Original Article

The structure and properties of pre-alloyed NiAl-Cr(Co,Hf) spherical powders produced by plasma rotating electrode processing for additive manufacturing


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ABSTRACT

The structure and properties of pre-alloyed Ni$_{41}$Al$_{41}$Cr$_{12}$Co$_6$ spherical powders (the 40–160 μm fraction) produced using the plasma rotating electrode processing technology were studied. The evolution of the fine structure of pre-alloyed Ni$_{41}$Al$_{41}$Cr$_{12}$Co$_6$ spherical powders under heating at 20, 350, …, 850 °C was investigated. Disk-shaped chromium-rich pre-precipitation zones 5–30 nm in size were detected in the temperature range of 450, …, 650 °C; they precede the formation of the dispersed chromium precipitate. Prism-shaped chromium nanocrystals with the characteristic longitudinal dimension ranging from 15 to 100 nm, whose nucleation process starts at prismatic dislocation loops, were found to be formed at 750, …, 850 °C. The Young's modulus, hardness, and elastic recovery of powder material were determined by nanoindentation measurements. The resulting powders are characterized by bulk density of 3.8 g/cm$^3$, excellent flow rate (3.5 s), and the angle of repose of 19.6°.

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1. Introduction

NiAl alloy is a promising basis for designing high-temperature materials for the aircraft and aerospace industries [1–3]. NiAl-based alloys are characterized by high melting point, high Young’s modulus, a relatively low density, and enhanced heat and corrosion resistance at temperatures above 1000 °C. Their thermal conductivity is much higher than that of the conventional nickel-based superalloys [3–5]. However, the industrial application of NiAl is limited by low ductility and crack resistance at room temperature, as well as low heat and creep resistance at elevated temperatures [5–7]. Furthermore, fabrication of final items from NiAl-based alloys is characterized by high melting point, high Young’s modulus, a relatively low density, and enhanced heat and corrosion resistance at temperatures above 1000 °C. Their thermal conductivity is much higher than that of the conventional nickel-based superalloys [3–5]. However, the industrial application of NiAl is limited by low ductility and crack resistance at room temperature, as well as low heat and creep resistance at elevated temperatures [5–7]. Furthermore, fabrication of final items from NiAl-based alloys is characterized by high melting point, high Young’s modulus, a relatively low density, and enhanced heat and corrosion resistance at temperatures above 1000 °C. Their thermal conductivity is much higher than that of the conventional nickel-based superalloys [3–5]. However, the industrial application of NiAl is limited by low ductility and crack resistance at room temperature, as well as low heat and creep resistance at elevated temperatures [5–7]. Furthermore, fabrication of final items from NiAl-based
alloys using the conventional metallurgy methods is complicated due to high hardness and wear resistance of NiAl, as well as the tendency of materials based on this alloy toward crack formation and spalling when being machined [6,8].

These shortcomings can be eliminated using an integrated approach that involves (1) optimization of the system for doping NiAl in order to enhance its mechanical properties and (2) transition from the conventional metallurgy methods to the technologies minimizing the machining stage. These technologies include net-shape powder metallurgy by hot isostatic pressing (HIP) [9–13] and modern additive technologies (AT), such as selective laser melting (SLM), electron beam melting (EBM), and direct metal deposition (DMD) [13–20].

Pre-alloyed spherical powders are the rare materials for using the methods listed above; stability of the manufacturing process and quality of a final item largely depend on their grade [21–23]. The spherical shaped particles that ensures the maximum packing density and high flow rate is the key requirement of AT [23–25]. Furthermore, the powders need to be characterized by high chemical homogeneity, the minimal oxygen content and contain no satellites or gas porosity defects [24,26,27]. The granulometric composition of powders can vary depending on the type of AT equipment and the material used [18,20,22,28–31].

Various atomization techniques such as water atomization, gas atomization (GA), plasma atomization, plasma rotating electrode processing (PREP), and centrifugal atomization are used to produce spherical powders [24,32–40]. Thus, it was demonstrated in studies [41–44] that the use of PREP powders ensures the microstructure with higher quality and better properties of the final items compared to GA powders.

