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X-Ray Studies in the System $ZrNi_{5-x}Al_x$

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X-ray and micrographic investigations in the system $ZrNi_{5-x}Al_x$ revealed the existence of a continuous series of solid solutions $ZrNi_5$ — $ZrNi_4Al$. The lattice parameter increases monotonously from 6.710 to 6.748 A. Beyond the composition $ZrNi_4Al$ the samples are of a two phase nature. The X-ray intensity calculations confirmed the postulated substitution of nickel atoms in the position 4(c) in the space group $F\bar{4}3m$ (No. 216). A possible influence of oxygen upon the formation of these compounds is briefly discussed.

INTRODUCTION

Some years ago a paper describing the substitution alloying behaviour of $ThNi_5$ and aluminum showed that the atoms of the third component (Al) are distributed in a very special way[1]. Because there are two structural variants of the AB_5 phases, *i. e.* the hexagonal $CaCu_5$ and the cubic UNi_5 type, we felt that the convincing results as obtained on the system $ThNi_{5-x}Al_x$, should be tested on the cubic analogue, also. The crystallographically different positions in both polymorphs were the basis for this study. In the hexagonal variant there are two positions for the element B, *i. e.* 2 (c) and 3 (g) (S. G. P6/mmm). The same situation is found in the cubic form where two sets of the tetrahedral voids are alternatively filled with isolated nickel atoms or their tetrahedral clusters.

MATERIALS AND METHODS

Sample Preparation

All samples in the system $ZrNi_{5-x}Al_x$ were prepared by arc-melting in an argon atmosphere using the following materials: zirconium (Koch-Light Ltd. 99.7%), aluminum (Koch-Light Ltd. 99.99%) and nickel (Koch-Light Ltd. 99.99%). Titanium metal was used as a »getter«. After the annealing treatment in evacuated quartz tubes at 800 °C for 700 hours, buttons were cut in halves, one part being used for micrographic and the other for X-ray analyses.

X-Ray Measurements

X-ray patterns were taken on a Philips diffractometer PW-1010/30 using nickel filtered CuK radiation and a scintillation counter. All samples were previously crushed and ground to a fine powder in an agate mortar under benzene in order to prevent oxidation.

Micrographic Examination

As mentioned above, one half of each specimen used for micrography was embedded in »Duracryl« (Spofa-Dental, Prague, ČSSR), ground on a series of emery

papers, polished with a diamond paste (1/2 μ) on a silk cloth, and photographed at 100x magnification using an »Officine Galileo« reflecting microscope.

Microhardness values were obtained on a PMT-3 metallographic microscope of Soviet origin. The applied load was 100 p. All measurements were done at least three times. Since the indentations were regular, only one diagonal length was measured and the microhardness was computed using the expression

$$H_V = 1.8544 \frac{P}{d^2} \text{ kp/mm}^2.$$

RESULTS AND DISCUSSION

The results of the X-ray and micrographic examinations clearly indicate that the maximum content of aluminum which enters the crystal structure substitutionally is about 16.7 per cent., corresponding to the chemical formula $ZrNi_4Al$. The lattice parameter changes from 6.710 to 6.748 and, as seen from Fig. 1, obeys Vegard's rule. The atomic positions of zirconium and nickel atoms in the crystal structure of $ZrNi_5$ (UNi_5 type S. G. $F\bar{4}3m$; No. 216) are:

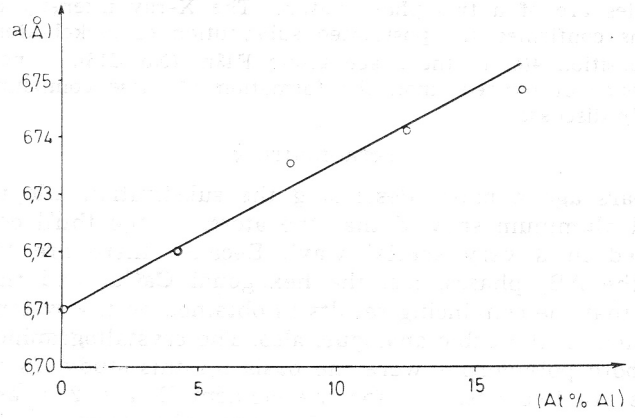

Fig. 1. The lattice parameter variation in the single phase region.

4 Zr in 4 (a) 000
4 Ni in 4 (c) 1/4, 1/4, 1/4 and
16 Ni in 16 (e) xxx, $x\bar{x}\bar{x}$, $\bar{x}x\bar{x}$, $\bar{x}\bar{x}x$
$x = 0.625 \pm 0.005$

It is fairly obvious that the most probable atomic site to be substituted is 4 (c). Fig. 2 illustrates this possibility which is further substantiated by the experimental results.

