Jeol Superprobe-733 (JEOL, Japan) equipped with X-ray detectors (EDX and EPMA) was used to recognise feedstock powder morphology (particle size and shape) and microstructure as well as to get basic information about particle/particle bonding achieved in cold-sprayed and extruded samples. Differential scanning calorimetry (DSC) together with X-ray diffraction (XRD) analysis using Cu K_{α} radiation and transmission electron microscopy (TEM) observation were employed to study thermal stability of the quasicrystalline phase under elevated temperatures. TEM images and selected area electron diffraction (SAED) patterns were performed using JEM 2100 F (JEOL, Japan) microscope.

Microhardness measurements were performed using conventional microhardness machine equipped by standardised Vickers pyramid and determined under indentation load as high as 1.0 N. Plasticity characteristic δ_H as dimensionless parameter that can vary in the range from 0 (for "pure" elastic contact) to 1 (for "pure" plastic contact) was derived by calculations through microhardness measurement results and Young's modulus, E [14]. Microtester capable for load-displacement measurements and equipped by Berkovich pyramid was used to determine Young's modulus, E, according to the test method procedure originally proposed by Oliver and Pharr [15]. In addition, plasticity characteristic δ_A, which is physically close to that denoted by δ_H was derived from loading and unloading data according to demands of International standard ISO 14577-1:2002 (E). Yield stress, σ_y, was extracted from 'stress-strain' curve constructed by a set of trihedral pyramids with different angles at the tip γ_1 (ranged from 45° to 85°) according to the test method procedure [16].

RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns recorded for the feedstock WA powder, as-extruded rod, and cold-sprayed alloy.

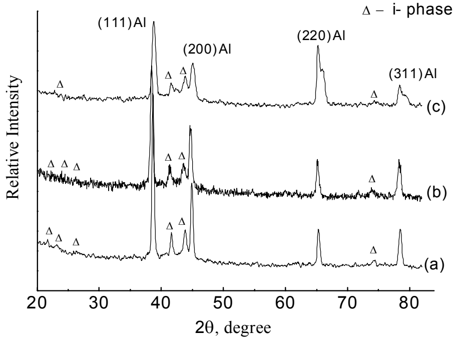
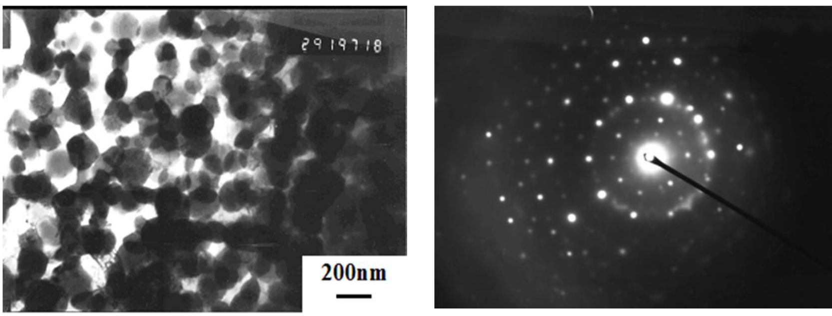


Fig.1 – XRD patterns of (a) feedstock powder, (b) cold-sprayed material, and (c) extruded rod, all performed by $Al_{94}Fe_3Cr_3$ alloy

In all of the XRD patterns the presence of the X-ray peaks for α-Al is clearly seen together with those indexed as i-phase using Cahn's indexation scheme [17].

