The Characterization of HIP and RHIP Consolidated NiAl Intermetallic compounds Containing Chromium Particles

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NiAl intermetallics with dispersive Cr particles consolidated by the Hot Isostatic Press (HIP) and Reactive HIP (RHIP) techniques, has been investigated. Mechanical properties of HIPed and RHIPed materials with various Cr concentrations ranging form 0 to 30 mass%Cr, were examined at various temperatures. The consolidation temperature of RHIP materials decreases with Cr addition; when RHIPing NiAl+xCr compounds with 25 mass% has attained remarkable high ductility over 17% elongation and over 400 MPa tensile strength at 873 K. A very high tensile strength of HIPed NiAl+20 mass%Cr over 600 MPa with 10% elongation at 873 K can be achieved at 873 K.

1. Introduction

The Intermetallic compound NiAl is one of the most promising candidate materials with lightweight, high melting point and oxidation-resistance. It has a potential for light-weight and high temperature structural materials such as helium gas turbine for 600 MWt HTGR-GT system, in which a single turbine and compressor rotor shaft has a weight limit in its design due to rotor dynamics and lift-up capacity limit of magnet bearing on the service.[1–3] However, its lower temperature ductility and high creep rates limit the practical use of NiAl. A lot of works have been done to improve these weak points.[4–13] In recent years, significant improvements of ductility were reported.[4–8] Various techniques were also developed to improve the high temperature strength.[9–15] However, their effects on mechanical properties of NiAl materials at elevated temperature have only been investigated to a limited extent.

Hot Isostatic Press (HIP) and Reactive HIP (RHIP) techniques have the advantages in minimizing micro-segregation and contamination of the elemental powders at its consolidated process, and in achieving small grain size of NiAl matrix with the solid solubility of the ternary additions. These advantages are expected to improve low temperature ductility and high temperature strength of NiAl intermetallics.

The purpose of the present study aims for improvement of low temperature ductility and strength of NiAl intermetallic compound by adding Cr addition and its consolidation by HIP and RHIP techniques.

2. Experimental Procedure

2.1 Materials

Both Ni+Al(1 : 1)elemental mixed powder and NiAl pre-alloyed powder with mixing addition of chromium powder were prepared in the present study. Ni(mean particle size, 7 μm 3600 mesh) and Al elemental powders(mean particle size, 20 μm 635 mesh) are supplied by VALKO WERKST-OFF TECHNOLOGGIE GMBH(Germany) and H.C. Starch

Table 1 Chemical compositions and impurity levels of as-received NiAl pre-alloyed powder.

C	Al	B	Si	S	O	Ni
			(mass%)			
0.02	30.3	0.12	0.06	<0.01	0.04	Bal.

GMBH(Germany), respectively. A coarse Cr powder (particle size > 150 μm) was grained using mechanical alloying before mixing with the starting powders. The chemical composition and impurity levels of as-received NiAl pre-alloyed powder are listed in Table 1.

The content rate of Cr in the powders are changed from 0 mass% to 30 mass% by 5 mass% step and seven compositions of the powders of NiA+xCr and Ni+Al+xCr are prepared. The compositions of the powders used in present experiment are listed in Table 2.

2.2 Hipping procedures

These mixed powders were filled in stainless steel cans of 14 mm diameter, 2 mm thick, 20 mm long and stainless steel tubes of 14 mm in diameter, 2 mm thick, and 600 mm long. These capsules were evacuated at heated for out gassing at 673 K-6 h prior to HIP. After evacuation, every sample was encapsulated and then consolidated by HIP equipment.

Reactive HIP (RHIP) process in present study is defined as reaction process between elemental Ni and Al powers capsulated in the capsule above-mentioned during HIP procedure. RHIP technique of NiAl compound has the advantages in minimizing contamination of the elemental powders and consolidation process, and in obtaining small grain size and the solid solubility of the ternary element, such as Cr.

HIP and RHIP consolidation of NiAl+xCr powders and Ni+Al+xCr powders were performed in the following ways. Pattern (a); heated up by 0.25 K/s and holded at 1523 K with 172 MPa for 4 h, Pattern (b); heated up to 973 K by 0.25 K/s and hold for 900 s or Pattern (c); raised temperature by 0.02 K/s from 723 to 873 K, then raised up to 1523 K and

Table 2 The composition of pre-alloyed and elemental powders with Cr additions; (a) Pre-alloyed powder compositions and (b) Elemental powder compositions.

