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Constitutional and structural studies of the intermetallic phase, ZrCu

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Constitutional and structural studies have been carried out on the equiatomic percent alloy ZrCu, using magnetic susceptibility measurements, metallography and X-ray diffraction. The high-temperature magnetic susceptibility measurements and the metallographic studies indicate the presence of two solid state transformations in this alloy, a martensitic transformation with $M_s = 440 \pm 5$ K and a eutectoid transformation with $T_E = 985 \pm 5$ K. Thus, if the high-temperature ZrCu phase is metastably retained to lower temperatures then the martensitic transformation is observed, whereas prolonged annealing just below T_E produces a eutectoid mixture; the metallographic studies indicate that this mixture is lamellar in nature. The X-ray diffraction studies indicate that the high-temperature ZrCu phase has the b c c CsCl-type structure.

1. Introduction

According to the published Zr–Cu phase diagram of Lundin and co-workers [1, 2], the phase ZrCu has a congruent melting point of ~ 1208 K and is bounded by the congruent phases Zr_2Cu_3 and Zr_2Cu. The phase diagram has been modified by subsequent work [3, 4] and in the more recent literature [4] the phase which was originally stated to be Zr_2Cu_3 (40 at % Zr) is given as Zr_7Cu_{10} (41.2 at % Zr) and is reported to have the Zr_7Ni_{10} structure. There is no detailed information on equilibrium-type phase stability below 1173 K (as opposed to metallic glass studies) and the crystal structure of the ZrCu phase does not appear to have been determined.

The work reported in this paper is part of a general investigation into the structure and phase stability of zirconium-based intermetallic phases. The constitutional and structural characterization of the phase ZrCu is an essential preliminary to the investigation of some pseudo-binary alloys based on this material and the results of the studies on the ternary alloys will be reported in a later publication. In the present work, magnetic susceptibility measurements, metallography and X-ray diffraction have been used to investigate the nature of the equiatomic percent alloy ZrCu, after a variety of thermal treatments and it will be seen that these techniques provide complementary information on the character of this alloy.

2. Materials and experimental methods

The zirconium and copper used to prepare the ZrCu alloy were provided by Koch-Light Laboratories Ltd, and had purities of ≥ 99.9 at % and 99.999 at %, respectively. The alloy was prepared by arc-melting the constituents in a carefully purified argon atmosphere and the resultant button was inverted and remelted to improve the homogeneity. The alloy was then homogenized further by annealing at 1173 K for 1 week in a vacuum of better than 10^{-5} torr. In addition to the alloy button, a rod sample of ZrCu was produced by vacuum casting into a copper mould within the arc-furnace and this procedure effectively quenches the alloy from the liquid region.

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The sample dimensions were such that the rod could be examined directly in a standard 11.483 cm diameter) Debye–Scherrer camera.

A portion of the homogenized alloy button was used to study the variation of the magnetic susceptibility of ZrCu as a function of temperature and of various heat treatments. A magnetic balance was employed for this purpose and this has been described in a previous publication [5]. The magnetic susceptibility readings were checked for any field dependence due to the presence of ferromagnetic impurities [6] but all the measurements were found to be field independent. The equipment was capable of a maximum resolution of $0.004\,\mu\text{emu}\,\text{g}^{-1}$ in the magnetic susceptibility using samples of ~ 0.1 g weight and the balance could be evacuated to a vacuum of better than 10^{-5} torr, thus ensuring that there was no oxidation of the sample at high temperatures. Any oxidation would be evident from a permanent weight gain of the sample and changes in weight of $\pm 5 \times 10^{-7}$ g could be detected using this system.

Sections of the alloy button were metallographically examined after subjecting the alloy to various heat treatments. The metallographic samples were prepared by conventional techniques and particular care was taken to remove any surface artefacts produced as a result of the polishing treatment. The samples were examined in both the unetched and etched* conditions.

Powder from the homogenized alloy button was vacuum annealed for 2 h at 973 K and then slowly cooled to room temperature. An X-ray diffraction pattern was obtained from this powder using a Debye–Scherrer camera and Co$K\alpha$ radiation. A diffraction pattern was also obtained from the vacuum-cast rod of ZrCu mentioned earlier using the same camera and Co$K\alpha$ radiation.