This article continues the previous publications [45,46] focused on optimization of the composition of NiAl-based alloy and development of the integrated technology for producing electrodes for PREP. In study [45], the structure and mechanical properties of NiAl-based alloys doped with chromium and cobalt at total content (Cr + Co) = 18 at.% were studied and the Ni41Al41Cr12Co6 alloy was shown to possess the best properties. In study [46], the structural transformations and mechanical behavior of the Ni41Al41Cr12Co6 alloy were investigated at elevated temperatures and the electrode manufacturing technology including synthesis of the alloy preforms by centrifugal SHS casting followed by vacuum induction melting was proposed.

This study was aimed at fabricating pre-alloyed spherical Ni41Al41Cr12Co6 powders by the PREP technology and studying their composition, structure, mechanical and processing properties. Special attention was paid to the investigation of the evolution of powder microstructure when heated to 850°C.

2. Experimental procedure

Powders of heat-resistant Ni41Al41Cr12Co6 alloy were produced by plasma rotating electrode processing (PREP) on an UTsR-91 setup (PAO Elektromekhanika, Russia). Cylindrical preforms, 60 mm in diameter and 550 mm long, manufactured using the technology thoroughly described in [45] were used as the initial electrode. The electrodes were sputtered in a mixture of inert Ar and He gases taken at a 1:9 ratio. The granulometric composition of pre-alloyed powders was determined by laser diffraction in a liquid medium using an ANALYSSETTE 22 MicroTec plus particle size analyzer (FRITSCH, Germany) in accordance with ISO standards 13320:2009. The target powder fraction with particle size of 40–160 μm was isolated using a combination of sieves 200 mm in diameter (sieve size, 160 and 40 μm) on a BA 200N sieve shaker (CISA, Spain).

The phase composition was determined by X-ray powder diffraction (XRD) on a DRON-3 diffractometer (Russia) using Co-Kα radiation at angles 2θ = 100–140°. The contents of gas impurities (O, N) were measured using the reduction melting method on a TC-436 analyzer (LECO, USA). The cross-sectional microstructure, surface morphology, and elemental composition of the powders were examined using an S-3400N scanning electron microscope (SEM) (Hitachi, Japan) equipped with a NORAN X-ray energy-dispersive spectrometer. The fine structure of the powders at room temperature and the structural transformations occurring in the material under heating were studied in real time by high-resolution transmission electron microscopy (HRTEM) on a JEM-2100 microscope (Jeol, Japan). Foils made of the powders for HRTEM were prepared by dual beam ion etching using a PIPS II System setup (Gatan, USA). Foils were heated in a Gatan Heating in situ holder model 652 (USA) directly in the microscope column at a heating rate of 100°C/min. The structure was recorded under isothermal exposure to 20, 350, 450, 550, 650, 750, and 850°C for 20–25 min.

Hardness (H), Young’s modulus (E), and elastic recovery (R) of the structural components of NiAl-based pre-alloyed spherical powders were determined by indentation measurements on a Nanohardness tester (CSM Instruments, Switzerland) at a load of 20 mN, the loading rate of 40 mN/min, and load exposure of 5 s. The nanoindentation curves were processed using the Oliver–Pharr method.

Bulk density of the powders was determined using a funnel with a diameter of 2.5 mm in compliance with the ISO standard 3923-1:2008. The flow rates of the powders were determined in accordance with the ISO standard 4490:2014.

3. Results and discussion

3.1. The morphology and granulometric composition of pre-alloyed Ni41Al41Cr12Co6 spherical powders

Examination of the morphology (Fig. 1a) and microstructure of the surface (Fig. 1b) of the pre-alloyed Ni41Al41Cr12Co6 powder (fraction 40–160 μm) produced by PREP demonstrated that all the particles have an ideal spherical shape with the mean ratio between the larger and smaller radii (the so-called equiaxiality ratio) Ks = 1.017 ± 0.029 and were characterized by the absence of satellites or large pores on the surface. During PREP, melt droplets are detached from the electrode end being fused with a plasma flow and acquire spherical shape under surface tension. The melt droplets contact with the gas medium being sputtered to result in rapid crystallization at rates of ~104, . . ., 106 K/s [47], while their spherical shape is retained. The microstructural studies of the surface of the pre-alloyed spherical powder showed that the surface of each particle typically consisted of individual grains having a dendritic structure (Fig. 1b).
3.2. The composition and microstructure of pre-alloyed Ni_{44}Al_{41}Cr_{12}Co_{6} spherical powders

The XRD patterns of the pre-alloyed Ni_{44}Al_{41}Cr_{12}Co_{6} spherical powder shown in Fig. 2 confirm that nickel monoaluminide (the bcc system) is formed as the main phase and chromium-based solid solution also crystallizing in the bcc system is formed as well. Superposition of the radiation intensity peaks in the main crystallographic directions observed in the XRD pattern when identifying the NiAl and Cr phases is related to the fact that they are characterized by the cubic crystal system with very close lattice parameters. Therefore, it is difficult to quantitatively assess the contents of phase components of pre-alloyed Ni_{44}Al_{41}Cr_{12}Co_{6} spherical powders according to the XRD pattern.

