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A BRIEF STUDY OF NICKEL-RICH
ALLOYS OF THE Ni-Hf-C AND
Ni-Zr-C SYSTEMS

D. C. BRIGGS

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH

RESEARCH REPORT

R 142

Price 50 cents

PHYSICAL METALLURGY DIVISION

NOVEMBER 1964

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ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery
Ottawa, Canada

1965

Mines Branch Research Report R 142

A BRIEF STUDY OF NICKEL-RICH ALLOYS OF THE
Ni-Hf-C AND Ni-Zr-C SYSTEMS

by

D. C. Briggs*

ABSTRACT

A brief study has been made of the incidence, form and stability of carbides of hafnium and zirconium in a nickel-base system. Alloys were studied in the Ni-Hf-C system up to 1 at. % C and 1 at. % Hf and in the Ni-Zr-C system up to 1 at. % C and 1 at. % Zr. In each system a second phase was found that was extracted electrolytically and identified by X-ray diffraction techniques as a monocarbide of the reactive metal. Both HfC and ZrC were found to lack stability with changes in temperature; both ternary systems exhibited mild ageing response.

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Rapport de recherches R 142

Direction des mines

BRÈVE ÉTUDE DES ALLIAGES RICHES EN NICKEL
DANS LES SYSTÈMES Ni-Hf-C ET Ni-Zr-C

par

D. C. Briggs*

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RÉSUMÉ

La présence, la forme et la stabilité des carbures de hafnium et de zirconium dans un système à base de nickel ont fait l'objet d'une courte étude. Celle-ci a porté sur des alliages du système Ni-Hf-C contenant jusqu'à 1 at. de C pour cent (d'alliage) et jusqu'à 1 at. de Hf pour cent, ainsi que sur des alliages du système Ni-Zr-C contenant jusqu'à 1 at. de C pour cent et 1 at. de Zr pour cent. Une deuxième phase a été trouvée dans chaque système, extraite par électrolyse, et identifiée par les techniques de diffraction aux rayons X comme étant des monocarbures du métal réactif. On a découvert que le HfC et le ZrC manquaient de stabilité lors des variations de température; les deux systèmes ternaires ont montré de faibles réactions de vieillissement.

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INTRODUCTION

In recent years, workers at Imperial Metal Industries, Ltd., Birmingham, U. K., have studied the properties of hafnium-carbide (HfC) in a niobium matrix. A dispersion of hafnium carbide was observed to resist agglomeration at hot-working temperatures and this behaviour was expected to extend to higher temperatures. Hafnium carbide was thought to be more resistant to agglomeration than zirconium carbide. The alloys studied were formed by melting rather than by powder metallurgy. This report describes efforts to establish a similar dispersion of HfC or ZrC in nickel.

A search of the literature revealed no information on the ternary systems Ni-Hf-C and Ni-Zr-C but yielded adequate data for the five binary systems involved. With this information and knowledge of the Ni-Ti-C system it is possible to speculate as to the general form of the constitution diagrams of the two pertinent ternary systems.

Nickel forms a metastable carbide, Ni_3C , which can be retained only by rapid cooling⁽¹⁾. The stable phases are nickel and graphite. The solubility of carbon in nickel is a maximum of 3.0 at. % at the eutectic temperature 1318°C (2405°F) and falls to 1.2 at. % at 1000°C (1832°F) and 0.4 at. % at 700°C (1290°F).

Kirkpatrick and Larsen⁽²⁾ have established the phase diagram of the Ni-Zr system and, in the same work, have investigated the Ni-Hf system sufficiently to indicate that it is exactly analogous to the Ni-Zr system. They give the maximum solubility of zirconium in solid nickel as less than 2 wt % and other work suggests much lower limits^(3,4). The maximum solubility of hafnium in solid nickel has been placed at about 0.7 at. %⁽⁵⁾. The intermetallic compounds Ni_5Zr and Ni_5Hf appear when the solubility limits are exceeded⁽⁶⁾.

The existence of ZrC and HfC has been established, and ZrC appears to be the only carbide of zirconium that occurs⁽¹⁾. Similarly, by analogy with the Zr-C and the Ti-C systems, it is expected that HfC is the only carbide of hafnium that occurs.