3. Results

3.1. Magnetic susceptibility studies

The variations of the mass magnetic susceptibility (χ_g) with temperature for the ZrCu alloy after a variety of thermal treatments are shown in Figs. 1 and 2.

The sample was quenched from 1200 K (i.e. very close to the reported melting point), to the temperature of liquid nitrogen (77 K) and then reheated at a very slow rate which, above room temperature, involved holding the sample at each measuring temperature for approximately 10 min. The behaviour on heating is shown in Fig. 1 and it can be seen that there is a sharp increase in the susceptibility between 500 and 550 K, followed by an approximately linear decrease up to 750 K. There is then a broad minimum in the variation which begins at about 750 K and ends at about 1000 K. The susceptibility then exhibits another linear decrease with temperature up to the maximum temperature of 1205 K, with a very similar slope to that of the earlier temperature range (550 to 750 K).

Fig. 1 also shows the behaviour on furnace-cooling the sample from the highest temperature attained on the heating cycle. The cooling rate

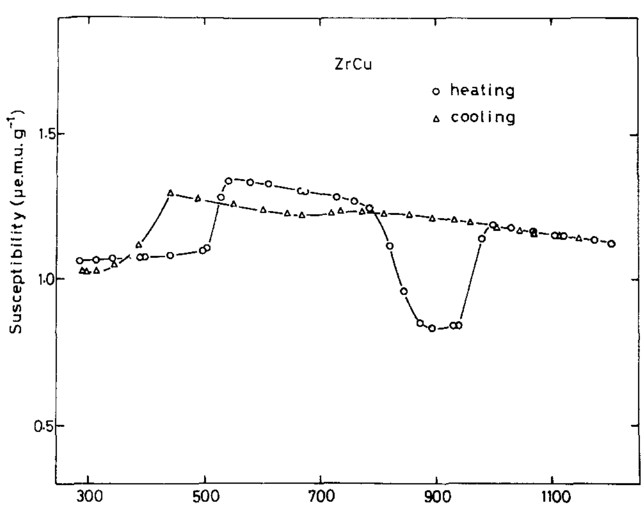

Figure 1 The variation of the magnetic susceptibility with temperature for the ZrCu alloy. ○ heating data for the sample quenched from 1200 K. △ cooling data for the sample furnace cooled from 1205 K, holding at 720 K for $1\frac{1}{2}$ h and then further cooling to room temperature.

*Using a mixture of nitric acid, hydrofluoric acid, glycerol and water.

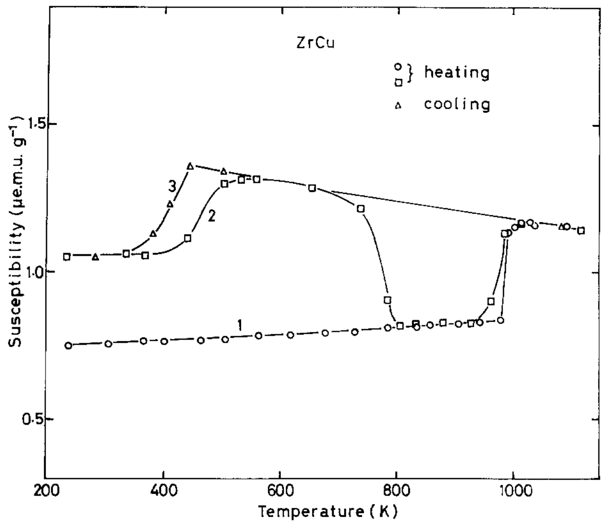

Figure 2 The variation of the magnetic susceptibility with temperature for the ZrCu alloy. The numbers indicate the sequence followed on heating and cooling. Before 1 the sample had been annealed at 973 K for 24 h and then furnace-cooled to room temperature. Between 1 and 2 the sample had been furnace-cooled to room temperature. After 2, no readings were taken between 1117 and 501 K.

