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Formation of the Laves phases in Co/Fe–V–Zr and their magnetic and superconducting properties*

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Abstract

The structure, microstructure, magnetic and superconducting properties of the arc-melted ternary alloys $Co_{67-x}V_xZr_{33}$ and $Co_{50}Fe_{17}Zr_{33}$ are investigated. Substitution of cobalt on vanadium sites in $V_{67}Zr_{33}$ ($MgCu_2$-type structure) transforms the structure to $MgZn_2$ type for cobalt concentrations higher than 9 at.%, but for cobalt concentrations higher than 50 at.% the alloys again transform to the $MgCu_2$-type structure. $MgCu_2$-type structure alloys have large magnetic susceptibility and possess magnetic moments. The negative Curie temperatures indicate that the alloys would order antiferromagnetically at low temperatures. Only vanadium-rich alloys of $MgCu_2$-type structure are superconducting.

1. Introduction

Most of the Laves phase alloys have either an $MgCu_2$-type (C15) or an $MgZn_2$-type (C14) structure. These Laves phase alloys and their hydrides have interesting mechanical and superconducting properties with potential for applications. Because of their high melting temperature and outstanding strength at elevated temperatures, these alloys may be used as high-temperature structural materials and a typical example is $TiCr_2$ [1]. The vanadium-, hafnium- and zirconium-based $MgCu_2$-type structure alloys exhibit superconducting transition temperatures in the range 8–11 K and show high critical magnetic fields and current densities [2, 3]. They are also insensitive to neutron irradiation [4] and absorb large amounts of hydrogen [5, 6]. The other characteristic features of these alloys are that they show lattice instability at low temperatures [7, 8], have high electronic density of states at the Fermi surface and show the presence of spin fluctuations [9, 10]. Substitution of ferromagnetic metal atoms such as cobalt and iron on the vanadium sites in the binary $MgCu_2$-type structure $V_{67}Zr_{33}$ causes a change in the crystal and electronic structures. The magnetic properties of the binary $MgCu_2$-type structure Co_2Zr have been reported by Aoki *et al.* [11]. The $MgCu_2$-type

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structure Laves phase formation and their magnetic and superconducting properties were reported earlier [12]. This paper reports the formation of the Laves phases in the Co/Fe–V–Zr system and their magnetic and superconducting properties.

2. Experimental details

Eleven alloys of composition $Co_{67-x}V_xZr_{33}$ ($0 \leqslant x \leqslant 67$) and an alloy of composition $Co_{50}Fe_{17}Zr_{33}$ were prepared by arc melting on a water-cooled copper hearth in an argon atmosphere. The arc-melted alloys were homogenized by a heat treatment at 1500 K in a vacuum of 10^{-6} Torr for a period of 24 h. The crystal structure of the alloys was determined by X-ray diffraction of powdered samples and the lattice parameters were calculated from the X-ray diffractograms taken at room temperature using Cu Kα radiation. The phase distribution and composition of the alloys were investigated by optical microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA) techniques. The temperature-dependent mass magnetic susceptibility χ in the temperature range 90–300 K was measured by the Faraday technique. The superconducting transition temperature T_c and the transition width ΔT_c were determined down to 2 K from inductance measurements using an a.c. inductance bridge working at 18 kHz.

3. Results and discussion

The distribution of the ternary $MgCu_2$-type (C15) and $MgZn_2$-type (C14) structure alloys in the Co–V–Zr system is shown in Fig. 1.

The ternary cobalt-rich alloys $Co_{63}V_4Zr_{33}$ and $Co_{58}V_9Zr_{33}$ and the vanadium-rich alloy $Co_4V_{63}Zr_{33}$ have $MgCu_2$-type structure. Four alloys with composition $Co_{67-x}V_xZr_{33}$ ($17 \leqslant x \leqslant 50$) have $MgZn_2$-type structure. $Co_9V_{58}Zr_{33}$ consists of two phases of $MgCu_2$- and $MgZn_2$-type structures. The cell volume of the phases is plotted as a function of composition in Fig. 2(a). The cell volume decreases almost linearly with increasing cobalt concentration, as expected, because the atomic radius of cobalt (1.25 Å) is smaller than that of vanadium

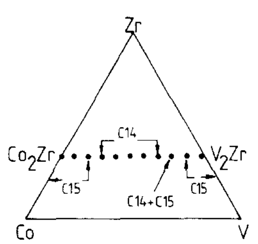

Fig. 1. Distribution of $MgCu_2$-type (C15) and $MgZn_2$-type (C14) structure Laves phases in ternary $Co_{67-x}V_xZr_{33}$ system.

