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Coefficients of thermal expansion of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys ($x=0\ldots 0.2$)

P. J. Masset*, D. Texier and M. Schütze

The coefficients of thermal expansion (CTEs) of Ni–Al–Hf alloys have been investigated due to their potential as corrosion resistant coatings in aggressive environments at high temperature. The CTEs of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys ($x=0\ldots 0.2$) were measured between 473 and 1073 K (200–800°C) and range between 8 and $15 \times 10^{-6} \text{ K}^{-1}$ depending on temperature and alloy composition. The temperature dependence of the CTE was found to be properly described by a simple expression: $(19.982 - 0.24016X_{\text{Hf}})[0.15182 + 1.8287 \times 10^{-3}(T/K) - 2.12378 \times 10^{-6}(T/K)^2 + 8.87011 \times 10^{-10}(T/K)^3]$. It was shown that the CTE of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys varies linearly with the amount of Hf in the alloy which allows the control of the CTE. Within the $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloy composition range ($x=0\ldots 0.2$) it covers the CTE range of most of the austenitic and ferritic steels and the CTE of the coatings can be adjusted to those of the substrate to be protected without inducing additional strains at the coatings/substrate interface.

Keywords: Coefficients of thermal expansion, CTE, NiAl alloys, Al–Ni–Hf, high temperature

Introduction

In high temperature processes, materials can face aggressive chemical environments sometimes even under mechanical load. Usually, the construction materials are designed to offer the best mechanical properties to fit the industrial requirements. However, they do not always sustain aggressive environments, e.g. chlorine containing atmospheres in waste combustion processes. As an alternative, coatings may be applied onto the material surface and act as a physical barrier against the environment to reduce the degradation rate. The selection of the coating material should fit the following two requirements:

- (i) it should be more resistant against the environment than the base material
- (ii) the coefficient of thermal expansion (CTE) should match that of the material to be coated.

For processes where the environment contains chlorine, it has been shown that NiAl based thermal sprayed coatings were resistant against high temperature corrosion attack.¹ However the CTE of NiAl does not fit all of the CTEs range of the ferritic and austenitic stainless steels.^{1,2}

The properties of NiAl + X alloys (X = Hf, Cr ...) have been extensively investigated for their use as high temperature structural materials. Hafnium was found to be an effective solid solution strengthener for NiAl alloys at high temperature.^{3–5} The phase diagram of the Al–Ni–Hf system^{6–9} exhibits three ternary intermetallic phases which can be in equilibrium with the β -NiAl phase, namely, NiAlHf (Laves), Ni₂AlHf (Heusler) and Ni₇(Hf, Al)₂. The solubility of Hf in the β -NiAl phase

was found to be <5 at.-%.¹⁰ Very recently, the ternary system has been optimised and thermodynamic data were made available, especially in the Ni rich corner.⁹ Although these alloys have been widely investigated for their mechanical properties, reported values of the CTEs of Al–Ni–Hf alloys are scarce^{11–13} and need further investigation. The evolution of CTEs of NiAl, NiAl₃ and NiAlHf alloys with temperature is plotted in Fig 1 with data taken from the literature.^{11–13} The available CTE data for the ternary alloys are only for very low Hf content and does not show any influence of the hafnium content. In addition predictive models developed to calculate CTEs of multi-element alloys do not reproduce the experimental data with a high level of confidence.

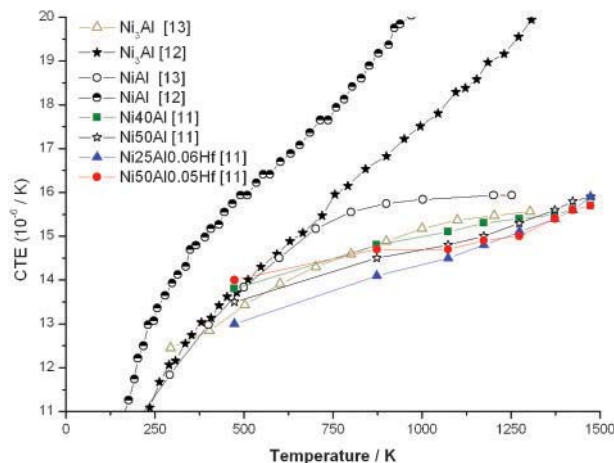
It is apparent that new experimental measurements may bring new data to be used as a basis for further modelling. Therefore, the aim of the present work is to investigate the composition and temperature dependence of the CTE of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys (x varies from 0 to 0.2) through the substitution of NiAl by Hf.