As a starting point for this study, the general form of the Ni-Zr-C and Ni-Hf-C systems has been assumed to be similar to that of the Ni-Ti-C system. In the latter, a two-phase region exists between the nickel solid solution and TiC, and thus TiC can occur at high nickel contents, e. g. up to 94.5 at. % Ni at 1000°C (1832°F)⁽⁶⁾. Similar features have been incorporated in the speculative diagram for the Ni-Zr-C system shown in Figure 1. The only documented point in this diagram is the solubility limit of carbon in nickel. The Ni-Hf-C diagram should have similar form but show greater solubility of hafnium in nickel.

EXPERIMENTAL PROCEDURE

The nominal compositions of the alloys that were investigated are listed in Table 1 and, in the case of the Ni-Zr-C alloys, are shown in Figure 1.

TABLE 1
Nominal Compositions of Experimental Alloys
 (Atomic per cent)

	<u>Zr</u>	<u>C</u>	<u>Hf</u>
NZC-2	1.0		
NZC-3		0.2	
NZC-4	1.0	0.2	
NZC-6	1.0	0.5	
NZC-9	0.5		
NZC-10	0.5	0.5	
NZC-11	1.0	1.0	
NHC-1			0.5
NHC-2		0.5	0.5
NHC-3		1.0	1.0