The agreement between the calculated and the observed intensity values does not seem very convincing, but if this result is compared with the one obtained on UNi_5 and pure $ZrNi_5$ (Table I and II) it is acceptable.[2,3] Notice the last column where observed values from the original paper are given for comparison. Any other assumption concerning the distribution of nickel or aluminum atoms always leads to absurd results. In our opinion, one possible cause for such a poor agreement is the preferred orientation due to cleavage parallel to the octahedral plane (in pure $ZrNi_5$) or 311 ($ZrNi_4Al$). Another possible reason is the presence of oxygen atoms in some positions in the

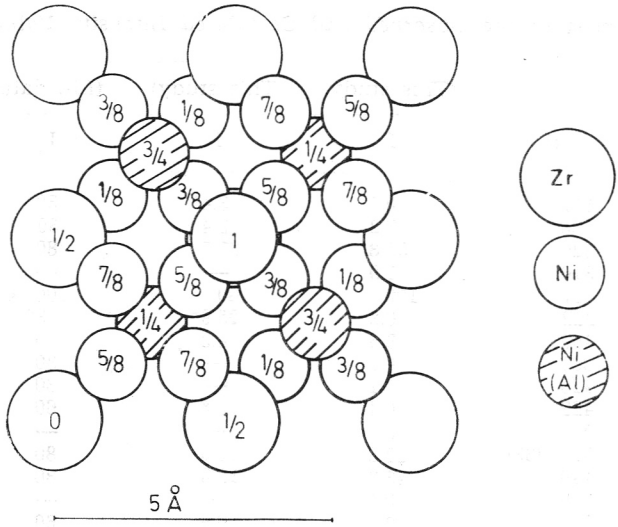

Fig. 2. The projection of the unit cell of $ZrNi_4(Ni,Al)$.

structure. By introducing oxygen atoms in the positions 4 (c) the agreement is improved. This was further confirmed by controlled oxidation of samples of the composition $ZrNi_4$ up to $ZrNi_4O$ (single phase)[4].

TABLE I

The List of the Observed and Calculated Intensity Values for $ZrNi_4Al$

The literature data for UNi_5 are given for comparison

	$ZrNi_4Al$		UNi_5	
hkl	I_c	I_o	I_c	I_o
111	0.1	—	22.4	m
200	16.9	3.1	23.8	m
220	36.3	14.1	131.6	s
310	1.9	—	—	—
311	100	100	331.6	vs
222	3.9	5.5	78.3	m
400	6.9	2.8	1	Abs.
331	0.1	—	40.6	m
420	5.2	3.1	54.6	m^+
422	9.1	4.9	143.4	s
510	0.7	—	—	—
511 (333)	22.8	4.3	250.8	s^+
440	35.8	6.1	60.8	m
530	0.1	—	—	—
533	12.1	3.1	158.9	m^+
622	1.7	—	113.1	m

TABLE II

The Comparison of the Observed and Calculated Intensity Values for $ZrNi_5$

	(This study)	(This study)	(Lit. data)
hkl	I_c	I_o	I_o
111	0.1	3.4*	30
200	3.2	3.4	30
220	59.8	27.7	80
310	1.9	—	—
311	100	100	100
222	0.8	25.9*	80
400	3.6	4.3	30
331	0.1	—	30
420	1.1	—	30
422	16.4	10.6	60
510	0.7	—	—
511 (333)	22.8	20.0	80
440	43.3	12.8	80
530	0.1	—	—
533	12.1	8.9	60
622	0.4	7.7*	60

Microhardness values clearly show that the series of solid solutions ends at the composition $ZrNi_4Al$, (Fig. 3). In our previous paper on the substitution alloying behaviour in the system $ThNi_{5-x}Al_x$ we noticed that there is a marked change of the basic crystallographic parameters and hardness at the composition $ThNi_4Al$ but we could not find any sign of an ordered distribution of the elements in question. Further experiments are underway in order to clear up the whole problem.

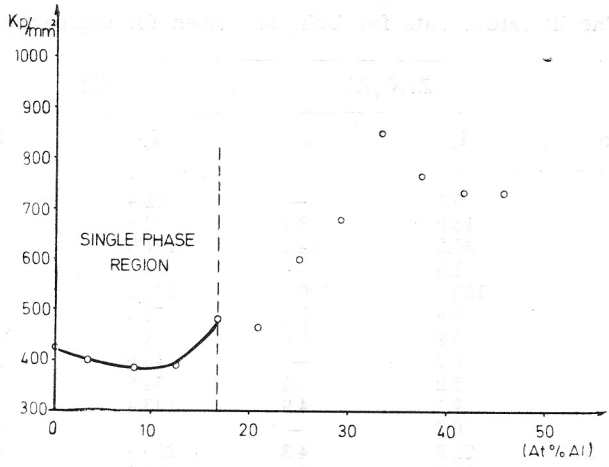

Fig. 3. Microhardness values for all samples in the system $ZrNi_5$—$ZrNi_2Al_3$.

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IZVOD

Rendgenografsko istraživanje sistema $ZrNi_{5-x}Al_x$

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Rendgenografskim i mikrografskim istraživanjem sistema $ZrNi_{5-x}Al_x$ utvrđeno je postojanje neprekinutog niza čvrstih otopina u rasponu ZrNi—$ZrNi_4Al$. Promjena parametara elementarne ćelije pokorava se Vegardovom pravilu i monotono raste od 6,710 do 6,748 A. Računanjem intenziteta difrakcijskih linija zaključeno je da dolazi do unaprijed postuliranog rasporeda atoma nikla, tj. 4 (c) u prostornoj grupi $F\bar{4}3m$. Ukratko je spomenut utjecaj kisika na nastajanje tih spojeva.

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