Journal of the Less-Common Metals, 66 (1979) 59 - 66

THE INTERMETALLIC COMPOUND Ni_3Zr*

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(Received November 17, 1978)

Summary

The intermetallic compound Ni_3Zr has been isolated; it is stable at room temperature but decays by a peritectoïd reaction at 940 °C according to: $4Ni_3Zr \longrightarrow Ni_7Zr_2 + Ni_5Zr_2$. Ni_3Zr is a hexagonal close-packed compound of the Ni_3Sn type ($DO19$), space group $P6_3/mmc$. The lattice parameters are a = 5.309 Å and c = 4.303 Å.

1. Introduction

In earlier studies of the Ni–Zr phase diagram several authors have pointed out the existence of the intermetallic compound Ni_3Zr [1 - 3]. This phase was not observed in later work [4 - 6], but was noted by Van Vucht [7] in a study of the $Ti_xZr_{1-x}Ni_3$ alloys. We have prepared this compound [8] and determined its stability field and its crystallographic structure; experimental results have been obtained from metallographic examination, electron probe microanalysis and X-ray powder diffraction using Cu K_α radiation.

2. Synthesis

2 g ingots of mean composition Ni_3Zr were prepared by melting the components (99.99% pure Ni and Zr) in an induction–levitation furnace and then quenching them in a copper ingot mould. The furnace was filled with argon to exclude oxygen and nitrogen and to reduce evaporation losses. The alloys obtained in this manner are in fact a mixture of the two phases Ni_5Zr_2 and Ni_7Zr_2; the compound Ni_3Zr was prepared by annealing the ingots for 2 d at 860 °C under high vacuum (10^{-4} Pa).

*Presented in a poster session at the fourth European Crystallographic meeting, University of Oxford, England, 30 August - 3 September, 1977.

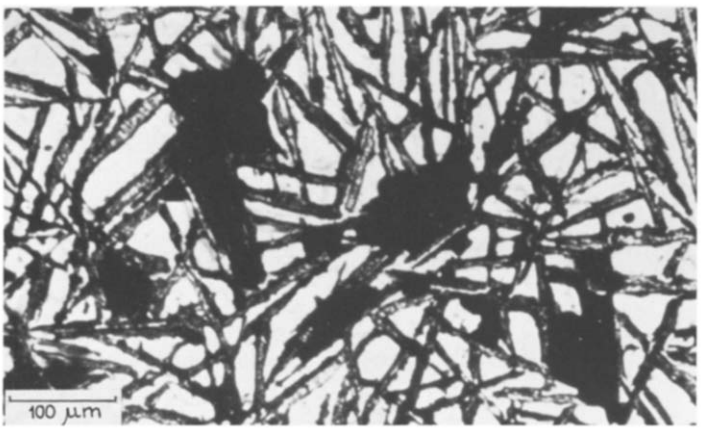

Fig. 1. Photomicrograph of a sample annealed at 960 °C. The two phases have been identified by electron microprobe analysis: the light one is Ni_5Zr_2 and the dark one Ni_7Zr_2.

TABLE 1

Results of electron microprobe analysis

Sample preparation	Phase analysed	Composition (wt.%)			
		Ni		Zr	
		Experimental	Calculated	Experimental	Calculated
Annealed at 920 °C	Ni_3Zr (homogeneous)	67.6	65.9	33.5	34.1
Annealed at 960 °C	Ni_5Zr_2 (light)	61.2	61.7	37.9	38.3
	Ni_7Zr_2 (dark)	67.2	68.9	31.8	31.1

3. Characterization of the material and its stability field

Specimens which were quenched after melting or were annealed at 960 °C or higher temperatures were soft alloys; they were strongly cold worked by the pulverization. The X-ray diffraction lines are rather diffuse and overlapping; this can be explained by the superposition of the Ni_5Zr_2 and Ni_7Zr_2 diffraction lines. Metallographic examination confirms the presence of two phases (Fig. 1). The results of electron microprobe analysis of these two phases agree with the calculated values (Table 1).

Specimens which were annealed at 920 °C or at lower temperatures are very brittle and easily pulverized. The X-ray diffraction lines are sharp; they point to the existence of the new phase Ni_3Zr whose crystal structure is described below. The samples appear homogeneous under both microscopic