According to the XRD data, the lattice parameter of the bcc phase (0.2882 nm) is somewhat underestimated compared to its reference value (0.2887 nm) for equiatomic nickel monoaluminide due to the reduced aluminum content and replacement of some atoms in the NiAl lattice with Cr and Co atoms. The contents of oxygen and nitrogen impurities in the powder according to chemical analysis are not higher than 0.0043 and 0.00061 wt. %, respectively.

Examination of cross sections (Fig. 3a) showed that the resulting spherical powder (the 40–160 μm fraction) has a dendritic structure. The characteristic transversal dimension of dendrites is 2–4 μm, being an order of magnitude smaller than that in cast electrodes [46]. The porosity of spherical particles is less than 0.3 vol.%; pore diameter is less than 0.5 μm. EDS analysis (Fig. 3b) of the structural components of the Ni_{44}Al_{41}Cr_{12}Co_{6} alloy showed that dendrites consisted of NiAl with the approximately equivalent contents of dissolved Cr and Co. Cr concentration in intermetallic grains is about 6 at.%, close to the solubility limit. The excessive Cr content in the alloy results in formation of thin (350–500 nm) interlayers of Cr-based solid solution in the interdendritic space. Hf precipitates as dispersed nanoparticles (Fig. 3b) ~100 nm in diameter, which are predominantly localized in thin interlayers of Cr-based solid solution.

The results of investigating the fine structure of spherical particles of the pre-alloyed Ni_{44}Al_{41}Cr_{12}Co_{6} powder by HRTEM are shown in Fig. 4. It is clear from the microimages (Fig. 4a and b) that the grains of dendritic aggregates contain no dispersed Cr nanoparticles that are observed in the cast alloy [46]. The different contrast in some alloy regions in the TEM image is caused by fluctuations in Cr concentration emerging during melt crystallization and due to its increased content in the melt, being higher than the solubility limit in the NiAl phase. Cooling of spherical powders at a rate of ~10^4 K/s inhibits the diffusion processes that result in precipitation of excessive Cr as dispersed particles; in this connection, zones with different Cr concentration in the NiAl phase remain in the intermetallic grain (Fig. 4). The cumulative effect of crystallization parameters and high Cr concentration in the two-phase Ni_{44}Al_{41}Cr_{12}Co_{6} alloy also gives rise to thermal stress, high density of packing defects, and distortion of the NiAl phase lattice.

The diffraction data (Fig. 4c) suggest that the lattice parameter of the intermetallic alloy is 0.2885 nm and corresponds to the NiAl phase, being consistent with the XRD data (Fig. 3). In addition, the XRD pattern of the alloy region under study contains no additional reflection, thus indicating that there is no second phase.

3.3. Evolution of the microstructure of pre-alloyed Ni_{44}Al_{41}Cr_{12}Co_{6} spherical powders under heating

The structural changes in the powders emerging under isothermal exposure to temperatures ranging from 350 to 850 °C in the column of the electron microscope for 20 min, with an increment of 100 °C, were studied by TEM and HRTEM. Three temperature intervals (20–450; 450–650, and 650–850 °C) where the most significant structural changes take place (Fig. 5) were revealed during the study. Diffusion processes resulting in nucleation of Cr-rich pre-precipitation zones (Guinier–Preston zones) at concentration fluctuations are activated in the 20–450 °C interval (Fig. 5a). The resulting pre-precipitation zones are uniformly distributed over the bulk of the NiAl-phase grain and have a disk shape, with diameter ranging from 4 to 30 nm. Further increase in temperature to 650 °C causes collective recrystallization of large (20, ...,
30 nm) Cr-rich pre-precipitation zones due to intensive diffusion of Cr atoms from pre-precipitates less than 15 nm in size, toward the matrix-large pre-precipitate interface boundary. This process is caused by the tendency of the system to reach the minimum free energy by decreasing surface energy. As a result, fine-grained pre-precipitates disappear, while the coarser-grained ones increase from 20, . . . , 30 to 38, . . . , 43 nm. An increase in temperature to 850 °C (Fig. 5b) shifts the solubility limit of Cr in the NiAl phase toward higher concentrations; as a result, Cr-rich pre-precipitation zones are gradually dissolved and completely disappear (the region shown as a circle in Fig. 5b). Nevertheless, some Guinier–Preston zones give rise to Cr spherical nanoparticles ∼50 nm in size, which are stable in the 650–850 °C temperature range.