Experimental

Alloys were prepared from 99.99%Ni, 99.99%Al and Hf (containing <1 at.-%Zr). Five compositions of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys were prepared by centrifugal casting in an induction furnace and solidified in an Ar cooled copper mould. Cylindrical ingots (10 cm in length and 15 mm in diameter) of ~40 g were obtained. Their nominal compositions are reported in Table 1. For each a small portion was used for microstructural analyses. For the microstructural characterisation the specimens were mechanically polished with 4000 grit SiC abrasive paper and then ultrasonically washed in acetone and ethanol for 10 min. The samples were post-experimentally investigated by metallography and

Karl Winnacker Institut der Dechema e.V., Theodor Heuss Allee 25, 60486 Frankfurt am Main, Germany

*Corresponding author, email masset@dechema.de



1 Coefficients of thermal expansion values of NiAl, Ni₃Al and NiAl–Hf alloys taken from literature

scanning electron microscopy (SEM). Before observation, the samples were gold sputtered, electrochemically coated with Ni and embedded in an epoxy resin. Scanning electron microscope images were taken by an XL40 electronic microscope from Philips coupled with energy dispersive analysis of X-rays (EDAX). In addition, X-ray diffraction (XRD) patterns were recorded on a Siemens D500 using a Cu K_{α} cathode ($\Theta/2\ \Theta$ mode) every 0.02° .

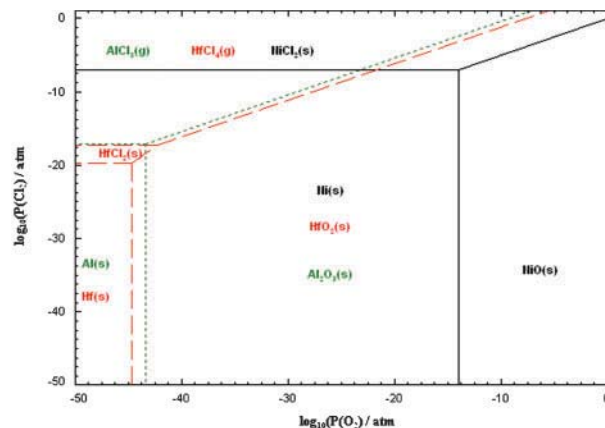
The as cast specimens for thermal expansion measurements were machined via electrodischarge machining to parallelograms of dimension $2 \times 10 \times 15$ mm. Expansion measurements were made between room temperature and 800°C and with a heating and cooling rate of $3\ \text{K}\ \text{min}^{-1}$ using a Linseis1500 dual push rod differential dilatometer. Data were recorded at 30 s intervals. The dilatometer was of horizontal configuration with push rods and sample holder constructed of high density alumina. A platinum/Pt–10%Rh type S thermocouple was used to monitor the sample temperature. Oxidation of the samples during the dilatometer runs was minimised by maintaining under a reductive Ar–5% H_2 atmosphere

Table 1 Nominal and measured (in brackets) compositions of produced alloys by centrifugal casting

Alloy	Nominal composition (measured composition), at.-%		
	Ni	Al	Hf
Ni _{0.5} Al _{0.5}	50.0 (50.5)	50.0 (49.5)	–
Ni _{0.49} Al _{0.49} Hf _{0.02}	49.0 (50.4)	49.0 (47.5)	2 (2.1)
Ni _{0.475} Al _{0.475} Hf _{0.05}	47.5 (44.6)	47.5 (50.6)	5 (4.8)
Ni _{0.45} Al _{0.45} Hf _{0.1}	45.0 (45.1)	45 (44.4)	10 (10.6)
Ni _{0.4} Al _{0.4} Hf _{0.2}	40.0 (39.8)	40 (42.0)	20 (18.2)