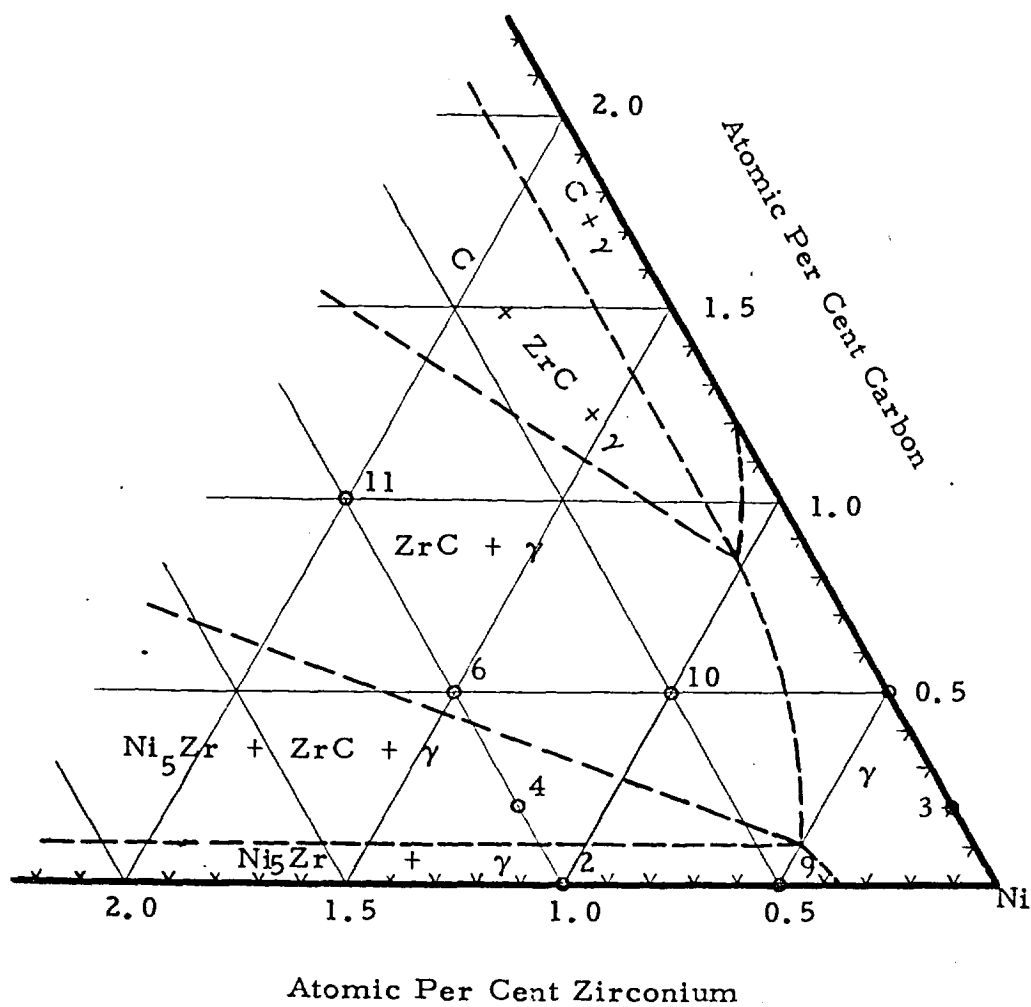


Figure 1 - Speculative constitution diagram of the Ni-Zr-C system for 1000°C (1832°F)

The starting materials for these alloys were the following:

- Nickel: Sherritt-Gordon powder, Grade C, 99.9% Ni,
major impurities Co, Fe, S
- Zirconium: sponge supplied by Wah Chang Corp., 99.8% Zr,
major impurities O, Fe, Hf, Si
- Hafnium: sponge supplied by The Carborundum Co., 97.2% Hf,
major impurities Zr (2.8%), O, Fe, Ta
- Carbon: foundry graphite.

The zirconium and hafnium were added as master alloys of stoichiometric composition Ni_9Zr and Ni_9Hf respectively.

The alloys were melted in a tungsten-electrode arc furnace with a water-cooled copper crucible and argon atmosphere. After an initial alloying melt, each alloy was melted at least three additional times to promote homogeneity. No chemical analyses were made of the alloys but a close check was made of the weights of constituents or button before and after melting.

The product of each final melt was a cigar-shaped ingot about 3/8 in. thick. This was swaged to 0.28 in. at 800°C (1470°F) for alloys of the zirconium series up to NZC-10 or at 900°C (1650°F) for NZC-11 and alloys of the hafnium series. The swaged bar was machined to 1/4 in. diameter to remove scale and surface contamination.

Solution heat treatment for all alloys consisted of annealing for one hour in an atmosphere of flowing argon, followed by quenching in water. Several ageing treatments were used, all in air. All hardness measurements were made on electrolytically-polished surfaces.

During preparation of samples for metallographic examination, electropolishing was used when possible, but whenever this method proved unsatisfactory vibratory polishing was used. Details of the metallography are as follows:

Electropolishing: 20% perchloric acid in ethanol;
 10-15 amp/sq in. at 25 v
 1 min after preparation on 600 grit or
 4 min after preparation on 220 grit

Mechanical polishing (vibratory):

Preparation on 600 grit paper
 20 min on silk with Linde A and water, 350 g weight.
 20 min on microcloth with Linde B and water,
 350 g weight.
 10-20 min on microcloth with Linde B and water,
 no weight.

Etchant: 0.4 mg potassium permanganate
 10 ml sulphuric acid
 90 ml water
 20 amp/sq in. at 6 v
 2 sec.

One alloy from each series (NZC-11 and NHC-3) was chosen for identification of the secondary phases by X-ray diffraction techniques. The minor phases were extracted electrolytically, using a 10% solution of hydrochloric acid in methyl alcohol, with a current density of 1 amp/sq in. at 1.5 v. Sufficient residue was obtained after four hours of extraction.

X-ray diffraction powder photographs were taken of the residues, using CuK_{α} radiation for the residues of alloy NHC-3 and CrK_{α} radiation for that of NZC-11. Exposure times were 4-4 $\frac{1}{2}$ hr.

RESULTS

Hardnesses measured for various heat-treated conditions of the alloys are listed in Table 2. An indication of the ageing response of alloy NZC-10 and of NHC-2, the analogous alloy with hafnium, can be seen from the data of Table 3.