Double dislocation loops (Fig. 6a) with a packing defect inside produced by a vacancy cluster are detected in the NiAl matrix at temperatures above 650 °C. The resulting double dislocation loops have a characteristic prism shape and are 20–100 nm long. Smallman and Ngan [48] reported that these clusters were capable of further diffusion growth at elevated temperatures. These dislocation loops can presumably act as nucleation centers for the Guinier–Preston zones (GP zones). The mechanism of nucleation of GP zones at concentration fluctuations under variation of the temperature solubility limit of one of the dopants in the alloys within the Al–Cu, Al–Zn systems has been thoroughly studied [49–51]. However, the mechanism of nucleation of GP zones at dislocations and packing defects remains poorly studied.

Thorough investigation of structural changes occurring in the powders under isothermal exposure to 750 and 850 °C (Fig. 6) revealed characteristic regularities in the order of structure formation. The dissolution of disk-shaped Cr-rich pre-precipitation zones detected within the temperature range from 650 to 850 °C starts from their fragmentation into subgrains (Fig. 6b), since the increase in surface area of subgrain boundaries increases their dissolution rate and the system reaches the minimum free energy more rapidly. Nanocrystal aggregates (Fig. 6c and d) of elongated prismatic shape identical to that of double dislocation loops were formed.
at 850 °C. The transversal dimension of nanocrystals ranged from 15 to 100 nm.

Some typical features in the structure of Cr nanocrystals were revealed by HRTEM (Fig. 6d). The central portions of all nanocrystals (Fig. 6d) have a characteristic plate-shaped structure, while the vertices of the prismatic nanocrystal crystallize in the ordered bcc system. Initially, most nanocrystals have a plate-like structure because the deformation energy factor is the least for this shape [48]. Hence, the plate-shaped structure of crystals ensures the minimum surface energy of the alloy at the initial stage of nanocrystal nucleation. The initial observed structural heterogeneity gradually disap-

pears as the duration of isothermal exposure is increased. The revealed structural features (size, shape, and structure) of Cr nanocrystals allow one to suggest the staging and the mechanism of their nucleation in the NiAl powder matrix. Formation and diffusion growth of double dislocation loops accompanied by dissolution of Cr-rich pre-precipitation zones due to the change in temperature solubility limit of Cr in the NiAl phase takes place during the first stage (750 °C). Nucleation of plate-like solute-rich GP zones at double dislocation loops presumably occurs at the second stage (750, . . . , 850 °C). By analogy with [48], this process is caused by the increased concentration of Cr atoms along dislocation loops and lower diffusion activation energy than in the grain bulk, as well as the presence of a packing defect that can act as a nucleation center of a new Cr phase under certain conditions (the new phase has the same crystal lattice as the packing defect). Therefore, the double dislocation loops formed in the alloy under study act as nucleation centers for the GP zones. The final stage (850 °C) involves the intensive diffusion growth of the GP zones resulting in formation of nanocrystals having an ordered bcc lattice. The initial stage of formation of Cr nanocrystals was detected at 750 °C (Fig. 6a); it confirms the proposed mechanism. Cr-rich crystals are typically formed on the (211) crystallographic planes of the NiAl matrix, preferably along the [224] directions, which is related to the mechanism of nucleation of GP zones at double dislocation loops.

3.4. Mechanical and processing properties of pre-alloyed Ni₄₁Al₄₁Cr₁₂Co₆ spherical powders

In order to study the mechanical properties of pre-alloyed spherical powders, we conducted nanoindentation measurements along the cross-sectional centerline of a spherical particle ~150 μm in diameter. The hardness (H), Young’s modulus (E), and elastic recovery (R) were measured. The indent projection size ranged from 1.5 to 2.5 μm (Fig. 7), being smaller than the cross-sectional area of NiAl phase dendrites but larger than thin interdendritic interlayers of the Cr phase. Therefore, when the indenter tip penetrated into the Cr phase, the data derived from the indentation curves were averaged over properties of the two phases of the Ni₄₁Al₄₁Cr₁₂Co₆ alloy. Resistance to plastic (H²/E²) and elastic (H/E) deformation was also calculated.

