Synthesis and Compression Property of Oxidation-Resistant Ni–Al Foams

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Abstract Three different Ni–Al foams were synthesized by vapor aluminizing with control of aluminizing time. Oxidation tests under 1100 °C and compression tests were conducted to evaluate the oxidation resistance and compression properties of the foams. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) tests were carried out to study the phase composition and microstructure of Ni–Al foams before and after oxidation. Results showed that vapor aluminizing process did not change the foam macro- and microstructure, and the phase composition became from β/γ' -phase to single β -phase as the aluminizing time extending. The Ni–Al foams possessed excellent oxidation resistance, and decreased Al content increased oxidation weight gain and altered oxidation products. Foams containing single β -phase presented obvious brittleness under compression tests, but the foam with β/γ' -phase exhibited elasticity and toughness to a certain extent. The elasticity and toughness of the foams significantly can be improved after oxidation because of the phase changing in matrix during oxidation, and the pre-oxidized high-Al-content Ni–Al foams exhibited good compression properties, as well as excellent oxidation resistance.

KEY WORDS: Ni–Al foams; Vapor aluminizing; Oxidation; Compression

1 Introduction

On account of their cellular structure, high specific surface area, low specific weight, high stiffness, and other characteristics, open-cell metallic foams have been widely applied at ambient temperature [1, 2], including heat exchanger, support for catalysts, filtration, and separation. At elevated temperatures, open-cell metallic foams hold potentials for applications as heat shield for aircraft exhaust

and cooling systems in the burning chamber of turbines [3], high-temperature catalyst substrate, or filter or heat exchanger subjected to high temperature [4]. For these high-temperature applications, it is important for the metallic foams to exhibit good resistances to oxidation. However, all existing pure metallic foams behave poorly in oxidation under elevated temperatures. Thus, numerous efforts have been applied on alloyed nickel foam, due to its high melting point, good mechanical properties, and satisfactory oxidation resistance.

Yang et al. [5] prepared oxidation-resistant NiCrAl–Al coatings on nickel foams by electrophoresis co-deposition, while Smorygo et al. [6] fabricated $\text{TiB}_2\text{--Al}_2\text{O}_3$ oxidation-resistant coatings on nickel foams by combustion. The largest disadvantage of these two methods is that the inner surface of struts could not be protected during oxidation as protective layer could only form on outer surface.

Choe et al. [7] synthesized Ni–Cr foams through pack-cementation, and the Ni–Cr foams showed good oxidation

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resistance at 1000 °C and both the compressive yield stress at ambient temperature and creep resistance at 825 °C increased with chromium content. Choe [4] alloyed nickel foams with 8–9 wt% Al or 14–18 wt% Cr and 5–9 wt% Al, and found their mechanical properties improved apparently because of the γ/γ' structure. Pang *et al.* [8, 9] synthesized Ni–Cr–Fe and Ni–Cr–Fe–Al alloy foams by pack-cementation co-deposition and reported that the formation of continuous protective oxide film provided good oxidation resistance up to 1000 °C, and alloying improved the mechanical properties of foam both at ambient and elevated temperatures. In these studies, oxidation temperature was not more than 1000 °C, and Cr was used to form protective oxide films. But because of thermal stress, Cr_2O_3 spalls easily from the substrate and volatilizes when temperature exceeds 900 °C, i.e., these foamed alloys cannot be applied beyond 1000 °C [10].

When applied beyond 1000 °C, Ni-based alloys are protected by aluminizing to form Al_2O_3 ; therefore, aluminide coating is widely used as oxidation-resistant coating on jet blade. But when applied on nickel foams, almost all substrate will become nickel aluminide due to the thin strut wall, and then, their mechanical properties will be deteriorated on account of the brittleness of nickel aluminides. Hodge and Dunand [11] prepared nickel–aluminide foams by pack aluminization and subsequent homogenization and consequently obtained a single-phase NiAl structure for 80 pores per inch (ppi) foams, and Omar *et al.* [12] aluminized nickel foam by a slurry coating process, but no data of their oxidation resistance and mechanical properties were given.

Since aluminum is consumed during oxidation, the composition and microstructure of the Ni–Al foams will be changed on account of the thin strut wall. It means that the mechanical properties may change after oxidation, so pre-oxidation may serve a new way to improve the mechanical properties of Ni–Al foam. Therefore, this study involves synthesis of several Ni–Al foams with different components by vapor aluminization, and assessment of the oxidation behavior of the foams at 1100 °C and compression properties at ambient temperature before and after oxidation.