was approximately 1.5 K min^{-1} and unlike the behaviour on heating, a much more regular variation of χ_g with temperature is observed over most of the temperature range. There is a progressive increase in χ_g in the range 1150 to 735 K but with a gradually reducing slope. At 720 K the cooling process was arrested and the temperature held constant for $1\frac{1}{2}$ h before resuming the cooling treatment. As a result of this interruption in the cooling sequence, a slight decrease in χ_g can be observed at 720 K and on subsequent cooling there is an approximately linear increase of susceptibility with temperature in the range 670 to 440 K with a slope which is significantly greater than that of the range 900 to 735 K and which is similar to that of the heating range, 550 to 750 K. A sharp fall is observed at 440 K which appears to level out around 300 K. The value of the mass magnetic susceptibility at room temperature of 1.027 μemu g^{-1} is slightly less than the mass magnetic susceptibility of the sample in the quenched condition (1.065 μemu g^{-1}). The values of the room-temperature mass magnetic susceptibilities of the ZrCu alloy after the various heat treatments are summarized in Table I.

TABLE I The room-temperature mass magnetic susceptibility of the ZrCu alloy after various heat treatments

χ_g (μemu g^{-1})	Thermal history
1.065	Quenched from 1200 K
1.027	Furnace-cooled from 1205 to 720 K, $1\frac{1}{2}$ h at 720 K and then furnace-cooled to room temperature
0.752	24 h at 973 K and then furnace-cooled to room temperature
1.049	Furnace-cooled from 1100 K

All the above observations can be interpreted in terms of the ZrCu phase only existing in a high-temperature stability range and decomposing by a eutectoid reaction below about 1000 K. If, however, the proposed high-temperature phase is metastably retained to lower temperatures, then the susceptibility data would be consistent with the occurrence of another phase transformation which exhibits a clearly defined hysteresis loop and is probably martensitic in character. The fact that the susceptibility data on heating and cooling only correspond within the high-temperature range 1000 to 1200 K, can be explained in terms of the different cooling rates, with the quenching treatment giving complete retention of the high-temperature phase which then persists on subsequent heating up to the beginning of the proposed eutectoid decomposition, whereas the furnace cool resulted in a partial decomposition of the high-temperature phase into its eutectoid constituents with a resultant fall in the total susceptibility. Such a conversion on furnace cooling the sample would explain the decreasing slope of the appropriate χ_g versus T variation below about 1000 K (see Fig. 1) where the increase in χ_g due to the temperature dependence of the host ZrCu phase is partially counteracted by the formation of the decomposition products which have a lower total magnetic susceptibility. The fall in χ_g on holding at 720 K is also explained and the linear increase in χ_g with T in the lower temperature range prior to the appearance of the lower temperature transformation, (with a slope similar to that characteristic of the high-temperature region above 1000 K) can be understood in terms of the arrest of the diffusion-controlled eutectoid reaction in the lower temperature range so that the magnetic behaviour is influenced solely by the temperature dependence of the magnetic susceptibility of the alloy; the small decrease in the room-temperature magnetic susceptibility and the values of $d\chi/dT$ indicated that the high-temperature ZrCu phase still predominates in the alloy after the furnace cool.

In order to investigate these ideas further, the ZrCu alloy was annealed in the magnetic balance for 24 h at 973 K, i.e. at a temperature judged to be just below that of the proposed eutectoid reaction. Such a treatment should ensure the complete conversion of the high-temperature phase into the eutectoid mixture. The alloy was then furnace-cooled to room temperature and it was found to exhibit an appreciably lower room-temperature susceptibility ($0.752\,\mu$emu g^{-1}) compared with that of the sample in the quenched condition ($1.065\,\mu$emu g^{-1}); this represents a 29% fall in the mass susceptibility (see Table I). On slowly heating the sample (see Fig. 2), the magnetic susceptibility exhibited a slight linear increase with temperature up to 977 K, and this is in marked contrast to the magnetic behaviour of the quenched sample on slowly heating to 1000 K (see Fig. 1). Between 977 and 990 K, a sharp increase in χ_g was observed (Fig. 2) with the original high-temperature susceptibility behaviour finally being attained at 1010 K. Above this temperature the alloy again exhibited a negative temperature dependence of the susceptibility. The alloy was then furnace-cooled to room temperature without holding at an intermediate temperature (unlike the previous furnace cool) and a value of $1.049\,\mu$emu g^{-1} was obtained for the room-temperature magnetic susceptibility, thus indicating a small proportion of eutectoid mixture in the sample after cooling in this way.