Table 2 Measured compositions of phases in alloys (Ni_{0.5}Al_{0.5})_(1-x)Hf_x by EDAX

Alloy	Phase 1			Phase 2			Phase 3		
	Ni	Al	Hf	Ni	Al	Hf	Ni	Al	Hf
Ni _{0.5} Al _{0.5}	50.5	49.5	–	–	–	–	–	–	–
Ni _{0.49} Al _{0.49} Hf _{0.02}	50.3	49.7	–	58.7	30.2	11.1	56.7	39.4	3.9
Ni _{0.475} Al _{0.475} Hf _{0.05}	55.4	44.6	–	34.3	38.3	27.4	46.2	31	22.8
Ni _{0.45} Al _{0.45} Hf _{0.1}	45.2	53.3	1.5	35.1	35.4	29.5	46.8	30.9	22.3
Ni _{0.4} Al _{0.4} Hf _{0.2}	39.8	42	18.2	–	–	–	–	–	–



2 Stability diagrams of pure metals Al (green dotted line), Hf (red dashed line), Ni (black full line) function of chlorine and oxygen partial pressures at 1073 K (800°C) (For the full colour version of this paper go to www.ingentaconnect.com)

(flow: $5\ \text{mL}\ \text{min}^{-1}$) a slight overpressure. The error due to the growth of an oxide layer was found to be $<3\%$ and was neglected. Three measurements from 20 to 800°C were made on all the specimens to ensure repeatability.