2 Experimental

2.1 Initial Nickel Foams

The nickel foams employed in this study were produced by electro-deposition and acquired commercially from Kunshan Jiayisheng Electronics Co., Ltd. The foams exhibited a 3D reticulate structure consisting of hollow struts of $\sim 84\ \mu\text{m}$ diameter and $\sim 7.5\ \mu\text{m}$ average strut wall

thickness. The cell size was $\sim 0.34\ \text{mm}$ (75 ppi), and the relative density was about 1.6% ($0.14\ \text{g/cm}^3$). Raw nickel foams with 3 mm thickness were cut into 12-mm-diameter circles by electro-discharge machining and then ultrasonically cleaned successively by metal detergent, distilled water, alcohol, and petroleum ether.

2.2 Aluminization Process

Vapor aluminizing was used to obtain Ni–Al foams. The aluminization media consisted of 20 g Ni-50 wt% Al powders as Al source and 0.8 g NH_4Cl powders as activator. After thorough mixing by a mortar, the media were divided into two parts. One part was placed at the bottom of a corundum crucible with a volume of about 80 mL, and the other part was placed in a stainless steel cross vessel fixed at the top of the corundum crucible. The samples were placed at the middle of the corundum crucible supported by a network of Ni20Cr wires. The crucible, with a suitable lid attached by Ludox, was placed in a tube furnace, heated to 1024 °C (at 10 °C/min) in an argon atmosphere, then maintained at such temperature for a given time, and subjected to furnace cooling. After cooling to room temperature, the samples were removed and weighed to determine the mass gain.

2.3 Oxidation Test

Static oxidation tests were carried out in a muffle furnace with a static air atmosphere under 1100 °C. After the furnace was heated to a set temperature, the samples placed in corundum crucibles were transferred to the furnace chamber and maintained for up to 60 h, with periodic movement to ambient temperature to measure the mass changes of samples.

2.4 Compression Test and Characterization

The compression tests were conducted at room temperature using UMT-2 multifunctional tribometer with a cross-head speed of 0.01 mm/s. The total deformation in height was over 70%. Apparent stress and strain rather than true stress and strain were used to construct the stress–strain curves (SSCs).

Field emission scanning electron microscopy (FESEM) was used to observe the microstructures and sectional features of the foams. The foams were mounted in epoxy, ground to 1200 grit, and polished with a 2.5- μm diamond polishing paste for the observation of cross-sectional morphology under FESEM. Energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were also carried out to analyze the chemical composition and phases in foams.

3 Results and Discussion

3.1 Microstructure and Composition of the Ni–Al Foams

Figure 1 shows the microstructure and sectional micrographs of the nickel foams before and after aluminization. Similar to the nickel foams, the Ni–Al foams maintained a 3D reticulated structure with hollow struts, illustrating that the vapor aluminizing did not change the structures of the nickel foams. Comparing Fig. 1c with d, it is obvious that the strut wall thickness increased after aluminization. This can also be confirmed by comparing Fig. 1a with b. Both masses increased with aluminum deposition and low density by forming new phases lead to a volume increase in foams, which reflected on the increase in the wall thickness. Similar phenomenon was found in Ref. [11].

The aluminizing time, average weight gain, and calculated Al atomic percentage of three kinds of Ni–Al foams used in this study (foam A, B, and C) are shown in Table 1. Apparently, the weight gain and Al atomic percentage of the samples increase with the aluminizing time.

To verify the existing phases in the Ni–Al foams, XRD were carried out. All phases in the foams rather

than those near outer surface can be distinguished on account of the thin strut wall. As shown in Fig. 2, foam A consists of a single β -NiAl phase, while foam B consists of β -NiAl and bits of γ' -Ni₃Al. However, in foam C, the quantity of γ' -Ni₃Al is much larger. The findings indicated that the resultant Ni–Al foams consisted of β/γ' -phases when aluminizing time was short, and gradually became single β -phase as the aluminizing time extended. Therefore, if aluminizing time was short enough, γ -Ni phase must have existed as substrate.