Fig. 2 displays representative bright field TEM image showing the microstructure of the $Al_{94}Fe_3Cr_3$ alloy fabricated via different routes. All kinds of the $Al_{94}Fe_3Cr_3$ alloy show the similar microstructure composed of quasicrystalline particles embedded in α-Al matrix, as shown in *Fig. 2a*. Quasicrystals have the clear and characteristic spherical shape with a diameter roughly about 200 nm and smaller. Selected area diffraction patterns (SAED) reveal five-fold reflection spots indicative of i-phase, as can be seen in *Fig. 2b*.



a) b)

Fig.2 – (a) Bright field TEM image and (b) SAED pattern of the $Al_{94}Fe_3Cr_3$ alloy

However, intensity of diffraction peaks attributed to i-phase in the XRD pattern for as-extruded rod is much smaller, suggesting reduced fraction volume of metastable quasicrystalline particles. The proper are thought to be partially decomposed under combined effect of high pressure and enhanced temperature during extrusion process. This assumption is confirmed by the presence of the addition reflections for α-Al overlapping those typical for α-Al recorded in the feedstock powder and as-sprayed alloy. This is because of two α-Al solid solutions of different elementary composition were formed in the matrix after extrusion. As could be seen in Table 1, one of them has reduced lattice parameter a_o, indicating enrichment of α-Al by solute Fe and Cr. In addition, broadening of diffraction peaks for α-Al matrix, which could be resulted from combined effect of delaminating the α-Al solid solution and dislocation activity, are seen in the XRD pattern of as-extruded bar.

Table 1 – Lattice parameter a_o of elements and α-Al solid solutions in $Al_{94}Fe_3Cr_3$ alloy performed via different routes

Material	Al	Fe	Cr	Feedstock powder	Extruded rod	CS-alloy
a_o, nm	0.4049	0.2866	0.2885	0.4041	0.4045/0.4006	0.4045

Notice: CS – cold spray

The results of DSC analysis shown in *Fig. 3* are helpful to estimate the diminishing the fraction volume of quasicrystalline particles resulted from powder consolidation via extrusion process.

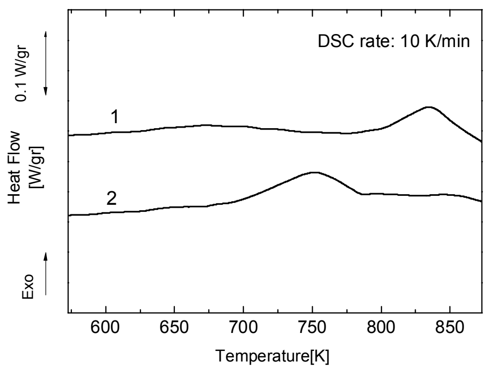
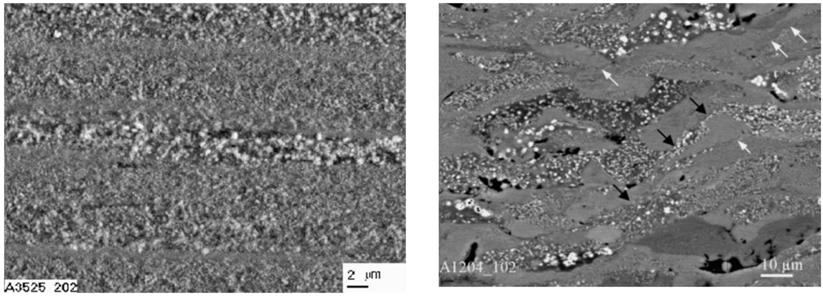


Fig. 3 – DSC traces reordered at the heating rate 10 K/min for (1) $Al_{94}Fe_3Cr_3$ feedstock powder and (2) as-extruded $Al_{94}Fe_3Cr_3$ alloy

It is easy to show that heat flow of exothermic reaction associated with decomposition of quasi-crystalline phase in the as-extruded $Al_{94}Fe_3Cr_3$ alloy are smaller by roughly about 23% than that for quasicrystalline feedstock powder of the same composition. Moreover, a shift of the main exothermic peak toward lower temperature after extrusion indicates increased kinetic of quasi-crystalline particles decomposition. Dislocation activity in α-Al matrix, which has been indicated by XRD analysis of as-extruded rod, can principally facilitates dissolution of alloying elements released from decomposed metastable quasicrystalline particles.