The alloy was then heated again to the high-temperature region (>1100 K) and the low-temperature and high-temperature transformations were again observed with the reproducible high-temperature variation of χ_g with T being attained at around 1010 K. The alloy was then furnace-cooled to 501 K without taking any susceptibility readings and measurements were then taken on cooling to room temperature. It can be seen from Fig. 2 that the hysteresis curve for the proposed martensitic transformation is clearly evident without the displacement of the heating and cooling curves seen in Fig. 1 which was due to the different degrees of decomposition of the parent phase due to the different cooling treatments (i.e. quenching and furnace-cooling). The heating data, designated 1 in Fig. 2 (obtained after annealing the sample for 24 h at 973 K and then furnace cooling to room temperature) can be regarded as the most reliable data for determining the proposed eutectoid temperature T_E and these data indicate that $T_E = 985 \pm 5$ K. The data on the proposed martensitic transformation indicate that $M_s = 440 \pm 5$ K.

It can be seen from Fig. 2 that the susceptibility values shown in curve 2 coincide with those shown in 1 in the range 800 to 925 K, thus indicating completion of the proposed eutectoid decomposition. The values of the room-temperature mass magnetic susceptibility can be used to estimate the extent of the proposed eutectoid decomposition in the sample after the two furnace cooling treatments, if the susceptibility data shown in 1 is taken to represent the magnetic behaviour of the alloy containing 100% eutectoid mixture and the room temperature susceptibility of the quenched alloy is taken to represent that of 100% retained high-temperature phase. Thus

$$\chi_{\text{total}} = (1-x)\,\chi_{\text{ZrCu}} + x\chi_{\text{E}}$$

where χ_{total} is the measured room-temperature magnetic susceptibility of the alloy, χ_{ZrCu} is the room-temperature magnetic susceptibility of the sample in the quenched condition and χ_E is the room temperature magnetic susceptibility of the sample containing 100% eutectoid mixture (after annealing sample at 973 K for 24 h), x is the proportion of eutectoid mixture in the sample.

The relationship gives, respectively, values of 12.2 and 5.2% for the proportion of the eutectoid mixture in the alloy after the first and second furnace-cooling treatments. A larger proportion is obtained in the sample after the first cool because the temperature was held at 720 K for $1\frac{1}{2}$ h.

3.2. Metallographic studies

The microstructures of the ZrCu alloy were examined after various heat treatments in order to provide further information on the nature of the solid state phase transformations indicated by the magnetic susceptibility measurements. Characteristic microstructures would be anticipated as a result of the proposed eutectoid reaction and