The data on nanoindentation of granules are summarized in Table 1; the indent numbering corresponds to their sequential arrangement in Fig. 7.

Sequential comparison of the results of each measurement (Table 1) with the proper location of the indent in the microimage (Fig. 7) gives grounds for saying that the difference in mechanical properties of the alloy microregions along the cross-sectional centerline of the particle depends only on what structural components the indenter tip has penetrated into; there is no hardness gradient from the particle surface toward its center. The mean H, E, and R are 7.56 ± 0.87 GPa, 170 ± 10.46 GPa, and 26.83 ± 2.30%, respectively. Zaitsev et al. [45] reported that the Ni₄₁Al₄₁Cr₁₂Co₆ cast alloy is characterized by hardness of ~7.1 GPa. The results are in good agreement with the values of hardness and Young’s modulus of NiAl-based alloys [52–55].

The angle of repose and bulk density are among the most important processing properties of powder materials that determine their applicability in additive technologies. The angle of repose characterizes the flow rate of a powder, depends on particle shape, and is minimal when the particles are shaped as an ideal sphere. The measurements have demonstrated that the resulting pre-alloyed Ni₄₁Al₄₁Cr₁₂Co₆ spherical powders (the 40–160 μm fraction) are characterized by a bulk density of 3.8 g/cm³, an excellent flow rate of 3.5 s, and angle of repose of 19.6°.

4. Conclusions

1. Pre-alloyed Ni₄₁Al₄₁Cr₁₂Co₆ spherical powders have been produced by PREP. The powders of 40–160 μm fraction have been found to possess an ideal spherical shape, porosity of less than 0.3 vol.%, high purity with respect to (O, N) impurities (their contents being 0.0043 and 0.00061 wt.%, respectively), and to contain no satellite defects.
2. It has been found that spherical powders have a fine-grained dendritic structure. The characteristic transversal

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Table 1 - The results of nanoindentation measurements along the cross-sectional centerline of fast-quenched Ni₄₁Al₄₁Cr₁₂Co₆ alloy granules.

<table>
<thead>
<tr>
<th>Indent</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>R (%)</th>
<th>(H/E)²</th>
<th>(H/E) 10²</th>
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<tr>
<td>1</td>
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<td>30.61</td>
<td>2.45</td>
<td>5.43</td>
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<tr>
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<td>1.78</td>
<td>4.71</td>
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<tr>
<td>3</td>
<td>7.62</td>
<td>159</td>
<td>29.04</td>
<td>1.75</td>
<td>4.79</td>
</tr>
<tr>
<td>4</td>
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<tr>
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<tr>
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<tr>
<td>8</td>
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</tr>
<tr>
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<td>179</td>
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Mean value 7.56 ± 0.87 170 ± 10.46 26.83 ± 2.30 1.56 ± 0.54 4.47 ± 0.50
dimension of dendritic branches is 2–4 μm; the interdendritic space is filled with thin (350–500 nm) interlayers of Cr-based solid solution.

3. The evolution of the microstructure of pre-alloyed NiAl1AlxCr12Cox spherical powders has been studied upon isothermal exposure to 350, 450, 550, 650, 750, and 850 °C. Formation of Cr-rich disk-shaped pre-precipitates (GP zones), 5–40 nm in diameter, has been found in the 450, . . . , 650 °C temperature range. Cr-rich pre-precipitates are intensively dissolved at 750 °C via fragmentation into subgrains. Prism-shaped Cr nanocrystals with the characteristic longitudinal dimension ranging from 15 to 100 nm are formed in the temperature range of 750–850 °C.

4. The resulting spherical powders are not characterized by hardness gradient along the cross-sectional centerline. The Young's modulus, hardness, and elastic recovery of spherical powders are 7.56 ± 0.87 GPa, 170 ± 10.46 GPa, and 26.83 ± 2.30%, respectively.

5. On the basis of their processing parameters, namely, bulk density of 3.8 g/cm³, flow rate of 3.5 s, and the angle of repose of 19.6°, the resulting spherical powders can be recommended for fabricating items by the SLM, EBM, DMD, and net-shape powder metallurgy by HIP methods, as well as for depositing heat-resistant coatings by laser or plasma deposition.

Conflicts of interest
The authors declare no conflicts of interest.

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