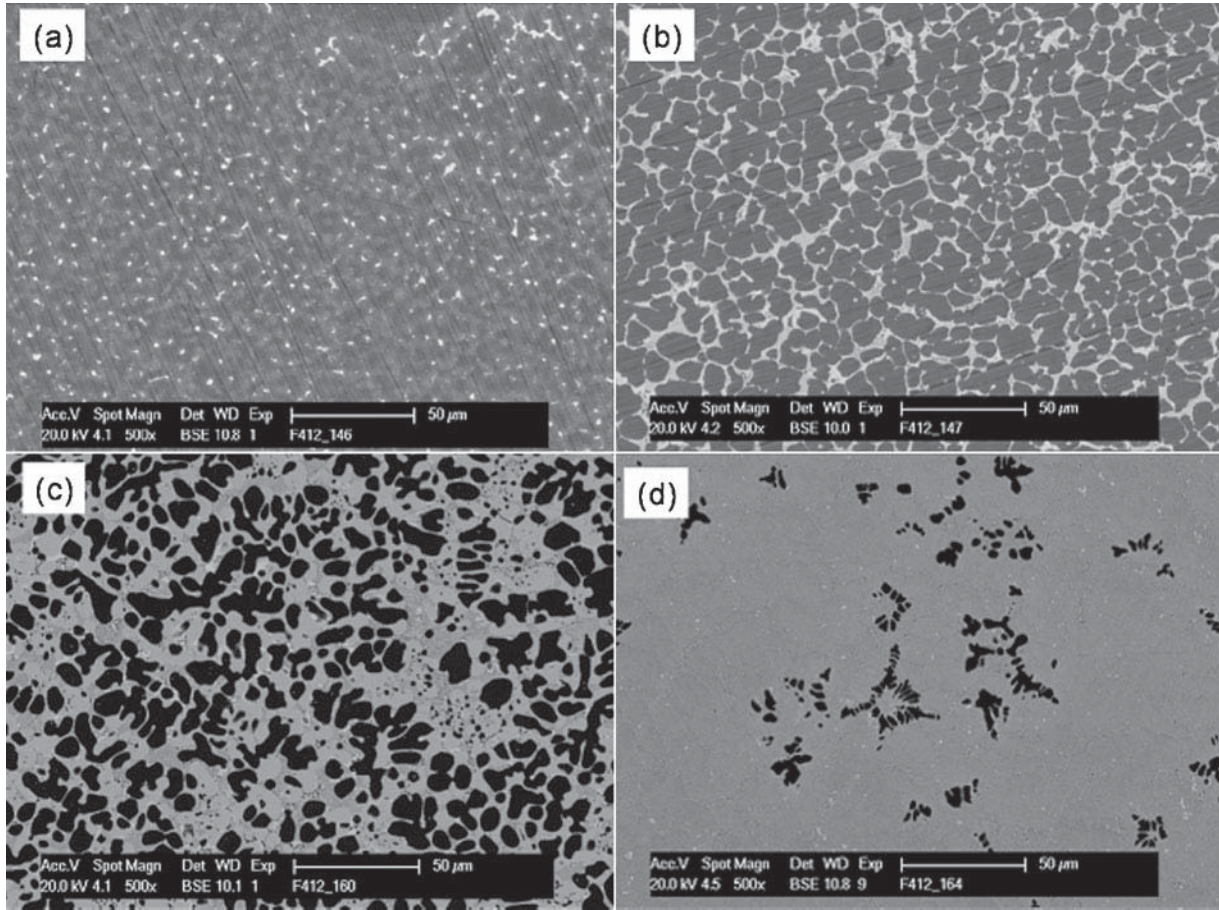
Results and discussion

Thermodynamic calculations

Thermodynamic calculations were carried out using the software FactSage. The stability diagrams of the pure elements (Ni, Al and Hf) were calculated as a function of the chlorine and oxygen partial pressures at 1073 K (800°C). This temperature represents the highest temperature for the application envisaged and from the point of view of corrosion. The computed stability diagrams were superimposed on each other in Fig. 2 to evidence the area of stability of the alloys studied. In these calculations, the activity of the elements was not taken into account. The stability area of HfO_2 is even slightly larger than that of alumina. It is therefore thought that hafnium should have a good corrosion resistance in chlorine containing atmospheres, even for low oxygen partial pressures. Considering the amount of Al in the prepared alloys the growth of a pure alumina layer is expected.

Alloy characterisation

The alloys of general composition $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ were prepared by centrifugal casting under vacuum or argon. The nominal and measured compositions of the prepared alloys were measured by means of EDAX and are summarised in Table 2. The differences in composition



a $x=0.02$; b $x=0.05$; c $x=0.1$; d $x=0.2$

3 Images (SEM) of alloy microstructures of composition $(\text{Ni}_{0.5}\text{Al}_{0.5})(1-x)\text{Hf}_x$

may be ascribed to the vaporisation of the pure metals during alloy processing at high temperature.

The microstructures of the as cast alloys are shown in Figs. 3 and 4. The local composition of each phase has been determined by EDAX measurements (Table 2). The microstructures of the alloys are of the β -NiAl and of the Ni_2AlHf Heusler type phases evidenced by XRD analysis (Fig. 5).

Coefficient of thermal expansion measurements

The CTEs of the $(\text{Ni}_{0.5}\text{Al}_{0.5})(1-x)\text{Hf}_x$ alloys were measured using a L75/1550 dilatometer from Linseis. The measurements were carried out between room temperature and 1073 K (800°C) under reducing Ar-5% H_2 atmosphere. This was conducted in order to minimise the formation of oxides which would hamper the determination of the true CTE of the materials. Reproducible results were obtained with heating rates $\leq 3 \text{ K min}^{-1}$. A blank measurement was carried out as reference by using the same thermal cycle and the measurements were repeated three times. The provided values are the mean values of three measurements and are reported in Table 3. Between room temperature and 1073 K (800°C) the CTEs of the alloys vary from 8 to $16 \times 10^{-6} \text{ K}^{-1}$ depending on the temperature and alloy composition. In the temperature range of the CTE measurements, no microstructural changes were expected, since the kinetics of the diffusion processes should be slow for this temperature range. This was confirmed by the good reproducibility of the CTE versus temperature curves. From the data analysis it was found