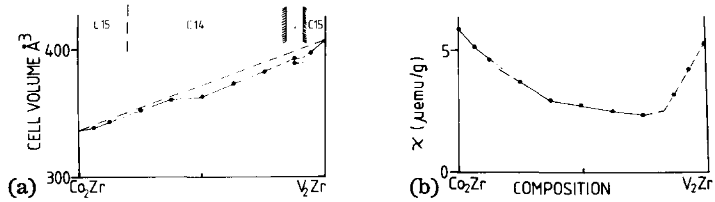

Fig. 2. (a) Cell volume and (b) room temperature mass magnetic susceptibility χ of $MgCu_2$-type (C15) and $MgZn_2$-type (C14) structure Laves phases as a function of composition in $Co_{67-x}V_xZr_{33}$.

TABLE 1

Lattice parameter, room temperature mass magnetic susceptibility χ (RT), effective magnetic moment μ_{eff}, Curie temperature θ_p, superconducting transition temperature T_c and transition width ΔT_c of $Co_{67-x}V_xZr_{33}$ ($0 \leqslant x \leqslant 67$) alloys

Alloy	Phase	Lattice parameter (Å)	χ(RT) (μemu g^{-1})	μ_{eff} (μ_B)	μ per Co atom (μ_B)	θ_p (K)	T_c (K)	ΔT_c (K)
$V_{67}Zr_{33}$	$MgCu_2$	$a = 7.43$	5.30	0.51		−160	8.0	1.2
$Co_4V_{63}Zr_{33}$	$MgCu_2$	$a = 7.38$	4.39	0.41	2.0	−132	8.4	1.4
$Co_9V_{58}Zr_{33}$	$MgCu_2$ +	$a = 7.35$	3.36	0.31	1.07	−130	2	1
	$MgZn_2$	$a = 5.19$ $c = 8.43$						
$Co_{17}V_{50}Zr_{33}$	$MgZn_2$	$a = 5.16$ $c = 8.37$	2.48					
$Co_{25}V_{42}Zr_{33}$	$MgZn_2$	$a = 5.10$ $c = 8.39$	2.60					
$Co_{34}V_{33}Zr_{33}$	$MgZn_2$	$a = 5.05$ $c = 8.25$	2.84					
$Co_{42}V_{25}Zr_{33}$	$MgZn_2$	$a = 5.04$ $c = 8.21$	3.02					
$Co_{50}V_{17}Zr_{33}$	$MgZn_2$	$a = 4.99$ $c = 8.15$	3.76					
$Co_{59}V_8Zr_{33}$	$MgCu_2$	$a = 7.00$	4.64					
$Co_{63}V_4Zr_{33}$	$MgCu_2$	$a = 6.96$	5.12	0.13	0.16	−29		
$Co_{67}Zr_{33}$	$MgCu_2$	$a = 6.94$	5.84	0.43	0.52	−82		
$Co_{50}Fe_{17}Zr_{33}$	$MgCu_2$	$a = 6.97$	16.80	1.30	3.67[a]	−163		

[a]Magnetic moment per ferromagnetic atom.

(1.34 Å). The alloy with two ferromagnetic components, $Co_{50}Fe_{17}Zr_{33}$, has a slightly larger cell volume and the Laves phase is of $MgCu_2$-type structure. The structure type and lattice parameters of all the Laves phases are listed in Table 1. Optical, SEM and EDXA investigations show in some cases a small amount of precipitation of secondary phases in the grains or at the grain boundaries which were not detected by X-ray diffraction.