(a)

Pre-alloyed powder compositions	NiAl	Cr
(mass%)		
NiAl	100	0
NiAl+5Cr	95	5
NiAl+10Cr	90	10
NiAl+15Cr	85	15
NiAl+20Cr	80	20
NiAl+25Cr	75	25
NiAl+30Cr	70	30

(b)

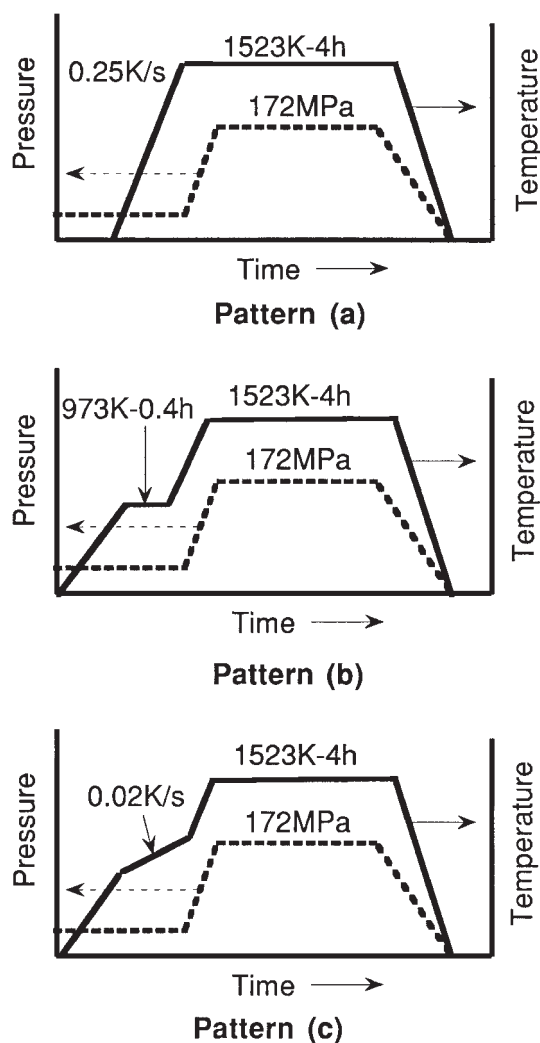| Elemental powder compositions	NiAl	Al	Cr
(mass%)			
NiAl	68.5	31.5	0
NiAl+5Cr	66.1	28.9	5
NiAl+10Cr	61.7	28.9	10
NiAl+15Cr	58.3	26.7	15
NiAl+20Cr	54.8	25.2	20
NiAl+25Cr	51.4	23.6	25
NiAl+30Cr	48.0	22.0	30

Fig. 1 HIP and RHIP schedules of Cr containing NiAl powders; Pattern (a) heated up by 0.25 K/s and holded at 1523 K with 172 MPa for 4 h, Pattern (b) heated up to 973 K by 0.25 K/s and holded for 900 s and Pattern (c) raised temperature by 0.02 K/s from 723 K to 873 K, then raised up to 1523 K and holded with the pressure of 172 MPa for 4 h.

holded with 172 MPa for 4 h. These hipping schedules are summarized in Fig. 1.

Prior to HIPing experiments of Ni+Al+xCr powders, these powders are CIPed (= Cold Isostatic Press) by 300 MPa for 900 s, then machined to the bar specimens(13 mm diameter with 18 mm or 500 mm in length) for encapsulation in the above-mentioned cans and tubes.

A HIP dilatometer technique[14] has been employed to measure the time dependent densification behavior of these intermetallics.

2.3 Strength tests

Tensile tests were performed at elevated temperatures up to 1073 K using an Instron type testing machine under controlled head speed. Strain rate was $3 \times 10^{-4}\,\mathrm{s^{-1}}$ at the strength test. Tensile specimens were machined from HIPed specimens into cylindrical test pieces with a gauge length of 17.6 mm and a diameter of 4.5 mm.

Microstructure of the consolidated intermetallics was studied by optical microscopy and energy dispersive spectroscopy(EDS). Metallographic specimens were prepared by mechanical polishing and chemical etching.

Vicker's hardness measurements were made on polished surface of the specimens cut from HIPed tubes or canned materials.

3. Results

3.1 HIPping tests

Prior to RHIP, CIPed Ni+Al+xCr elemental powders with 10, 15 and 30 mass%Cr are heated up to 1523 K in vacuum to define reactive temperature during RHIPing. Vacuum levels of farness was measured at elevating temperatures and it was

found that the disturbed points of vacuum level due to reaction between Ni+Al powers are observed at 838, 853 and 883 K corresponding to Cr contents of 10, 15 and 30 mass%Cr, respectively. These results indicated that the reaction temperature of Ni+Al powders are increased as increase of Cr contents in these powders. With these results, the first holding cycle at 973 K or every slow heating rate in the reactive HIPing schedule of (b) and (c) was decided in RHIP process, avoiding irregular re-heating due to the reaction with Ni and Al elemental powder under these temperatures.