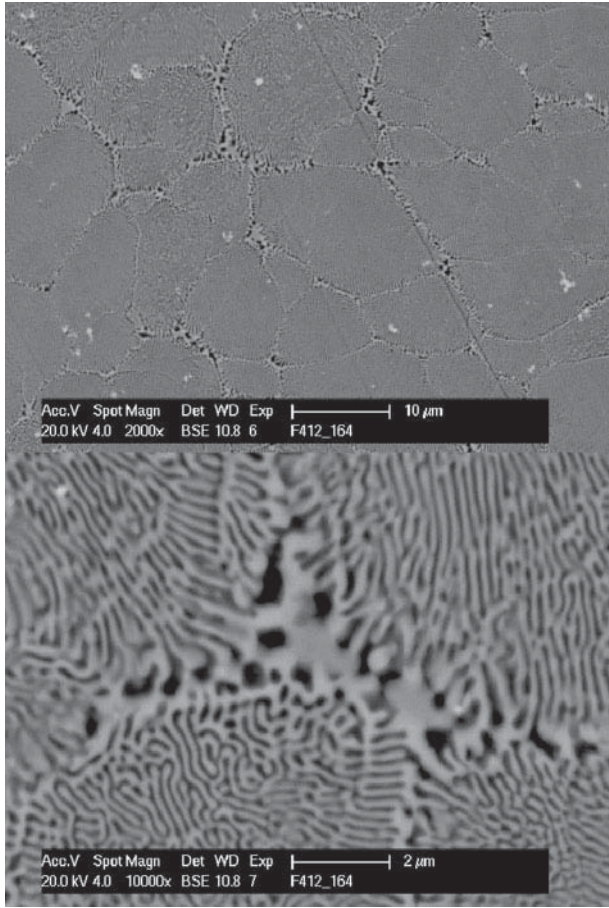
that the temperature and composition dependence could be considered separately. It means that the analytical expression of the CTE of the alloys investigated could be expressed as the product of a temperature and composition contribution (equation. (1)). The parameters were optimised using all the experimental data and the curves were fitted using a multilinear regression procedure.

$$\alpha_{\text{NiAlHf}}^T = (a_0 + a_1 X_{\text{Hf}})(b_0 + b_1 T + b_2 T^2 + b_3 T^3) \quad (1)$$

where T is the temperature (in K); a_0 and a_1 are the parameters which describe the concentration dependence; b_0 , b_1 , b_2 and b_3 are the parameters which represent the temperature dependence and X_{Hf} the hafnium molar fraction is expressed in at.-%. The expression of the CTE for the alloys $(\text{Ni}_{0.5}\text{Al}_{0.5})(1-x)\text{Hf}_x$ ($x=0 \dots 0.2$) is given by equation (2).

$$\alpha_{\text{NiAlHf}}^T = (19.982 - 0.24016 X_{\text{Hf}}) [0.15182 + 0.8287 \times 10^{-3} (T/K) - 2.12378 \times 10^{-6} (T/K)^2 + 8.87011 \times 10^{-10} (T/K)^3] \quad (2)$$

For each alloy composition the analytical expression of the CTE was derived from equation (2) and is reported in Table 4. The experimental points as well as the fitted curves are plotted in Fig. 6. The same trend was observed in all five curves. Between room temperature and 1073 K (800°C) the CTE values increase monotonously with the temperature. The curvature of the curve is given by equation (3).



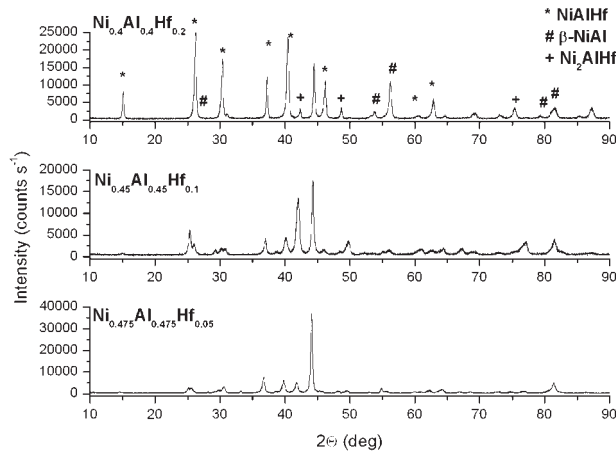
4 Detailed SEM images of alloy microstructure of alloy $(\text{Ni}_{0.5}\text{Al}_{0.5})_{0.8}\text{Hf}_{0.2}$

$$\left. \frac{\partial^2 \alpha_{\text{NiAlHf}}^T}{\partial T^2} \right)_{X_{\text{Hf}} = \text{CTE}} = (a_0 + a_1 X_{\text{Hf}})(2b_2 + 6b_3 T) \quad (3)$$