The sectional backscattered electron image of foam C is shown in Fig. 3. The outer part of the strut was composed of β -NiAl, and the γ' -Ni₃Al phase only existed near the inner surface of the strut. This result could be readily explained by the aluminizing process mainly from the outer to the inner surface of the strut, while the aluminizing process on inner surface also existed which could be confirmed by β -phase adjoined the inner side of γ' -phase (red arrow). Consequently, the Al content appeared in a concentration gradient across the strut wall. Outward diffusion of Ni is the primary process during aluminizing under this condition [13], and the voids in the strut were formed because of Kirkendall effect.

Fig. 1 Structures and sectional micrographs before **a, c**, after **b, d** aluminization

Table 1 Aluminizing time and weight gain of the three Ni–Al foams used in this study

	Aluminizing time (min)	Average weight gain (%)	Average Al atomic percentage (%)
Foam A	30	45.0 ± 2.0	49.4
Foam B	25	40.7 ± 1.4	46.9
Foam C	20	34.7 ± 0.7	43.0

Fig. 2 XRD patterns of aluminized foams **Fig. 4** Kinetics of oxidation weight gain of the original and Ni–Al foams **Fig. 3** Sectional backscattered electron image of foam C

3.2 Oxidation Performance of Ni–Al Foams

The kinetics of oxidation mass gain of pure nickel and Ni–Al foams under 1100 °C for 60 h are shown in Fig. 4. The weight of pure nickel foams increased rapidly as the test began and reached maximum at about 3.5 h, indicating that the pure nickel foams oxidized quickly and completely at ~3.5 h. By contrast, the Ni–Al foams showed excellent

oxidation resistance. The weight gain of the Ni–Al foams increased gradually in the initial 3.5 h, then became stable, and increased slowly in the remaining oxidation time. Foam A showed the best oxidation resistance; its weight gain was only about 7% after 60-h oxidation. The oxidation resistance of foam B and C decreased with decreasing Al content. The weight gains of foam B and C after 60-h oxidation were 7.9% and 11.1%, respectively. Compared with references [7] and [9], Ni–Al foams achieved better oxidation resistance than Ni–Cr and Ni–Cr–Fe foams despite the high oxidation temperature and specific surface area.

XRD were carried out to investigate the phase change and oxidation products of Ni–Al foams after 60-h oxidation (Fig. 5). The major phase of the oxidized foam A was β -NiAl and the minor phase comprised of the γ' -Ni₃Al, and the oxidation product was α -Al₂O₃. Compared with foam A, oxidized foam B was comprised of γ' -Ni₃Al as the major phase and β -NiAl as the minor phase. The main oxide was α -Al₂O₃, and a trace of NiAl₂O₄ spinel was found in the pattern. The phases in the oxidized foam C were more complex; γ -Ni and γ' -Ni₃Al became the major and minor phases in the matrix, respectively, and the oxides mainly comprised of α -Al₂O₃ and NiAl₂O₄ spinel. Meanwhile, some NiO was observed in the pattern.

Fig. 5 XRD patterns of the oxidized foam A **a**, B **b**, C **c**

Sectional backscattered electron images of the oxidized foams are displayed in Fig. 6. The images illustrate the oxidation process of the Ni–Al foams. Foam A achieved a simple structure after oxidation; a thin, continuous, compact α - Al_2O_3 film formed on the outer and inner strut surfaces (Fig. 6a) with an average film thickness of $\sim 1.8 \mu\text{m}$. Apparently, oxidation happened both on the outer and inner surfaces of the foams. A few voids (marked by white arrows) can be seen beneath the oxidation film. This is typical of Ni–Al oxidation [14]. These voids were formed mainly due to the inward diffusion of Ni after the consumption of Al during oxidation. These voids were generally thought to affect the adhesion of the oxidation film, especially when they enlarged substantially.

By contrast, the main difference between foams A and B after oxidation was the duplex-layer oxidation films on the inner surface of foam B (Fig. 6b). According to the EDS line-scan results in Fig. 7 and the XRD findings, the light-colored outer layer of the duplex oxidation film mainly consisted of Ni, Al, and O elements, highly likely corresponding to the NiAl_2O_4 spinel. Similarly, the melanocratic inner layer chiefly contained α - Al_2O_3 . This duplex oxidation layer usually appears when Al content is insufficient to form a continuous protective α - Al_2O_3 layer [15, 16]. The average thicknesses of the spinel and the entire oxidation film on the inner surface of foam B were ~ 1.6 and $\sim 4.1 \mu\text{m}$, respectively. The total thickness was much