TABLE 2
Hardness of Experimental Alloys

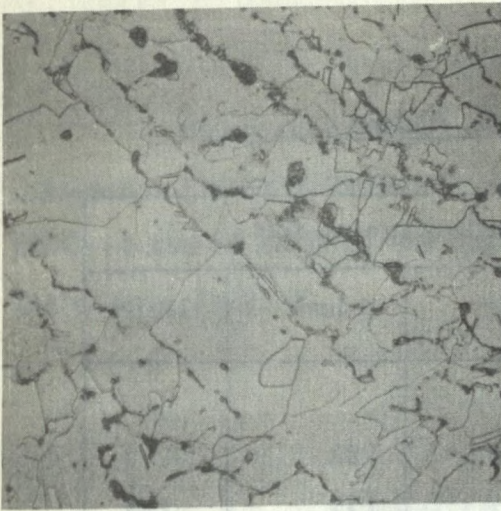
Alloy	Hardness, VHN, 20-kg load					
	As-Melted	Aged 800-4 hr	Solution-treated		Solution-treated and Aged	
			1100- 1 hr	1150- 1 hr	1100-1hr 800-4 hr	1150-1hr 700-4 hr
NZC-2	119	132	112			
NZC-3	87	68	70			
NZC-4	127	131	127			
NZC-6	135	123	137		134	
NZC-9			92		113	
NZC-10			115		122	157
NZC-11	136			137		191
NHC-1	106			90		104
NHC-2	113			106		140
NHC-3				134		162

TABLE 3
Ageing Response of Experimental Alloys

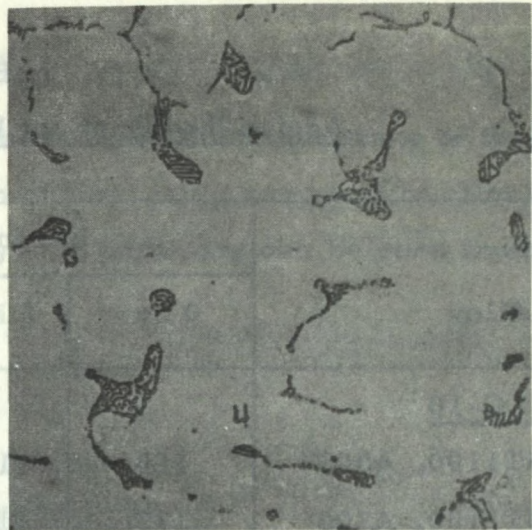
Alloy	Hardness (VHN) after ageing for				
	0 hr	$\frac{1}{2}$ hr	1 hr	4 hr	16 hr
<u>NZC-10</u>					
ST1100, A800*	115	116	124	122	
ST1100, A700	115	114	113	127	133
ST1150, A700			139	157	150
<u>NHC-2</u>					
ST1150, A700	106			140	137
ST1150, A800	106			123	

* Solution-treated at 1100°C (2010°F) and aged at 800°C (1470°F).

Figures 2 to 7 are photomicrographs of alloys NZC-11 and NHC-3 in the as-swaged, solution-treated, and solution-treated and aged conditions. Results of the X-ray diffraction determinations made on the residues of these two alloys are recorded in Table 4. The data include the spacings of the observed lines as well as the documented spacings for ZrC, HfC and Ni₅Zr lines, and calculated values for Ni₅Hf. The value of the unit cell dimension of Ni₅Hf used in the calculations is 6.68Å as found by Kirkpatrick and Larsen⁽²⁾. Both intermetallic compounds have a face-centred cubic structure. All the lines that were observed are listed in Table 4. The use of chromium radiation for the residue of NZC-11 precluded observation of higher angle reflections (smaller spacing) than those listed in Table 4.