HIPed specimens of pre-alloy and elemental powders were machined and measured the relative density. A fully density was achieved by the above-mentioned hipping schedules for all these materials, however, the long tubes of the elemental mixed powder with less than 20 mass%Cr were destroyed during hipping, whereas good as-hipped samples were obtained with the powder of more than 20 mass%Cr.
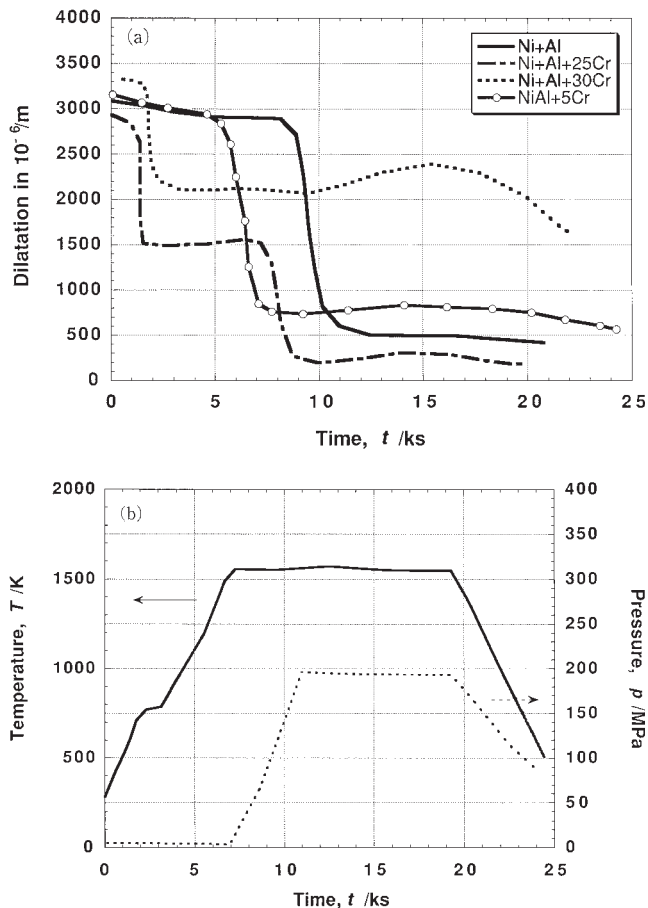
Fig. 2 Densification process of RHIPed and HIPed NiAl+xCr; (a) Shrinkage of canned Ni+Al+xCr and NiAl+xCr powders and (b) temperature and pressure change in HIP process.

Fig. 3 Microstructure of HIPed NiAl+25Cr; (a) Macroscopic and (b) microscopic photos.

3.2 Densification process

Figure 2 shows the typical HIP and densification processes of Ni+Al elemental mixed powders with 0, 25 and 30 mass%Cr and pre-alloyed powders of NiAl+5Cr under the HIPing. In Fig. 2(a), these lines are the length change of the canned specimen measured by the dilatometer system. A drastic shrinkage of Ni+Al powder mainly occurred at the temperature between 1273–1473 K, and of Ni+Al, Ni+Al+15Cr and Ni+Al+30Cr powders were observed at the temperature between 1373 and 1473 C. Two-step changes was found between 873 K and 973 K, and 1273 K and 1473 K in the case of Ni+Al+25Cr powder. These results indicate that the Cr content in Ni+Al powder has influence reactive behavior between Ni and Al elemental powers, that is, the reactive temperature decreases as Cr content in Ni+Al powder.

3.3 Microstructure of HIPed materials

Microstructure of the as-hipped NiAl pre-alloy and elemental mixed powders with Cr particle is complicated. NiAl pre-alloyed powder in present experiment essentially consists of metastable ordered matrix structure with dispersive Cr particles. Ni+Al elemental powder consists of a super-saturated Cr concentration matrix has the non-equilibrium solidification with dispersive Cr particles. The microstructure involved a change in characteristic microstructure from homogeneous to inhomogeneous structure.
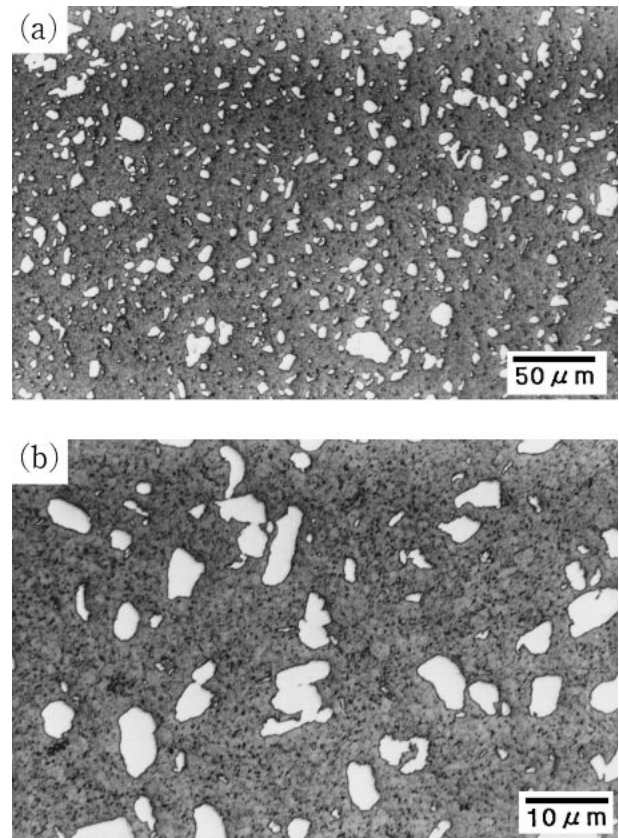
The dependence of microstructure development on HIPed NiAl+25Cr pre-alloy material is shown in Fig. 3. Each individual particle of NiAl and dispersive Cr particle remains its own identity and characteristic microstructure after HIPing. Microstructure of the as-hipped pre-alloy powder, as shown in the figure, is homogeneous with fine-grained structure (mean grain size < 35 μm). Population of Cr particles in matrix structure becomes higher and uniformly disturbed in matrix microstructure are in progress as increasing Cr additions. No reaction zone between original powder and Cr particle is observed in interparticle.