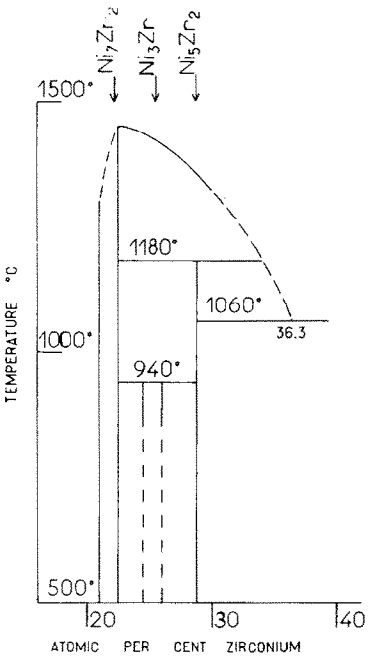

Fig. 2. Ni–Zr diagram between 20 and 30 at.% Zr. This diagram, published by Elliott [9], has been completed to show the Ni_3Zr phase.

examination and electron probe microanalysis; the measured weight percentage of Ni and Zr tally with the calculated values (Table 1); we have not been able to observe the grain boundaries. The Ni_3Zr compound is formed from Ni_5Zr_2 and Ni_7Zr_2 phases at 940 °C or below by a peritectoïd reaction: $Ni_7Zr_2 + Ni_5Zr_2 \longrightarrow 4Ni_3Zr$. With an annealing temperature of 860 °C, the alloy shows good ordering after 2 d as can be seen from the sharpness of X-ray diffraction lines; the same result can be obtained at lower temperatures by longer annealing times (96 h at 800 °C). The Ni_3Zr phase is still observed after slow cooling (37 °C h^{-1}) and remains stable at room temperature. This phase presents a narrow stability field: 24.5 - 26 at.% Zr. The alloys annealed at temperatures between 960 and 1150 °C always present the same features as the samples quenched immediately after melting: they are a mixture of Ni_5Zr_2 and Ni_7Zr_2 phases. Therefore we propose to complete the Ni–Zr diagram as shown in Fig. 2.

4. The crystal structure of Ni_3Zr

The new phase has the same structure as Ni_3Sn (*DO*19); the space group is $P6_3/mmc$ (Table 2); the parameters of the hexagonal unit cell are $a = 5.309$ Å and $c = 4.303$ Å. The d (*hkl*) values have been calculated for all observable reflections from these data; they are listed in Table 3 which also

TABLE 2

Crystal structure of Ni_3Zr, space group $P6_3/mmc$ or D_{6h}, No. 194 (lattice parameters: a = 5.3090 ± 0.0008 Å, c = 4.3034 ± 0.0012 Å)

Atom	Wyckoff's positions	Coordinates of equivalent positions		
Zr	2c	$\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$	$\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$	
Ni	6h	$x, 2x, \frac{1}{4}$	$2\bar{x}, \bar{x}, \frac{1}{4}$	$x, \bar{x}, \frac{1}{4}$
		$\bar{x}, 2\bar{x}, \frac{3}{4}$	$2x, x, \frac{3}{4}$	$\bar{x}, x, \frac{3}{4}$

TABLE 3

Observed reflections from a powdered Ni_3Zr sample

hkl	*d* (Å)	Reflections observed on diffractometer recording	Reflections observed on film	Calculated intensity including Lorentz factor
100	4.600			9
101	3.143	.	.	24
110	2.655	.	.	18
200	2.299	.	.	189
002	2.153	.	.	238
201	2.028	.	.	1000
102	1.950			12
210	1.738			1
112	1.672	.	.	27
211	1.612	.	.	54
202	1.572	.	.	241
300	1.533			12
301	1.444			3
103	1.370	.	.	14
212	1.352			3
220	1.328	.	.	362
310	1.275			8
302	1.249		.	19
311	1.223			26
203	1.218	.	.	462
400	1.150	.	.	67
222	1.130	.	.	522
401	1.111	.	.	374
213	1.107	.		32
312	1.097			12
004	1.077	.	.	77
320	1.055			12

(continued on facing page)

TABLE 3 *(continued)*

hkl	*d* (Å)	Reflections observed on diffractometer recording	Reflections observed on film	Calculated intensity including Lorentz factor
104	1.048			5
303	1.048			1
321	1.025	.	.	11
402	1.014	.	.	96
410	1.004			14
114	0.9976		.	13
411	0.9773			2
204	0.9749	.	.	86
313	0.9534			16
322	0.9474		.	18
214	0.9152		.	2
412	0.9096		.	21
501	0.8994	.	.	12
403	0.8973	.	.	186
330	0.8850		.	5
304	0.8810		.	9
420	0.8691	.	.	52
421	0.8519	.	.	277
323	0.8501			6
105	0.8465		.	5
224	0.8361	.	.	164
510	0.8259		.	<1
314	0.8226			4
413	0.8224		.	1
332	0.8185		.	6
511	0.8111		.	11
205	0.8065	.	.	88
422	0.8059	.	.	57
404	0.7858		.	18
503	0.7744			1
215	0.7717			1
512	0.7711			<1

gives the reflections actually observed either on a photograph taken with a Debye–Scherrer camera or on a diffractometer chart; all the observed reflections can be indexed. The parameters were computed by the least squares method; experimental data were obtained from Debye–Scherrer photographs and from diffractometer charts; from these two independent measures and their standard deviations we have calculated the most probable values of the parameters according to the method described in International Tables for X-ray Crystallography [10].