As opposed to extrusion process, cold spray technique allows one to retain entirely fraction volume of quasicrystalline phase created in powdered $Al_{94}Fe_3Cr_3$ alloy by rapid solidification. Processing temperature under cold spraying is much smaller than that for warm extrusion process. Despite of this cold spraying finds oneself capable to create effective intimate metallic bonding between the adjacent particles by breaking off the oxide films presented naturally on the feedstock Al-powder and promoting intimate contact between two clean surfaces the same as those in extrusion process. Actually, remnant agglomerations of broken oxide layer have been revealed by TEM observation at the particle/particle interfaces [12]. However, compared to extrusion process intimate bonding at the particle/particle interfaces under cold spraying is controlled by different mechanisms of deformation. Characteristic features observed in cross-sectional microstructures of cold-sprayed alloy and extruded rod are helpful to elucidate the matter at the issue above. With retaining the quasicrystalline particles of unchanged shape in deformation-induced structure, cold spraying causes powder particles to become flattened and heavily deformed in cross-sectional microstructure and get lens-like shape with aspect ratio $k_{fcs} \approx 4.7$ while extrusion process results in elongated powder particles of perfect fibred-like shape and aspect ratio $k_{fe} \approx 7.2$ that is the same as extrusion coefficient k_e, as shown in *Fig. 4a* and *Fig. 4b*.



a) b)

Fig. 4 – SEM images of cross-sectional microstructure for (a) extruded rod (b) cold-sprayed alloy, both performed by $Al_{94}Fe_3Cr_3$ -feedstock powder. Black arrows in (b) indicate the evidence of shear instabilities at the particle/particle boundaries whereas white arrows indicate the local metallurgical bonding between the powder particles due to impact fusion.

Homogeneous severe plastic deformation under extrusion results in elongation of powder particles that is assisted by two components of pressure such as longitudinal, P_l, and transversal one, P_t. By considering the accepted experimental conditions and following the calculation procedure reported previously in [10] components of pressure have been estimated as great as P_l = 1.42 GPa and P_t = 3.30 GPa. In contrast to extrusion process, two different kinds of deformation ensure intimate bonding at the particle/particle interfaces under cold spraying. Among them severe plastic deformation of powder particles results in their flattening and mechanical interlocking the splats by cold forging under forward pressure estimated in line with [10] as great as p_f=1.45 GPa. Nevertheless, flow jet or adiabatic shear instability resulted from localised deformation at the particle boundaries is commonly believed to be primary responsible for creating the mostly effective intimate metallic bonding between the adjacent particles under extremely high strain rate as a result of high impact velocity. Adiabatic interaction between particle/particle is based on the fact that the thermal diffusion distance is very small (on the order of 10^{-6} m) during the very short operational time of impact, i.e. 10^{-7} to 10^{-5}s [18]. This is the reason of that why kinetic energy is mainly dissipated as heat, causing material softening and shear localisation and promoting intimate contact between two adjacent particles by mechanical interlocking and even by impact fusion, as evidenced from *Fig. 4b*.

Mechanical characteristics of feedstock powder, extruded rod and cold sprayed material, all performed by $Al_{94}Fe_3Cr_3$-alloy, are listed in *Table 2*.

Several aspects resulting from mechanical performance of as-sprayed alloy could be mentioned here to clarify superior advantages of cold-spraying technique in comparison with extrusion process.

Table 2 – Mechanical characteristics of feedstock powder, extruded rod and cold sprayed material, all performed by $Al_{94}Fe_3Cr_3$-alloy

Parameter / Material	E, GPa	HV, GPa	Plasticity δ_H/δ_A	Yield stress $\sigma_{0,2}$, MPa
Feedstock powder*	–	0.91±0.3	0.92/0.92	–
Extruded rod	87.5±2.3**	1.62±0.04	0.90/0.89	380
Cold sprayed alloy	90.0±2.5	2.19±0.02	0.86/0.87	515

Notice: * – adopted from [10]; ** – adopted from [4]