The curvature changes and becomes positive for higher temperatures when the second derivative annuls, i.e.

$$\left(\frac{\partial^2 \alpha_{\text{NiAlHf}}^T}{\partial T^2} \right)_{X_{\text{Hf}} = \text{CTE}} = 0$$

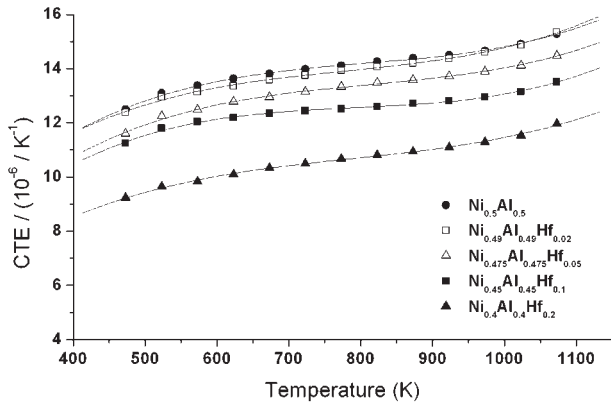
This occurs at temperature T_c independent of hafnium content, i.e. X_{Hf} , when T_c is equal to $-2b_2/6b_3$. Using the optimised set of parameters, the calculation of T_c leads to the value of 797 K (524°C). One of the reasons for these



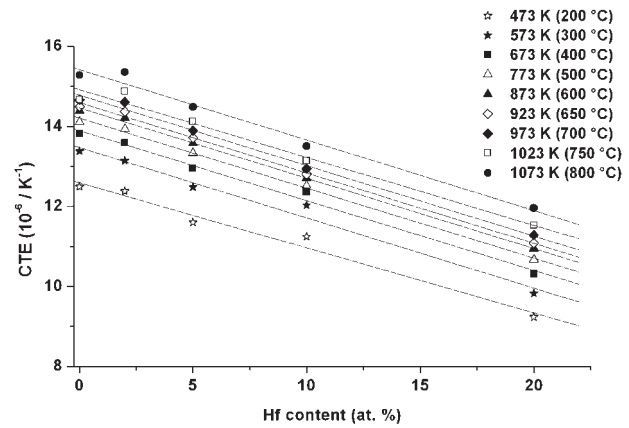
5 X-ray diffraction spectra of alloys $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$

Table 3 Experimental values of CTE of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys

Nominal composition, at.-%	CTE, 10^{-6} K^{-1}												
	200	250	300	350	400	450	500	550	600	650	700	750	800
$\text{Ni}_{0.5}\text{Al}_{0.5}$	12-49(1)	13-09(9)	13-37(8)	13-62(9)	13-80(8)	13-98(9)	14-11(0)	14-26(0)	14-38(5)	14-50(6)	14-66(4)	14-91(3)	15-28(0)
$\text{Ni}_{0.49}\text{Al}_{0.49}\text{Hf}_{0.02}$	12-379(4)	12-95(2)	13-14(3)	13-35(7)	13-58(1)	13-74(6)	13-93(2)	14-05(6)	14-20(2)	14-37(0)	14-60(5)	14-87(5)	15-35(3)
$\text{Ni}_{0.475}\text{Al}_{0.475}\text{Hf}_{0.05}$	11-60(1)	12-24(4)	12-47(9)	12-77(9)	12-95(1)	13-13(9)	13-32(8)	13-48(1)	13-57(7)	13-71(3)	13-89(2)	14-11(8)	14-48(3)
$\text{Ni}_{0.45}\text{Al}_{0.45}\text{Hf}_{0.1}$	11-24(3)	11-79(7)	12-03(1)	12-18(8)	12-34(9)	12-44(2)	12-51(8)	12-60(0)	12-70(2)	12-80(7)	12-94(1)	13-14(0)	13-50(3)
$\text{Ni}_{0.4}\text{Al}_{0.4}\text{Hf}_{0.2}$	9-23(5)	9-643(1)	9-82(7)	10-09(3)	10-32(5)	10-49(2)	10-67(1)	10-81(6)	10-94(1)	11-08(4)	11-28(5)	11-53(2)	11-96(1)