The sample for the intensity measurements was prepared by sprinkling powder over a lightly greased glass plate in order to assure the best possible random orientation of the crystals; the sample was kept oscillating with an

TABLE 4

Structure refinement (reliability factor $R = \Sigma \left| \frac{F_0 - F_c}{F_0} \right| = 0.06$; atomic position parameter (not fixed by symmetry) for Ni: $x = 0.829$; values of B in the temperature factors: Zr, $B_1 = 1.67 \times 10^{-16}$ cm^2; Ni, $B_2 = -0.07 \times 10^{-16}$ cm^2)

hkl	101	110	002	201	112	220	222	401	403	421	224
F_0	121	92	1181	929	142	843	757	602	473	406	481
F_c	128	155	1102	923	109	803	698	594	471	439	498

amplitude of one degree during the experiment. We have determined by point counting the intensities of eleven reflections chosen as the strongest and not overlapping other reflections; from these values we have deduced structure factors. The refinement was carried out by the least squares method; the *DO*19 structure involves only one atomic position parameter not fixed by the symmetry, so we have been able to resolve the complete system of normal equations [11]. The results obtained in Table 4 were obtained after eight iterations. The values of the Debye temperature factor B have no physical meaning; this could be accounted for by extinction (we have not made any correction) and/or by a dispersion effect; as a matter of fact the true dispersion correction for the Ni atom with Cu K_α radiation is uncertain [12].

5. Magnetic properties

We have determined the magnetization of a polycrystalline Ni_3Zr sample between room temperature and 4.2 K, using the facilities of the Magnetism Laboratory in Grenoble. Ni_3Zr remains paramagnetic down to 4.2 K; its magnetic susceptibility is about 1.4×10^{-6} u.e.m. g^{-1} at this temperature. The measurements were carried out according to the extraction process; the sensitivity of this method is very poor for paramagnetic samples, so the susceptibility value presents considerable uncertainty; nevertheless it is in the range of the Pauli paramagnetism.

6. Discussion

Ni_3Zr is a hexagonal close-packed intermetallic compound with a triangular type of order in the close-packed layers. Comparing its structure with that of the isoelectronic alloy $TiNi_3$ (*DO*23) we can support Van Vucht's hypothesis [7] for AB_3 intermetallic compounds: hexagonal stacking is increasingly favoured as the atomic radius ratio differs from unity; so the $TiNi_3$ alloy with $r_{Ti}/r_{Ni} = 1.16$ presents an ABAC (or hc) stacking sequence, but in the $ZrNi_3$ alloy with $r_{Zr}/r_{Ni} = 1.27$ the stacking sequence is

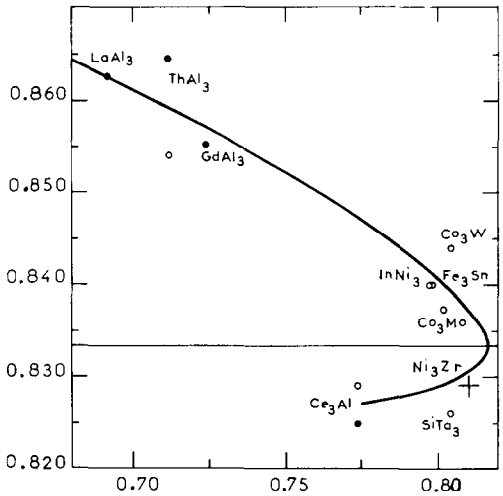

Fig. 3. Values of the atomic parameter x of the Ni_3Sn-type structure calculated as a function of the c/a ratio. This figure has been reproduced from ref. 13; our experimental value for Ni_3Zr is indicated by a cross.

strictly hexagonal AB (or h). The peritectoïd decay of Ni_3Zr at 940 °C shows a delicate balance between this phase and the Ni_7Zr_2–Ni_5Zr_2 mixture.

Havinga [13] has proposed for AB_3 intermetallic compounds of the Ni_3Sn type a model including short-range repulsive energy between nearest neighbours; he was able to deduce a relationship between the atomic position parameter and the c/a ratio; the values we have found for Ni_3Zr are in good agreement with this model, as shown in Fig. 3.

Acknowledgments

We thank R. Lemaire and his colleagues for their hearty welcome to the Laboratoire de Magnétisme of the C.N.R.S. in Grenoble. We are grateful to Mr. Roche, technician in the Laboratoire de Physique du Métal, E.N.S.M, who carried out the electron probe microanalysis.

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