higher than that of foam A, which explains why foam B yielded a higher oxidation weight gain. The voids under the oxidation layer in foam B were large and numerous, and the cracks between the layer and matrix (black arrow) are clearly displayed in Fig. 6b. These voids were generated on account of excessive consumption of Ni and Al, thus weakening the adhesion between the oxidation film and substrate, which would lead to the formation of cracks under thermal stress. This finding denotes that the adhesion of the oxidation layer to the inner surface of foam B was weak and may cause further oxidation of the matrix. Moreover, at some corners of foam B, the oxides grew and totally penetrated through the matrix (marked by circles). This phenomenon ensued because the stress concentration at the corner of the oxidation layer led to cracking and spalling of the layer, enabling the oxygen to enter and form new oxides. However, the new oxides formed on the Al-consumed matrix were insufficiently dense to prevent further oxidation effectively. Hence, the oxidation continued until the matrix at the corner was penetrated.

Foam C exhibited a similar sectional structure to foam B after oxidation (Fig. 6c). In the duplex-layer oxidation film, the light-colored outer layer of foam C was thicker and contained NiAl_2O_4 spinel and some NiO, according to the XRD results. The cracks in foam C were more obvious, indicating the aggravated spalling in the oxidation films and worse oxidation. The penetration of the oxides through

Fig. 6 Sectional backscattered electron images of the oxidized foam A **a**, B **b**, C **c**

Fig. 7 EDS line-scan of the oxidation film on the inner surface of foam B

the matrix was not only found at the corners but also at the straight portions where the oxidation film was thicker than the rest of the parts. The average thickness of the spinel and the whole inner oxidation film increased to ~ 2.1 and ~ 6.1 μm , respectively. All of these observations can explain the higher weight gain of foam C in Fig. 4.

Along with the earlier results, we noted that the outer part of the strut wall contained a higher Al concentration sufficiently to form $\alpha\text{-Al}_2\text{O}_3$. However, the Al content at the inner part of the strut wall decreased as the aluminizing time shortened, which led to different oxidation mechanisms and oxidation products on inner surface. In the end, such behaviors reflected on the kinetics of oxidation weight gain. For foams with low Al content, more consumption of Al occurred during oxidation, which made the Al content in oxidized foams B and C much lower. That is why the phase change was more remarkable in foams B and C after oxidation.

3.3 Compression Performance of the Ni–Al Foams

The SSCs of the original and Ni–Al foams are displayed in Fig. 8. The SSC of original foams was consistent with the typical SSC of ductile cellular metallic foams, which can be divided into three regions as follows: linear elastic, collapse, and densification regions [17, 18], and its yield strength was about 0.1 MPa.

The SSCs of foams A and B resembled each other, and both were characterized by a zigzag curve. This pattern was derived from the main $\beta\text{-NiAl}$ phase of the two foams, which was brittle and barely possessed deformation ability. Due to special net structure of foams, the struts at different positions may bear tension, compression, or bend stress during compressive tests. As the struts could not deform to disperse the pressure, stress concentration easily

Fig. 8 SSCs of the original and Ni–Al foams

accumulated and then cracks nucleated at weak places, such as defects on surface or voids in substrate. Due to the brittleness of $\beta\text{-NiAl}$, cracks propagated rapidly and rifted struts directly, as shown in Fig. 9a. The fracture appearance was even and presented typical brittle fracture. A crack could be seen in the middle of the strut wall, which was composed of tiny voids formed due to Kirkendall effects. These tiny voids formed a fast lane for crack propagation. Fracture of struts would lead to a dive in the SSC; continual repetition of this process generated the zigzag curve. During the test process, the curve rose slowly because of foam densification. Higher stress was required to obtain the same strain value for foam B than that for foam A because of the strengthening effect of the low amount of $\gamma'\text{-Ni}_3\text{Al}$ which performed as strengthening phase in $\beta\text{-NiAl}$.

By contrast, the SSC of foam C revealed a remarkably different pattern. The curve rose almost linearly from the

Fig. 9 Typical fracture appearance of foam A **a**, C **b**

origin and reached a higher point prior to a sharp drop. Then, the curve climbed undulately with some zigzag portions. The long linear elastic region indicated that the foam C possessed much higher elasticity and toughness than those of foams A and B and even those of the original foams. Nevertheless, foam C was fragile and sharply dropped in the SSC under stress beyond its elastic limit when a large-scale fracture occurred in the foam. The highest point prior to this fracture was noted as its breaking strength, which was about 0.3 MPa. Then, as the test progressed, the stress load and fracture repeated, and formed an undulating curve.