The mass magnetic susceptibility as a function of temperature for the alloys of composition $Co_{67-x}V_xZr_{33}$ ($0 \leqslant x \leqslant 50$) is shown in Fig. 3. $V_{67}Zr_{33}$ shows an anomaly in the χ–T curve in the temperature range 100–135 K

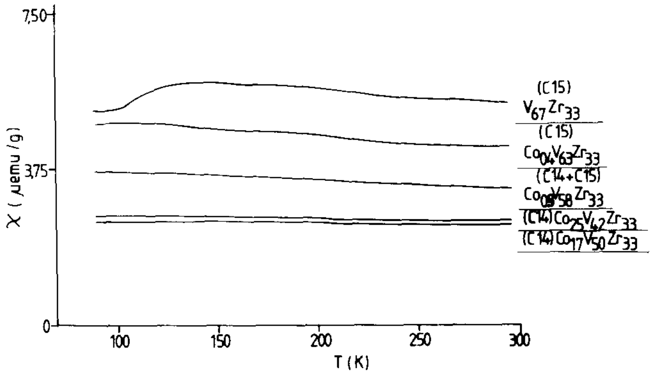

Fig. 3. Mass magnetic susceptibility χ as a function of temperature for $MgCu_2$-type (C15) and $MgZn_2$-type (C14) structure alloys in $Co_{67-x}V_xZr_{33}$.

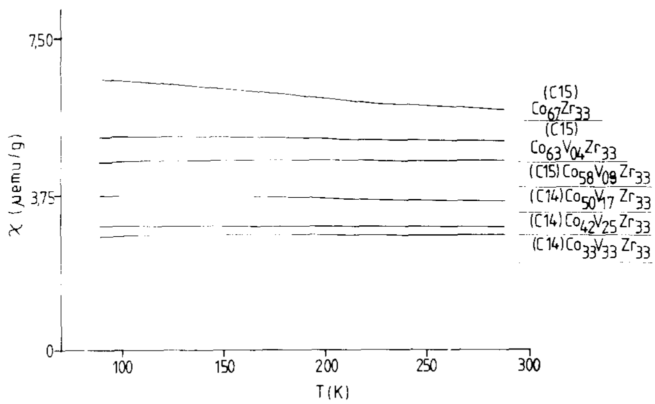

Fig. 4. Mass magnetic susceptibility χ as a function of temperature of $MgCu_2$-type (C15) and $MgZn_2$-type (C14) structure alloys in $Co_{67-x}V_xZr_{33}$.

which is associated with the cubic-to-rhombohedral phase transformation. This phase transformation is also confirmed by temperature-dependent X-ray diffraction studies and is consistent with earlier investigations [7, 8]. $Co_4V_{63}Zr_{33}$ does not show any anomaly, indicating that no phase transformation occurs in this alloy. $Co_4V_{63}Zr_{33}$ and $Co_9V_{58}Zr_{33}$ (mixed phase) have temperature-dependent χ and possess magnetic moments. The effective magnetic moments (μ_{eff}) and magnetic moments per cobalt atom of these alloys were determined from Curie–Weiss plots. Substitution of cobalt on the vanadium sites reduces the room temperature value as well as μ_{eff}. The room temperature χ, μ_{eff} and μ per cobalt atom values are listed in Table 1. The magnetic moment per cobalt atom in $Co_4V_{63}Zr_{33}$ is 2.0 μ_B, which is approximately two-thirds of the corresponding value for metallic cobalt (the effective magnetic moment of γ-Co is 3.15 μ_B). The $MgZn_2$-type structure alloys of composition $Co_{67-x}V_xZr_{33}$ ($17 \leqslant x \leqslant 50$) show temperature-independent χ (Figs. 3 and 4). The room temperature values are smaller than those of $MgCu_2$-type structure