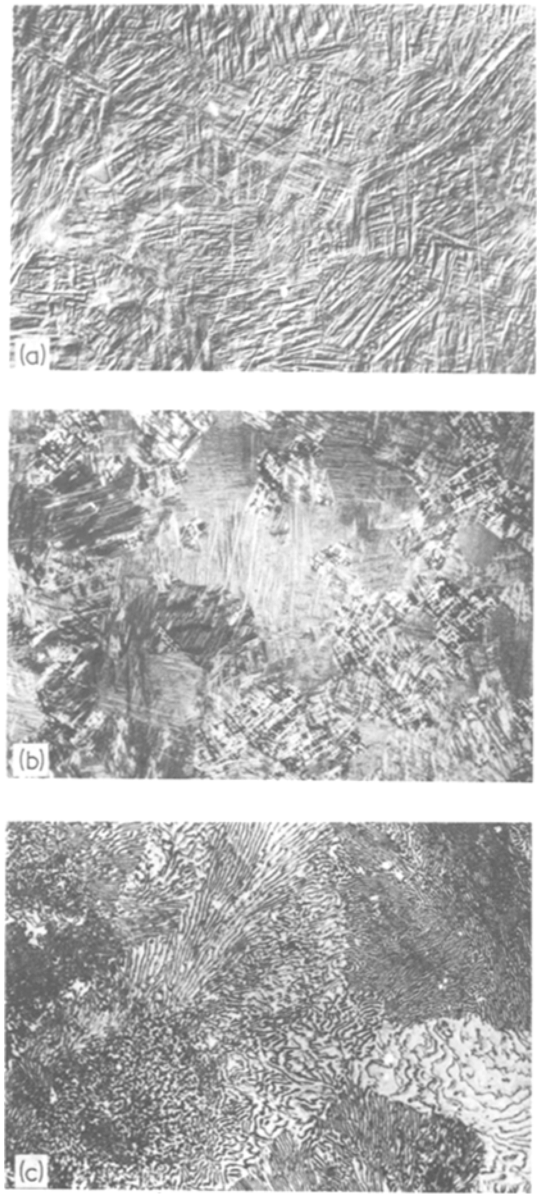

Figure 3 (a) ZrCu alloy annealed at 1173 K for 1 week and then quenched to room temperature. The alloy has been lightly etched and the microstructure is characteristic of a martensitically transformed phase; × 250. (b) The alloy in the same condition as (a) but examined under polarized light; × 250. (c) ZrCu alloy annealed at 900 K for 24 h and then furnace-cooled to room temperature. The alloy is in the etched condition and shows a typical eutectoid structure with alternative areas of the component phases; × 1000.

martensitic transformation. Thus the alloy was metallographically examined after quenching from 1173 K, i.e. from within the proposed high-temperature phase field, and after annealing at 900 K for 24 h, i.e. within the temperature range where extensive eutectoid decomposition was suggested.

The microstructures of the alloy after these treatments are shown in Fig. 3a, b and c and there is a marked contrast between their appearance. The microstructure of the quenched alloy (Fig. 3a and b) is characteristic of a martensitically transformed material and is, therefore, consistent with the susceptibility data shown in Figs. 1 and 2 which indicate a phase transformation at ~ 440 K on cooling. The microstructure of the alloy after annealing at 900 K for 24 h is shown in Fig. 3c and is a fine lamellar structure characteristic of a eutectoid-type decomposition process. This is an interesting example of a lamellar-type eutectoid mixture as reference to the Zr–Cu phase diagram [1, 2] indicates that it probably consists of a mixture of two intermetallic phases.

3.3. X-ray diffraction studies

The instability of the ZrCu alloy is also evident from the X-ray diffraction measurements. The diffraction pattern of the powdered material which had been annealed at 973 K for 2 h and then quickly cooled to room temperature, exhibited a large number of diffraction lines. Some of the stronger lines can be indexed according to the CsCl-type, b c c structure with $a = 3.2587 \pm 0.0005$ Å but there are many additional lines which could be due to the phases produced as a result of the partial eutectoid decomposition of the alloy and the martensitic phase change which occurs on cooling. The presence of two types of transformation and hence the possibility of four structural variations contributing to the diffraction pattern of the alloy would explain the complexity of the observed diffraction pattern.

The diffraction pattern of the vacuum-cast rod which has been quenched from the liquid region is much simpler than the previous case and of a much better quality. The pattern exhibits strong lines, all of which can be indexed according to the b c c CsCl-type structure; some additional, weak reflections can be observed at low angles. The diffraction data for the b c c structure are summarized in Table II and a lattice spacing of 3.2620 ± 0.0005 Å is obtained for this phase. The relative intensities of the reflections are in reasonably good qualitative agreement with the theoretically calculated values assuming the CsCl-type structure.

Thus the X-ray diffraction studies indicate

TABLE II The room-temperature X-ray diffraction data of ZrCu in the vacuum-cast condition (i.e. quenched from the liquid region). ZrCu has the CsCl-type b c c structure with a lattice spacing of 3.2620 ± 0.0005 Å

h k l	*d*-spacing (calculated) (Å)	*d*-spacing (observed) (Å)	Intensity observed
1 1 0	2.307	2.283	vs
1 1 1*	1.883	1.870	vw
2 0 0	1.631	1.621	m
2 1 0*	1.459	1.451	mw
2 1 1	1.332	1.326	s
2 2 0	1.153	1.150	ms
3 0 0, 2 2 1*	1.087	1.086	mw
3 1 0	1.032	1.030	s
3 1 1*	0.9835	0.9827	mw
2 2 2	0.9417	0.9413	m
3 2 0*	0.9047	0.9047	mw