This large alteration in the compression performance of foam C was attributed to the enhancement in ductility and toughness by γ' -Ni₃Al in β -NiAl. The mechanism may work from two aspects. On one hand, softer γ' -phase will serve dislocations for brittle β -phase through slip transfer at their interface, which will give some deformation ability to β -phase and improve the ductility of the foam [19]. On the other hand, β/γ' -phase interface can inhibit the propagation of cracks [19, 20]. As shown in Fig. 3, γ' -phase distributes along the strut inner surface, and cracks propagated from brittle β -phase will be inhibited at the phase interface. The larger deformation and higher stress are needed for cracks further propagating, which prevents rapid fracture of the strut and its toughness was improved. This could be verified by Fig. 9b, in which the fracture appearance was more fluctuant compared to Fig. 9a. The fracture was discontinuous from inner side to outer side of the strut, and a boundary (marked by arrows) separated the strut wall into two parts. It illustrated that cracks could not propagate through this boundary which should be β/γ' -phase interface. Each of the two parts had no obvious plastic deformation, which indicated the intrinsic brittleness of foam C. A series of Kirkendall voids and crack could also be seen in the middle of strut wall.

The SSCs of foams A, B, and C after 60-h oxidation are displayed in Fig. 10. These curves were similar to the SSC of foam C in Fig. 8, except for the sharp drop. The curves were smooth with much fewer zigzags, signifying the vast improvement in brittleness, especially in foams A and B. In these curves, a slow and limited decrease rather than a sharp drop was produced after the linear elastic region, which indicates the occurrence of small-scale rather than large-scale fracture. The breaking strength of the three curves was ~ 0.3 MPa, which varied minimally compared with that of foam C in Fig. 8.

Despite the large content of brittle oxides produced during oxidation, the foams did not increase in brittleness. This phenomenon can be explained by two reasons. Firstly, the brittle oxides barely had deformation ability and would fracture at low strain [21], so they would fracture easily during deformation; thus, with the addition of their thickness, the oxides were unable to significantly support the foams during the compression test. Secondly, the Al consumption during oxidation generated a phase change in the

Fig. 10 SSCs of the oxidized Ni–Al foams

matrix, particularly β/γ' , γ'/β , and γ/γ' for foams A, B, and C, respectively (Fig. 5). These new duplex-phase structures endowed the matrix with elasticity and toughness; hence, the SSC displayed elastic characteristics.

The SSC of foam A obtained after 1-h oxidation is presented in Fig. 10. This curve shows the substantially enhanced elasticity and toughness compared to that of foam A in Fig. 8. The breaking strength of foam A after 1 h of oxidation was almost equal to that after 60 h of oxidation. This result reveals a considerable improvement in compression property despite the inferior elasticity with respect to that after 60-h oxidation. After 1-h oxidation, foam A retained its excellent oxidation resistance. In other words, 1 h pre-oxidation will considerably improve the mechanical properties and will not change the oxidation resistance, which are of great significance for practical application.

4 Conclusions

- (1) The vapor aluminizing process does not change the foam microstructure; the obtained foams contained β -NiAl and an uncertain content of the γ' -Ni₃Al phase at different aluminizing times.
- (2) Ni–Al foams possess excellent oxidation resistance, but the oxidation performance of Ni–Al foams worsens as Al content decreases. All of the oxidation products on the outer surface are composed of dense α -Al₂O₃ film. However, the inner oxidation products changes from a dense α -Al₂O₃ film to a thicker duplex film containing NiAl₂O₄ spinel and α -Al₂O₃ as the aluminizing time decreases.
- (3) Single β -NiAl phase foams displayed obvious brittleness under ambient temperature compression tests. However, the foam containing β - and γ' -phases exhibit substantially improved elasticity and toughness which is attributed to the enhancement of elasticity and toughness in β -NiAl by γ' -Ni₃Al.
- (4) After oxidation, Ni–Al foams present much improved compression performance because of the phase change in the matrix caused by Al consumption during oxidation. Pre-oxidized high-Al-content Ni–Al foam displayed good compression performance as well as excellent oxidation resistance.

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