First of all it could be seen that the Vickers hardness, HV, of extruded rod and as-sprayed alloy is much higher than that of feedstock powder, suggesting material strain hardening upon consolidation. Compared to extrusion rod, Young's modulus is somewhat smaller whereas hardness number of the as-sprayed alloy is higher by roughly about 35%. The same is true for the value of yield stress of as-sprayed alloy that is by roughly 35% as high. The question is that what structural and processing parameters are responsible for enhanced strength properties of as-sprayed alloy. It is reasonable to though that retaining the entire number of quasicrystalline particles causes the strength of as- sprayed alloy to be greater than that for as-extruded material partly loosed quasicrystalline phase. The effect of quasicrystalline phase is intensified by extremely high values of strain rate (on the order of $10^5...10^7 s^{-1}$) sustained by powder particle under impact. As was pointed out in [10] strain rate of powder particle under cold spraying exceeds by several orders magnitude to that for extrusion process. Following the calculation procedure [10] the latter could be estimated for the present study as great as 15.2 s^{-1}. Apart from reduced at the least by 180 K processing temperature of cold-spraying causes yield stress, σ_y, to rise up, suggesting the decrease of material deformation when applied pressure is of the same value. Taking into consideration nearly the same pressure conditions ($P_l \approx p_f$), essential increase of yield stress, σ_y could play crucial role in decrease of aspect ratio for powder particle in the as-sprayed alloy compared to that revealed in as-extruded material. As notable characteristic, it is easy to show that the ratio of true deformation for powder particles of as-extruded rod to that of as-sprayed alloy is nearly the same as the ratio of aspect ratio for powder particle in extruded rods to that revealed in as-sprayed material, i.e. $e_e/e_{cs} \approx 1.7$ and $k_{fe}/k_{fcs} \approx 1.6$. This result justifies the validity of suggestion attributed to that the difference in deformation conditions applied to extruded rods and a cold-sprayed alloy causes the difference in their structural features.

Another aspect concerns ductility of $Al_{94}Fe_3Cr_3$-alloy fabricated via different techniques, i.e. water atomisation, extrusion, and cold-spraying. It is important that plasticity characteristics δ_H (δ_A) of feedstock powder are greater than critical value $\delta_H \geq 0.9$, indicating ductile behaviour of material in conventional tensile and bending tests [14] and, therefore, ensuring its good deformability under consolidation. That is why no evidences of delaminating and cracking have been observed in microstructure of as-received extruded rod and cold-sprayed alloy, see Fig. 4. It is also essential that despite of increased hardness numbers for both kinds of $Al_{94}Fe_3Cr_3$-alloy fabricated via extrusion process and cold-spraying keep the values of plasticity characteristics δ_H (δ_A) just about critical value, implying their workability under loading during exploitation. Thus, the essential advantage of both kinds of these metal matrix composites and especially that processed by cold spraying is their high hardness combined with rather high ductility valuable with respect to damage tolerance.

Among them composite performed by cold spraying gives mostly crucial benefit since its hardness number superior to that for hardest commercial Al alloys (Al-Cu-Mg-Fe-Ni) modified with 0.16 wt.% Sc and ascribed to series 7075-T6, which has been developed and successfully used for application under intermediate temperature (~ 230ºC). As reported in [18] Vickers hardness of 2618 Al alloy is about 1.45 GPa whereas cold-sprayed $Al_{94}Fe_3Cr_3$-alloy guarantees HV values by roughly 50 % as high. In addition, quasicrystalline Al-Fe-Cr -based alloys exhibit the thermal stability of mechanical properties at least up to 300º C [4], making them competitive with those of 2618 Al alloy for application in aircraft industry.

CONCLUSIONS

By using feedstock powder with nominal composition such as $Al_{94}Fe_3Cr_3$ the present study demonstrate significant advantages of cold-spraying in performance of composite Al-based coatings reinforced by metastable nano- and submicrometer-sized quasicrystalline particles as compared to currently employed warm extrusion process.

The main benefit of cold spraying is that the composite quasicrystalline structure of initial feedstock powder is entirely retained in as-sprayed material whereas extrusion process results in loosing by roughly about 23% of quasicrystalline phase. The latter is presumably decomposed under combined effect of elevated temperature and high pressure used in extrusion process.