*Superlattice reflections.
vs – very strong, s – strong, ms – medium strong, m – medium, mw – medium weak, vw – very weak.

that the high temperature ZrCu phase has the CsCl-type, b c c structure. These studies also indicate that annealing the powdered alloy for 2h at 973 K does not complete the eutectoid decomposition process and in the vacuum-cast rod the martensitic phase transformation has either not occurred or is largely incomplete. This could be due to compositional variations between the homogenized alloy and the vacuum-cast sample which could influence the value of M_s. The discrepancy in the lattice spacings reported above could indicate a compositional range of stabilities for the ZrCu phase at high temperatures which could correspond to some variation in M_s across the phase field.

4. Discussion

The magnetic susceptibility, metallographic and X-ray diffraction studies clearly indicate the presence of two solid state transformations in the equiatomic percent alloy, ZrCu. Thus, if the high-temperature b c c phase is metastably retained to lower temperatures then there is a martensitic-type transformation, whereas annealing at a temperature just below the high-temperature stability range results in the eutectoid decomposition of the high-temperature ZrCu phase. Reference to the existing phase diagram [1–4] indicates that a likely form of the eutectoid reaction is as follows:

$$13ZrCu \rightleftarrows Zr_7Cu_{10} + 3Zr_2Cu.$$

If this is the case then according to the Lever rule the eutectoid mixture should consist of 65% Zr_7Cu_{10} and 35% Zr_2Cu. It should be possible, therefore, to check this hypothesis by measuring the magnetic susceptibilities of these intermetallic phases to see what proportion of these phases are required to give agreement with the room-temperature magnetic susceptibility of the eutectoid mixture of $0.752\,\mu$emu g^{-1}. The relative average widths of the lamellae of the dark and light phases shown in Fig. 3c have been determined and the derived proportions of the two phases are in good agreement with the proposed eutectoid reaction if it is assumed that the light phase is Zr_7Cu_{10} and the dark phase is Zr_2Cu.

The fact that the susceptibility of the high-temperature ZrCu phase substantially exceeds that of the eutectoid mixture and the fact that $d\chi/dT < 0$ for this phase, both imply that the Fermi level of ZrCu is close to a peak in the density of states curve [7, 8]. It is interesting to compare the magnetic behaviour of ZrCu with that of the phases ZrCo and ZrNi, as the sequence ZrCo → ZrNi → ZrCu represents a regular sequence of increasing total electron concentration. The magnitude of the room-temperature susceptibility of ZrCu is similar to that of ZrNi (orthorhombic, CrB-type structure) but unlike ZrCu, this phase exhibits a slight positive temperature dependence of the susceptibility [9] ($d\chi/dT > 0$). The phase ZrCo (b c c CsCl-type) exhibits a much larger paramagnetic, room-temperature susceptibility than ZrCu [9] and a much greater negative temperature dependence of the susceptibility but in terms of the sign of $d\chi/dT$ it is similar to ZrCu. Thus it would appear that both phases have Fermi levels close to a maximum in the density of states curve and the larger magnetic effects observed in ZrCo are probably related to some exchange enhancement [10, 11] of the susceptibility of this phase.

There is some evidence from the present work (Fig. 1) that the martensitic phase of ZrCu exhibits a positive temperature dependence of χ and if this is the case then its magnetic behaviour would resemble that of ZrNi.

Finally, it is also of interest to compare the crystal structures of the phases, ZrCo, ZrNi and ZrCu. As mentioned above, ZrCo has the CsCl-type b c c structure whereas ZrNi has the CrB-type orthorhombic structure, despite the closely similar atomic diameters of cobalt (2.504 Å) and nickel (2.492 Å). The difference in structure of these phases has been attributed to the different electron concentrations [9] and on this basis alone the ZrCu phase would be expected to exhibit an orthorhombic structure instead of the observed b c c structure. It should be noted, however, that the atomic diameter of copper (2.556 Å) is significantly larger than that of cobalt or nickel and the larger radius ratio of the component atoms could influence the relative stabilities of the cubic and orthorhombic structures in the ZrCu alloy.

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