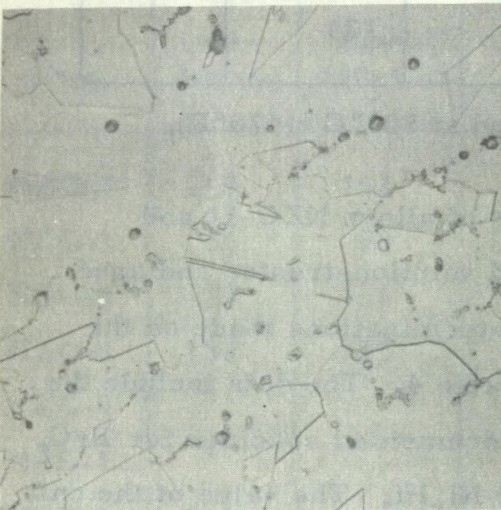
X500



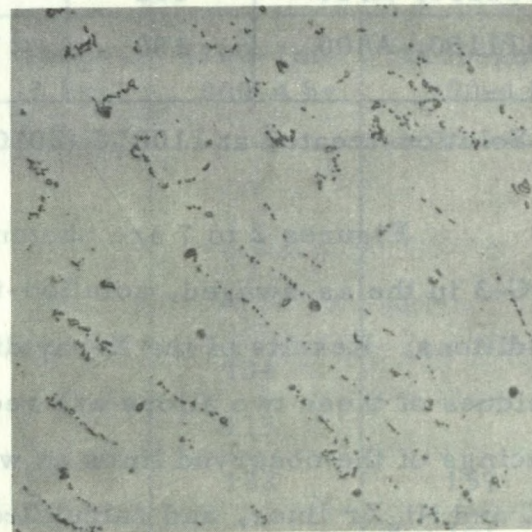
X500

Figure 2 - Alloy NZC-11 (1.0 Zr-1.0 C),
as-swaged.

Figure 3 - Alloy NHC-3 (1.0 Hf-1.0 C),
as-swaged.



X500



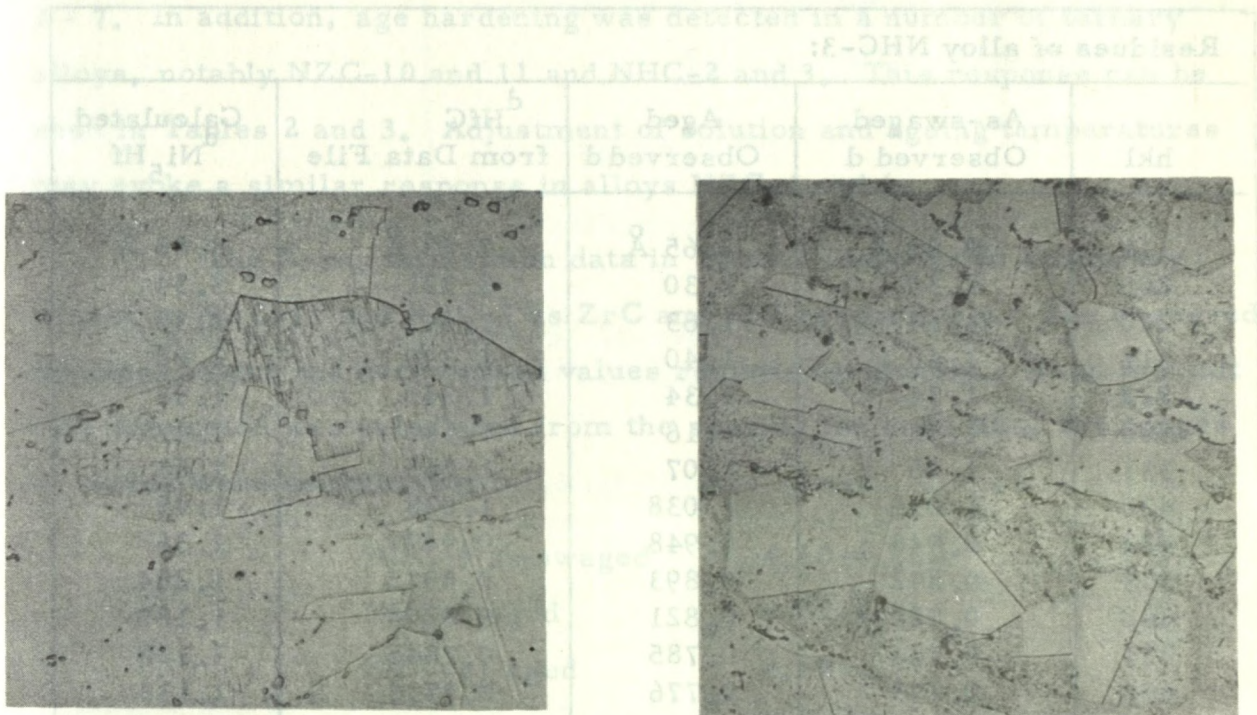
X500

Figure 4 - Alloy NZC-11, solution-treated
at 1150°C (2100°F) for 1 hr.