The microstructure of RHIPed elemental Ni+Al powder with 30 mass%Cr addition is shown in Fig. 4. A general view of microstructure of elemental materials is quite different from that observed in the 25Cr pre-alloy, as shown in Fig. 3. Homogeneous and well-developed eutectic network microstructure, which provides a very fine substructure size, is achieved in elemental materials.

3.4 Tensile tests

Tensile properties of the as-hipped pre-alloy and elemental materials at elevated temperatures of R.T. to 873 K are studied. The effect of Cr addition on the high temperature mechanical properties of the consolidated NiAl pre-alloy materials is shown in Fig. 5. In the figure, the stress-strain curves of as-hipped pre-alloy NiAl+xCr materials (x + 10–30 mass%) tested at the temperature ranging from room temperature (R.T.) to 873 K are shown. From these results,
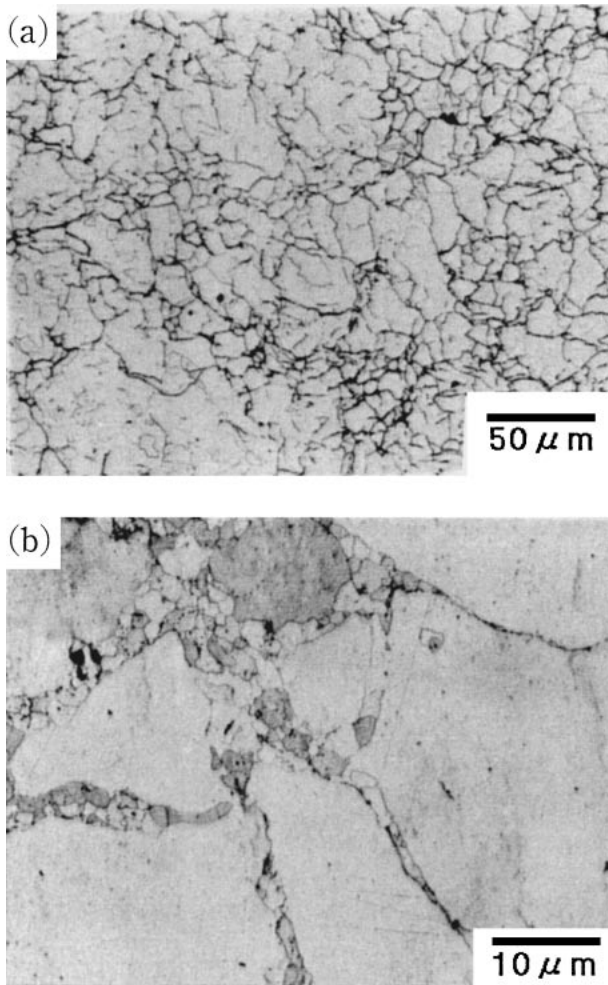
Fig. 4 Microstructure of RHIPed Ni+Al+30Cr; (a) Macroscopic and (b) Microscopic photos.
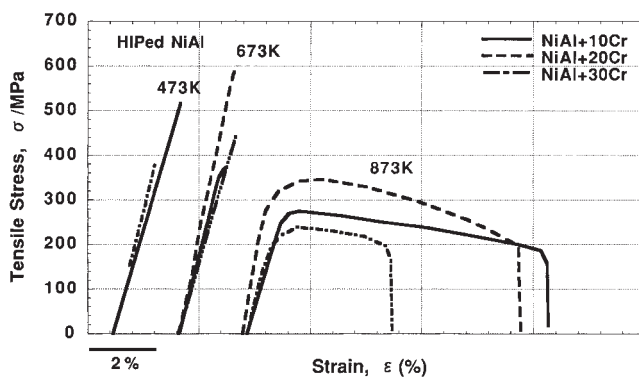

Fig. 5 Tensile stress and strain curves of HIPed NiAl+xCr tested at elevated temperatures.

tensile strength of these material decreased as increase of testing temperature and favorable elongation of these materials are observed at 873 K, but the ductility is very poor at 673 K. A very high strength can be obtained in NiAl+20Cr pre-alloyed material; tensile strength of about 600 MPa at 673 K and more than 300 MPa at 873 K.

