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Structure and properties of NiAl-Cr(Co,Hf) alloys prepared by centrifugal SHS casting. Part 1 – Room temperature investigations

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ABSTRACT

The structure and mechanical behavior of NiAl-based intermetallic alloys alloyed with Hf, Cr and Co at their total content $(Cr+Co)=18$ at% were studied. The alloys were prepared by centrifugal SHS casting from oxide raw materials. The mechanism of precipitation hardening is shown to take place at the Cr/Co ratios >0.5, leading to the formation of chromium-based inclusions and nanosized precipitates in the NiAl dendrite body. The resulting alloys have a three-level hierarchical structure with oxygen, nitrogen, and carbon impurity contents of 0.129, 0.0045, and 0.04 wt%, respectively, and the ultimate compressive strength at room temperature equal to 2300 MPa.

1. Introduction

NiAl intermetallic compound is a promising material for fabricating next-generation refractory alloys that operate at temperatures above 1100 °C. Nickel monoaluminide has an ordered CsCl (B2)-type body-centered cubic structure, high melting point (1640 °C), high Young's modulus (284 GPa), and the relatively low density (5.86 g/cm^3) [1]. Thermal conductivity of NiAl is 70–80 W/m K, which is 3–8-fold higher than that of nickel-based superalloys [2]. Furthermore, NiAl exhibits high resistance to oxidation at elevated temperatures and high corrosion resistance in aggressive environments [2,3].

However, the use of pure polycrystalline NiAl is limited as it has a near-zero plasticity at room temperature and low high-temperature strength above 800 °C [1,4,5]. These drawbacks of the NiAl can be eliminated by alloying. The elements used for alloying NiAl-based alloys can be conventionally divided into three main groups [6]:

- Mn, Cu and group VIII elements are highly soluble in NiAl and are prone to forming isostructural compounds [7–11];
- V, Re and subgroup VIB elements have low solubility in NiAl and form pseudobinary eutectic systems with stoichiometric NiAl, while the increased alloy plasticity is ensured by formation of the lamellar eutectic structure [12,13];
- IIIB, IVB, and VB subgroup elements have a very limited solubility in NiAl and form ordered ternary intermetallic compounds, such as Heusler phases Ni_2AlX and Laves phases NiAlX [14–17], which have a positive effect on high-temperature characteristics of the alloy.

For today, the eutectic alloys of the NiAl-9Mo [18–20] and NiAl-xCr-yMo ($x=28$–36; $y=3$–6 at%) systems [16,17,21–30] have been studied in most detail. The NiAl-xCr system, where $x=1$–34 at% [31–38], has also been studied over a broad alloying range. It has been revealed that inclusions based on α-Cr of different size can be formed in the NiAl matrix depending on chromium content and cooling conditions.

The methods for preparing of NiAl-based alloys include the conventional casting techniques (induction melting, arc melting) [16,17,19,29], rapid solidification techniques [23,24,26,27], powder metallurgy [6,39,40], and directed crystallization (the Bridgman method) [12,13,21,22,25,28,30]. All the afore-listed methods employ high-purity elements (alloy components or semi-products prepared using them) as starting materials.

A specific feature of this study is that centrifugal SHS (self-propagating high-temperature synthesis) casting, which allows preparing refractory and heat-resistant materials from oxide raw material, was used. The possibility of producing heavily alloyed NiAl-based alloys with low content of undesirable impurities was demonstrated in [41–45]. Highly exothermic mixtures of metal oxide powders with a reducing agent are employed as starting elements for synthesis. The use of energy of chemical reaction released during combustion makes SHS an energy-efficient

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Table 1
Specifications of initial components and functional additives.

No.	Substance	Grade	GOST state standard/technical specifications TU	Grain size, (μm)	Chemical composition, (%)
Key initial components					
1	NiO	Special purity grade	TU 6-09-02439-87	< 40	99.0
2	Al	PA-4	GOST 60-58-73	< 140	98.0
3	Cr_2O_3	Reagent grade	TU 6-09-4272-84	< 20	99.2
4	Co_3O_4	Reagent grade	GOST 4467-79	< 10	99.9
5	Hf	GFM-I	TU 48-4-176-85	–	–
Functional additives					
9	Electrocorundum Al_2O_3	White 25 A, F 320	GOST 28818-90	16–49	98–99
10	Na_3AlF_6	KP	GOST 10561-80	–	–

Table 2
Compositions of the alloys in the Ni-Al-Cr-Co-Hf system under study.

Alloy	at%/wt%				
	Ni	Al	Cr	Co	Hf
$Ni_{41}Al_{41}Cr_6Co_{12}$	41/53.35	41/23.50	6/6.79	12/15.4	0.25/0.97
$Ni_{41}Al_{41}Cr_9Co_9$	41/53.59	41/23.60	9/10.23	9/11.6	0.25/0.98
$Ni_{41}Al_{41}Cr_{12}Co_6$	41/53.83	41/23.71	12/13.71	6/7.77	0.25/0.98
$Ni_{41}Al_{41}Cr_{14}Co_4$	41/54.00	41/23.78	14/16.04	4/5.19	0.25/0.98

method for fabricating refractory materials. The drawback of SHS metallurgy is the limited cast product size; hence, an additional stage of remelting the SHS semi-product is required.