Figure 5 - Alloy NHC-3, solution-treated at
1150°C (2100°F) for 1 hr.

DISCUSSION

Results of the microstructural studies showed that in each of the ternary alloys examined a secondary phase occurs which can be partly or totally dissolved at elevated temperatures and reprecipitated at intermediate temperatures. This is illustrated for alloy NZC-11 and NHC-3 by Figures



X500

X500

Figure 6 - Alloy NZC-11, solution-treated at 1150°C (2100°F) for 1 hr and aged at 700°C (1290°F) for 4 hr.

Figure 7 - Alloy NHC-3, solution-treated at 1150°C (2100°F) for 1 hr and aged at 700°C (1290°F) for 4 hr.

The occurrence and behavior of ZrC in a series of ternary alloys in which zirconium was substituted for hafnium appear to be very similar to those of HfC.

TABLE 4
X-Ray Diffraction Results

Residues of alloy NHC-3:				
hkl	As-swaged Observed d	Aged Observed d	d_{HfC} from Data File	Calculated $d_{\text{Ni}_5\text{Hf}}$
111	2.67 Å	2.65 Å	2.68 Å	3.86 Å
200	2.30	2.30	2.321	3.34
220	1.64	1.63	1.641	2.36
311	1.40	1.40	1.399	2.02
222	1.34	1.34	1.340	1.93
400	1.16	1.16	1.160	1.67
331	1.06	1.07	1.065	1.53
420	1.035	1.038	1.038	1.49
422	0.946	0.948	0.9473	1.36
333	0.892	0.893	0.8932	1.284
440	0.820	0.821	0.8204	1.180
531	0.784	0.785	0.7845	1.128
600	0.775	0.776	0.7735	1.113
Residue of alloy NZC-11				
hkl	As-swaged Observed d	d_{ZrC} from Data File	$d_{\text{Ni}_5\text{Zr}}$ from Data File	
111	2.70 Å	2.70 Å	3.854 Å	
200	2.34	2.34	3.346	
220	1.66	1.65	2.358	
311	1.42	1.41	2.024	
222	1.36	1.35	1.928	
400	1.176	1.17	1.670	

DISCUSSION

Results of the microstructural studies showed that in each of the ternary alloys examined a secondary phase occurs which can be partly or totally dissolved at elevated temperatures and reprecipitated at intermediate temperatures. This is illustrated for alloys NZC-11 and NHC-3 by Figures 2 - 7. In addition, age hardening was detected in a number of ternary alloys, notably NZC-10 and 11 and NHC-2 and 3. This response can be seen in Tables 2 and 3. Adjustment of solution and ageing temperatures may evoke a similar response in alloys NZC-4 and 6.

The X-ray diffraction data in Table 4 identify the secondary phases in NZC-11 and NHC-3 as ZrC and HfC respectively. The observed spacings match the documented values reasonably closely. When the unit cell dimension was calculated from the spacing for each line, the ranges of values were as follows:

NHC-3 as-swaged	4.60-4.65Å
NHC-3 aged	4.59-4.66
NZC-11 aged	4.68-4.71

These values compare favourably with those documented in the X-ray Powder Data File, which are 4.641Å for HfC and 4.696Å for ZrC.

CONCLUSIONS

The formation of the monocarbide HfC has been established in Ni-Hf-C alloys containing up to 1 at. % Hf and 1 at. % C. HfC is not stable in a nickel matrix with change of temperature but, rather, can be dissolved at elevated temperatures and reprecipitated at intermediate temperatures.

The occurrence and behaviour of ZrC in a series of analogous alloys in which zirconium was substituted for hafnium appear to be very similar to those of HfC.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Mr. H. V. Kinsey, Head of the Refractory Metals Section, at whose initiative and under whose general guidance this project was carried out.

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