Figure 6 shows the stress-strain curves of Ni+Al+25 and 30Cr elemental materials and NiAl+25 Cr pre-alloys. Comparing to the results of NiAl+25Cr pre-alloy, a very
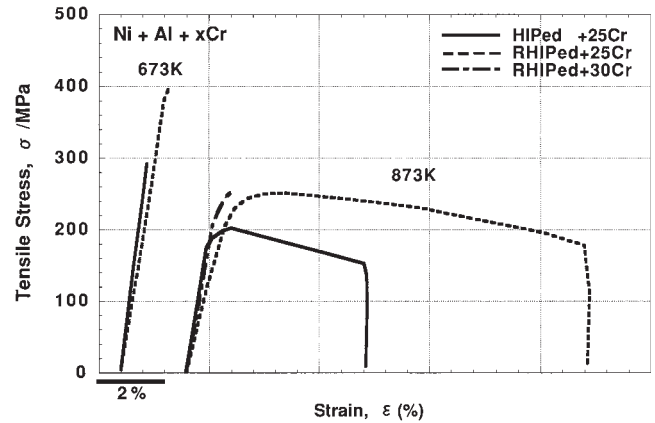

Fig. 6 Tensile stress and strain curves of RHIPed Ni+Al+xCr tested at elevated temperatures.

high tensile ductility of elemental Ni+Al+25 Cr is observed at 873 K, while the Ni+Al+30Cr elemental alloy has a very low tensile ductility.

4. Discussion

4.1 The effect of Cr additions on high temperature tensile strength

Figure 7 show the tensile strength of HIPed pre-alloyed and RHIPed elemental materials as a function of tested temperatures. For the HIPed pre-alloyed material with between 10 and 20 mass%Cr additions, tensile strength was decreased and HIPed NiAl+20 mass%Cr exhibited peak strength at the temperatures of 673 K and 873 K. Whereas that of the material with more than 20 mass%Cr was decreased with increasing of Cr concentration. The tensile strength of RHIPed elemental materials was also decreased with Cr additions.

The tensile strength of forged NiAl eutectic alloys in Ref. 15) at the temperature of 673 K and 873 K are also plotted in Fig. 7. This kind of experiments has been performed to testify the improvement of lower temperature ductility by ternary additives, as boron and another elements. [15] These forged eutectic NiAl materials with fine grain (grain size = 3 μm), in which grain size can not identified due
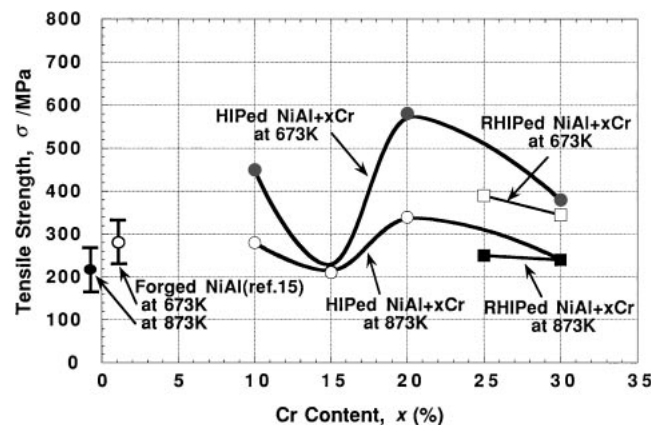

Fig. 7 Dependency of tensile strength of HIP and RHIPed NiAl+xCr on Cr addition as a function of testing temperature.

Table 3 Hardness and elongation of HIPed and RHIPed NiAl+xCr obtained at 673 K and 873 K.

Cr content (mass%)	Hardness (HV)		Tensile elongation (%)	
	Matrix	Particle	673 K	873 K
0 (Forged NiAl) Ref. 15)	318	-----	3.4	8.2
5	409	353	-----	-----
10	472	281	0	12.3
15	393	399	0	6.7
20	452	481	0.4	10.2
25	432	356	0	7.6
25(RHIP)	-----	-----	0.3	17.4
30	461	397	0.1	4.3
30(RHIP)	503	372	0.3	0.8

to the very complicated microstructure, are fabricated by electron beam melting method and forging technique.[15] These results indicated that tensile strength of dispersive Cr containing HIPed and RHIPed NiAl is superior to that of forged eutectic alloys at high temperatures, and comparing to the data of forged NiAl eutectic material with fine grain, structural reinforcement effect of dispersive Cr particle on NiAl matrix is clear.