Overall, hardness number and yield stress of cold-sprayed $Al_{94}Fe_3Cr_3$–alloy superiors nearly by 35 % to those of as-extruded material. Retaining the number of quasicrystalline particles at the most combined with extremely high values of strain rate sustained by powder particle under impact at the rather low processing temperature play crucial role in remarkable strain hardening of cold-sprayed alloy.

It was justified experimentally that essential advantage is combination of high hardness and rather high ductility valuable with respect to damage tolerance. Despite of strain hardening plasticity characteristics δ_H (δ_A) of cold-sprayed $Al_{94}Fe_3Cr_3$–alloy was determined to be just about critical value $\delta_H \cong 0.9$ indicated in literature [14] as criterion for ductile behaviour of material under conventional tensile and bending tests and, thus, quite enough for their workability under loading during exploitation.

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REFERENCES

[1] A. Inoue, Progress in Mater. Sci., 1998, Vol.43, P.365-520.
[2] A. Inoue, H.M. Kimura, J. Mater. Res., 2000, Vol. 15, No12, P. 2737-2744.
[3] A. Inoue, H.M.Kimura, Mat. Sci. Eng. A, 2000, Vol. 286, P. 1 -////.
[4] Yu.V. Milman, A.I. Sirko, M.O. Iefimov, and et al., High temperature materials and processes, 2006, Vol. 25, P. 19-29.
[5] D. Shechtman, Blech., D. Gratias, J.V. Cahn, Phys. Rev. Lett., 1984, Vol. 53, No20, P. 1951-1954.
[6] M. Galano, F. Audebert, I.C. Stone, D. Cantor, Acta Mater., 2009, Vol. 57, P. 5107-5119.
[7] M. Galano, F. Audebert, A. Garcia Escorial, and et al., Acta Mater., 2009, Vol. 57, P. 5120-5130.
[8] O.D. Neikov, V.G. Kalinkin, and et al., Patent Ru No 2078427, Information Bulletin, 1977, No. 12.
[9] A. Papyrin, V. Kosarev, S. Klinkov, A, Alkhimov, V. Fomin, Cold Spray Technology, Elsevier Science, 2006, 336 p.
[10] M.V. Semenov, M.M. Kiz, M.O. Iefimov, A. I. Sirko, A.V. Byakova, Yu. V. Milman. Nanosystem, Nanomaterials, and Nanotechnologies, 2007, Vol. 4, No 4, P. 767-783.
[11] M.M. Kiz, A.V. Byakova, A.I. Sirko, Yu. V. Milman, M. S. Yakovleva, Ukr. J. Phys., 2009, Vol. 54, No 6, P. 594-599.
[12] A.V. Byakova, M.M. Kiz, A.I. Sirko, M.S. Yakovleva, and Yu.V. Milman, High Temperature Materials and Processes, 2010, Vol. 29, No 5-6, P. 325-337.
[13] A.V. Byakova, Yu.V. Milman, A.A. Vlasov, Nanophysics, Nanosystems, and Nanomaterials, 2004, Vol. 2, No 1, P. 215-225.
[14] Yu.V. Milman, B.A. Galanov, S.I. Chugunova, Acta. Metall. Mater. 1993, Vol. 41, No 9, P. 2523-2532.
[15] W.C. Oliver and G.M. Pharr J., Mater. Res., 1992, Vol. 7, No 6, P. 1564-1583.
[16] B.A. Galanov, Yu.V. Milman, S.I.Chugunova, I.V. Goncharova, Superhard Materials, 1999, Vol. 21, No 3, P. 23-35.
[17] J.V. Cahn, D. Schehntman , D. Gratias, J. Mater. Res., 1986, Vol. 1, P. 13-26.
[18] Ajdelsztajn, A. Zuniga, B. Jodoin, E.J. Lavernia, Surf. Coat. Technol., 2006, Vol. 201, No 12, P. 2109-2116.