A combination of three alloying elements was selected in the present study to improve properties of NiAl: Co, to implement the mechanism of solid solution strengthening; Cr, to form the heterophase structure with disperse inclusions in the form of an α-Cr-based solid solution [35,37]; and Hf, to enhance thermal creep resistance.

The main aim of this work was to study the effect of the Cr/Co ratio on the microstructure and mechanical properties of the NiAl-xCr-yCo-0.25Hf alloys ($x = 6$–14; $y = 4$–12 at the total $x + y$ content remaining unchanged and equal to 18 at%) prepared by centrifugal SHS casting.

2. Experimental procedure

The powders with parameters listed in Table 1 were used to prepare alloys of the Ni-Al-Cr-Co-Hf system by centrifugal SHS casting.

The preparation scheme of the exothermic reactionary mixture included component dosing and mixing them in a ball mill for 20 min at a 1:15 ratio between the grinding balls and the material. The general form of the SHS reaction can be written as (1):

$$NiO+(\alpha)\,Cr_2O_3+(\beta)\,Co_3O_4+Hf+Al+(FA)\rightarrow[Ni_xAl_y-(Cr/Co)\text{-}Hf]+Al_2O_3+Q \qquad (1)$$

where α, β are the reaction coefficients;

FA – functional additives (Al_2O_3, $Na_3[AlF_6]$);
Q – the thermal effect of the reaction.
Al – the reducing agent.

The α and β coefficients were chosen so that the alloys with compositions listed in Table 2 were formed. To eliminate the effect of the stoichiometry of NiAl compound on solubility of Cr and Co, the Ni:Al atomic ratio for all alloys was chosen to be equal to 1:1. Hafnium content for all the investigated alloys was also fixed and equal to 0.25 at%.

The technological aspects of SHS casting of intermetallic alloys and the regularities in their combustion and gravity separation of synthesis products were discussed in detail in [41–45]. In the present study, SHS casting was performed in a cylinder-shaped graphite crucible 80 mm in diameter on a radial centrifugal SHS setup [42]. Crucible walls were preliminarily coated with a protective corundum layer. Combustion process was initiated using tungsten coil, which heated the surface layer of the mixture to the point of ignition. Synthesis was carried out in the combustion mode at a centrifugal acceleration of 50 ± 5g. The combustion rates of the mixtures under study were varied in the range from 1.2 cm/s (for $Ni_{41}Al_{41}Cr_{14}Co_4$) to 1.6 cm/s (for $Ni_{41}Al_{41}Cr_6Co_{12}$). The combustion temperature for the mixtures was 2200–2350 °C depending on their composition, which ensured complete melting of the synthesis products (metal alloy and aluminum oxide) and their gravity separation due to the difference between their specific weights. The synthesis products in as-cast state had two easily detachable layers: the lower part of the sample was the target intermetallic alloy (Fig. 1), while the upper part (slag) predominantly consisted of

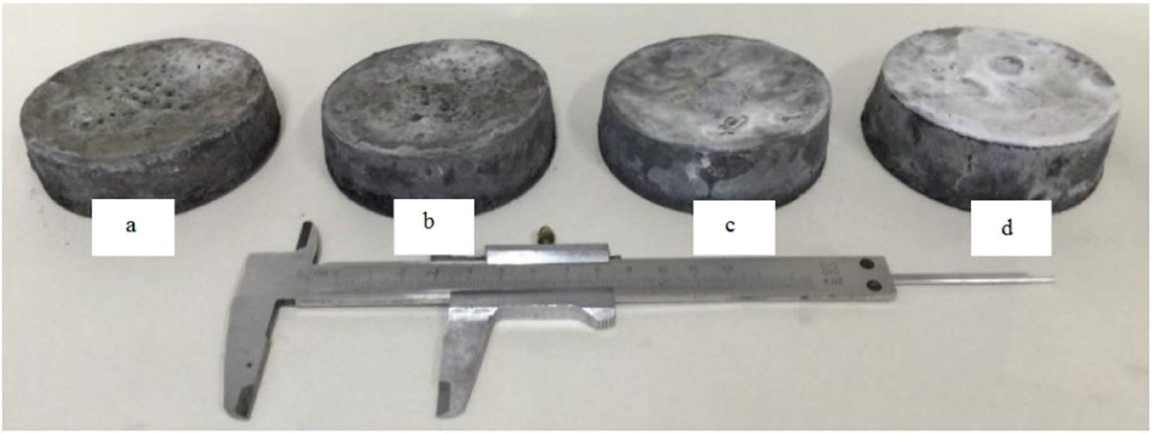

Fig. 1. The samples after SHS casting: a) $Ni_{41}Al_{41}Cr_6Co_{12}$ b) $Ni_{41}Al_{41}Cr_9Co_9$ c) $Ni_{41}Al_{41}Cr_{12}Co_6$ d) $Ni_{41}Al_{41}Cr_{14}Co_4$.

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