Micro hardness of NiAl matrix and dispersive Cr particle in HIP and RHIPed NiAl+Cr materials listed in Table 3. From the results, it is found that matrix hardning in HIPed NiAl+Cr materials occurred due to Cr particle addition and NiAl matrix hardness increases with increasing Cr addition and exhibits higher value than that of Cr particle in the case of Cr content less than 15 mass%. Whereas micro harness of Cr particle becomes larger than NiAl matrix in the case between 15 and 20 mass%Cr, and peak value of Cr particle was found in HIPed NiAl+20Cr material. However, micro hardness of Cr particle becomes lower than that of NiAl matrix again, but increases with Cr addition in the case of Cr addition more than 25 mass%.

With these results, it is found that change in NiAl matrix hardness of HIPed NiAl+Cr materials corresponds with the high temperature strength shown in Fig. 7. The reason why the HIPed dispersive Cr containing materials shows the higher strength, especially in the case of HIPed NiAl+20Cr is mainly due to its interparticle bonding and well harmonized mechanical properties between dispersive Cr particles and NiAl matrix.

From the SEM fractography examination of HIPed NiAl+10Cr and 20Cr materials tested at 673 K and 873 K, a mixed fracture feature of interparticle and transparticle fracture morphology with large spherical shape of Cr particles are observed both materials tested at 673 K, as shown in Figs. 8(a) and 9(a). The area fraction of transparticle fracture in these materials increased with increasing Cr additions, but in the 10Cr material tested at 873 K (Fig. 8(b)), only a fully matrix fracture is found. Whereas a mixed fracture is also observed in the 20Cr material, in which the shape of the particle is deformed from spherical to lanky particle at 873 K, shown in Fig. 9(b). SEM fractographs in
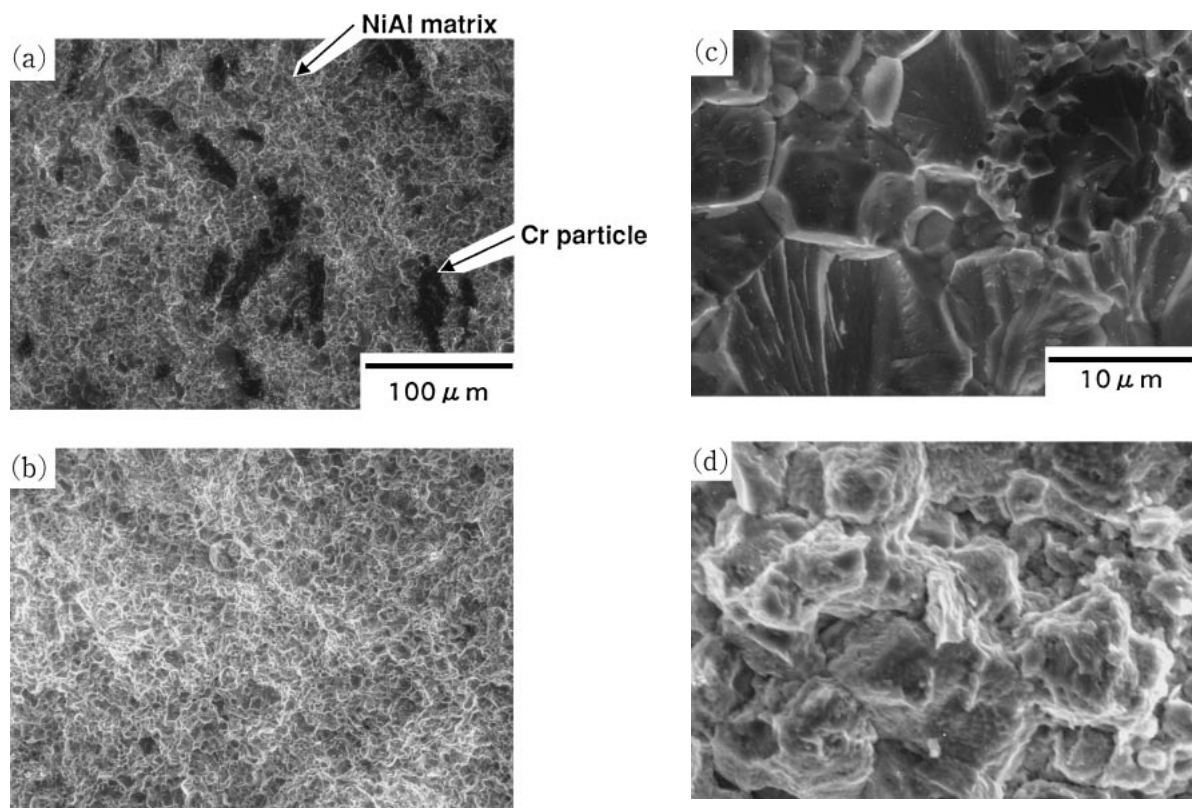