6 Coefficient of thermal expansion of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys versus temperature



7 Evolution of CTE of alloys versus Hf content

Table 4 Analytical expressions of CTE of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys

Nominal composition, at.-%	Expression of CTE versus T, K
$\text{Ni}_{0.5}\text{Al}_{0.5}$	$9.23 + 2.36 \times 10^{-2}T - 4.08 \times 10^{-5}T^2 + 2.52 \times 10^{-8}T^3$
$\text{Ni}_{0.49}\text{Al}_{0.49}\text{Hf}_{0.02}$	$9.51 + 2.08 \times 10^{-2}T - 3.61 \times 10^{-5}T^2 + 2.39 \times 10^{-8}T^3$
$\text{Ni}_{0.475}\text{Al}_{0.475}\text{Hf}_{0.05}$	$8.42 + 2.28 \times 10^{-2}T - 4.12 \times 10^{-5}T^2 + 2.33 \times 10^{-8}T^3$
$\text{Ni}_{0.45}\text{Al}_{0.45}\text{Hf}_{0.1}$	$8.21 + 2.26 \times 10^{-2}T - 4.12 \times 10^{-5}T^2 + 1.64 \times 10^{-8}T^3$
$\text{Ni}_{0.4}\text{Al}_{0.4}\text{Hf}_{0.2}$	$6.79 + 2.76 \times 10^{-2}T - 2.76 \times 10^{-5}T^2 + 1.80 \times 10^{-8}T^3$

changes with temperature may be ascribed to a possible disordering/ordering transition due to the magnetic contribution in the NiAl based alloy. However at that time no evidence is available to sustain this hypothesis.

The dependence of the CTE of the $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys on the hafnium content in the alloys was investigated as well. Figure 7 shows the evolution of the CTE versus Hf content for different temperatures. A linear dependence was observed between the CTE values and the Hf content in the alloy. The slopes for the variations of the CTE with Hf content appear almost constant with temperature and equal to $-0.2402 \pm 0.007 \text{ K}^{-1}/\text{at.}\% \text{Hf}$. According to these measurements the CTE of the $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys can be tuned by adjusting the hafnium content in the alloys. In addition, the variations of the CTE with the hafnium content appeared to be independent of the microstructure of the alloys and the phase arrangement.

The improvement of the corrosion behaviour is primarily linked to the alloy composition and its chemistry. The alloys produced can be considered as alumina formers as the aluminium content in the alloys is high. For the corrosion behaviour itself no change is expected from the modification of the CTEs. However, the CTEs of the coating can be adjusted to those of the substrate by adding hafnium. Since the stresses at the coating/substrate interface are proportional to the difference of the CTEs between coating and substrate, it can be expected that tendency for coating delamination or spalling can be reduced, especially under thermal cycling. In this respect, the whole system should offer a better corrosion protection of the substrate in chlorine containing atmospheres by combining optimised chemical and physical properties of the coating.

Conclusions

The main conclusions of this work are as follows.

1. $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys were cast using a centrifugal inductive furnace and their microstructures were investigated. For a substitution level of $x=0.2$ the alloy exhibits an eutectic type microstructure.
2. The coefficients of thermal expansion of $(\text{Ni}_{0.5}\text{Al}_{0.5})_{(1-x)}\text{Hf}_x$ alloys were measured between room temperature and 800°C and can be described by $(19.982 - 0.24016X_{\text{Hf}})[0.15182 + 1.8287 \times 10^{-3}(T/\text{K}) - 2.12378 \times 10^{-6}(T/\text{K})^2 + 8.87011 \times 10^{-10}(T/\text{K})^3]$
3. The CTEs of the alloys vary linearly with the hafnium content in the alloys.
4. The CTEs of the alloys may be tuned by adjusting the hafnium content.
5. The CTEs of the alloys seem to be independent of the alloy microstructure.

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