Fig. 8 Fractography of HIPed NiAl+10Cr; Macroscopic photos of (a) tested at 673 K and (b) 873 K, and microscopic photos of (c) tested at 673 K and (b) 873 K.
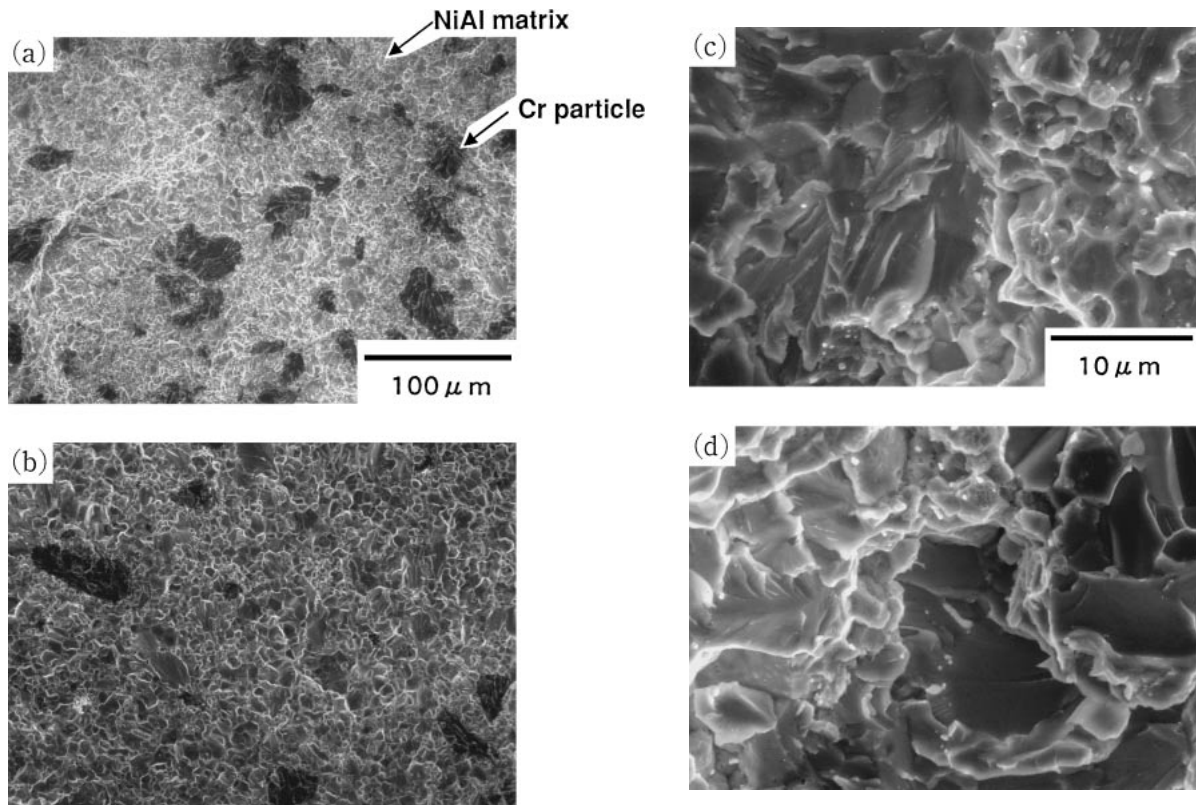
Fig. 9   Fractography of HIPed NiAl+20Cr; Macroscopic photos of (a) tested at 673 K and (b) 873 K, and microscopic photos of (c) tested
   at 673 K and (b) 873 K.

high magnification, shown in Figs. 8(c)–(d) and 9(c)–(d) reveal the details of the fracture surface of 10 and 20Cr materials. It is obvious that the brittle fracture occurred in inter- and transparticle in these materials tested at 673 K, while ductile fracture occurred in both of materials at 873 K, but a part of brittle fracture is still remained in Cr particles in 20Cr material.

This implied that the Cr addition less than 10 mass% in NiAl matrix is not enough which makes the powder particle boundaries become strong and contribute to improvement of the higher temperature strength. Whereas in higher Cr contents more than 20 mass%Cr, a sufficient strong inter-particle bonding can be achieved in interparticle, especially in 20Cr material.

However, the area fraction of NiAl matrix contributed to high temperature strength is monotonically decreasing with increasing Cr additions, then the high temperature strength of NiAl+xCr decrease with increasing Cr additions more than 20 mass%.

Tensile strength of RHIPed elemental materials measured at 673 K and 873 K are also shown in Fig. 7. Tensile strength of the RHIPed 25 and 30Cr elemental materials at higher temperature is a little bit lower that that of HIPed 20Cr pre-alloy material, but the degradation rate of high temperature strength of RHIPed 25Cr elemental material is almost the same value of that of 30Cr pre-alloy material. No remarkable difference in tensile strength is found between these materials with 25 and 30 mass%Cr additions.

Therefore, most important factor, which could influence the ultimate tensile strength of the alloy with dispersive Cr particle, is well micro structural matching and interparticle bonding between matrix and dispersive particles. With the these results, it is concluded that HIP process can fabricate a very high ultimate strength materials at high temperature with the concentration of dispersive Cr particle, of which the best concentration could be exist between 15 to 20 mass% and not exceeds more than 20 mass%Cr.

4.2   Effect of dispersive Cr particles on the ductility

The uniform elongation of HIPed pre- and RHIPed elemental alloys tested at 673 K and 873 K was listed in Table 3 as a function of Cr addition. For the HIPed pre-alloy materials, the results reveal that plastic elongation is decreased with increasing Cr addition and good correlation is obtained between elongation and Cr concentration. In The RHIPed elemental alloys, the same dependency of elongation on Cr concentration is also found, but the elongation values obtained in RHIPed 25Cr elemental alloy is two times higher than that of HIPed 25Cr pre-alloy in the figure. Higher tensile ductility is facilitated by the presence of large mount of the disordered γ phase and also a much homologous micro-structure in matrix.[14] Therefore, a factor that could influence the homogeneous plastic deformation could be well-homo-genized matrix microstructure and well development γ/γ' network structure, as shown in Fig. 4, which provides a very fine substructure size.

These results indicated that deformation feature of HIPed NiAl materials are very sensitive to the microstructure, that is, fineness of the microstructure of NiAl matrix is respon-sible for higher ductility at high temperatures, but ductility

behavior is also strictly controlled by the Cr concentration. These results are certainly associated with characteristic microstructure, that is, interparticle bonding between dispersive Cr particle and NiAl matrix developed during hipping process. As far as this point is concerned, most important factor is best plastic deformation matching between dispersive Cr particle and NiAl matrix. With the result of micro hardness measurement, as shown in Table 3, hardness mismatch between dispersive Cr particle and NiAl matrix, which will influence the inhomogeneous plastic deformation, can be observed in the as-hipped materials, which the hardness values of Cr particle is normally lower than that of NiAl matrix. Thus Cr particles behave more good ductility than that of NiAl matrix under the tensile stress and then large elongation mismatching occurred in interparticle, which induces micro cracking in the materials.

In present experiments, the Ductile-Brittle Transition-Temperature (DBTT) is defined by the temperature at which adequate tensile ductility of more than 0.2% is obtained during tensile strength tests. From the data shown in Table 3, the DBTTs of almost of these materials are not observed at less than 673 K, whereas adequate tensile elongation are only found at 873 K in HIPed 20Cr pre-alloy and RHIPed 25Cr elemental alloy, which are high tensile strength and high ductility material, respectively. These results indicated that the lower temperature ductility as can be achieved by the two factors, that is, high strength due to well fined microstructure provided by γ/γ' network found in elemental materials.

5. Conclusions

The present study mainly concerns the effect of dispersive Cr particles on the microstructure and mechanical properties of NiAl pre- and elemental alloyed intermetallics fabricated by the Hot Isostatic Press (HIP) and Reactive HIP (RHIP) techniques.

The effect of dispersed Cr particle on mechanical properties of HIPed NiAl materials is more complicated. For the HIPed pre-alloy materials, the hardness mismatching between matrix and Cr particles is found in the lower tensile strength materials, while higher strength at high temperature can be achieved by the materials with good micro structural matching between matrix and dispersed Cr particles.

Plastic elongation of pre-alloyed materials are decreased with increasing Cr concentration, but compared to the elemental materials, very high ductility can be observed in elemental materials. These results are associated with the deformation mismatching between fine homogeneous matrix structure and Cr particles.

Higher tensile strength and high ductility at higher temperatures are facilitated by the existence of large amount of the dispersive Cr particles. Moreover, it must be emphasized that the interparticle bonding and micro structural mismatching have to be treated as very important factors in determining mechanical properties of HIPed materials.

SEM examination of the fracture surfaces of the low Cr concentration materials suggested a transition from transparticle fracture to interparticle fracture of dispersive Cr particles with increasing testing temperature.

In conclusion, our results indicated that dispersive Cr concentration in NiAl materials should not exceed more than 20 mass% in mechanical properties, and very good ductility can be achieved by elemental materials consolidated by reactive hot isostatic press technique.

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