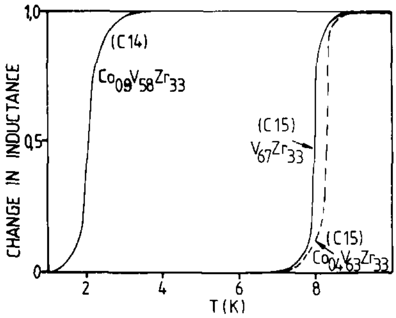

Fig. 5. Superconducting transitions of $V_{67}Zr_{33}$, $Cu_4V_{63}Zr_{33}$ and $Co_9V_{58}Zr_{33}$ alloys.

alloys and increase with increasing cobalt concentration. The room temperature values are listed in Table 1. The alloy of $MgCu_2$-type structure with composition $Co_{58}V_9Zr_{33}$ also has temperature-independent χ, but the room temperature value is higher than those of $MgZn_2$-type structure alloys and is comparable to that of the vanadium-rich alloys with $MgCu_2$-type structure.

The cobalt-rich alloys $Co_{63}V_4Zr_{33}$ and $Co_{67}Zr_{33}$ with $MgCu_2$-type structure show temperature-dependent χ (Fig. 4). The room temperature values are comparable to those of the vanadium-rich $MgCu_2$-type structure alloys but the magnetic moments are lower, as listed in Table 1. The room temperature χ value of $Co_{67}Zr_{33}$ and its weak temperature dependence agree with the data of Aoki *et al.* [11]. $Co_{50}Fe_{17}Zr_{33}$ ($MgCu_2$-type structure) shows temperature-dependent χ and the room temperature χ, μ_{eff} and μ per (Co+Fe) atom values are 16.80 μemu g^{-1}, 1.30 μ_B and 3.67 μ_B respectively. The variation in room temperature magnetic susceptibility χ as a function of composition is also shown in Fig. 2(b). The Curie temperatures (θ_p) of the $MgCu_2$-type structure alloys range between 29 and 163 K and are negative, indicating that these alloys would order antiferromagnetically at low temperatures. The θ_p values are also listed in Table 1. $V_{67}Zr_{33}$ [13] and $Co_4V_{63}Zr_{33}$ are superconducting with T_c (ΔT_c) values of 8.0 (1.2) and 8.4 (1.4) K respectively. $Co_9V_{58}Zr_{33}$ (mixed phase) has T_c (ΔT_c) values of 2 (1) K. The superconducting transitions are shown in Fig. 5.

4. Conclusions

Substitution of cobalt on the vanadium sites in binary $V_{67}Zr_{33}$ alloy of $MgCu_2$-type structure transforms the structure to $MgZn_2$ type for cobalt concentrations higher than 9 at.%, but for cobalt concentrations higher than 50 at.% the alloys again transform to the $MgCu_2$-type structure. The $MgCu_2$-type structure alloys (both vanadium and cobalt rich) have large magnetic susceptibility and possess magnetic moments. The negative Curie temperatures indicate that they would order antiferromagnetically at low temperatures. Only vanadium-rich alloys of $MgCu_2$-type structure are superconducting.

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References

1 G. Sauthoff, *Z. Metallkd.*, *80* (1989) 337.
2 K. Inoue and K. Tachikawa, *J. Jpn. Inst. Met.*, *39* (1975) 1274.
3 T. Kuroda, K. Inoue, H. Wada and K. Tachikawa, *IEEE Trans. Magn.*, *MAG-19* (1980) 410.
4 B. S. Brown, I. W. Hafstrom and T. E. Klippert, *J. Appl. Phys.*, *48* (1977) 1759.
5 D. Shaltiel, *J. Less-Common Met.*, *73* (1983) 329.
6 W. Däumer, H. R. Khan and K. Lüders, *Phys. Rev. B.*, *38*(7) (1988) 4427.
7 A. C. Lawson, *Phys. Lett. A*, *38* (1972) 379.
8 A. C. Lawson and H. Zachariason, *Phys. Lett. A*, *38* (1972) 1.
9 B. M. Klein, W. E. Pickett, D. A. Papaconstantopoulos and L. L. Boyer, *Phys. Rev. B*, *27* (1983) 6721.
10 H. Keiber, C. Geibel, B. Renker, H. Rietschel, H. Schmidt and H. Wühl, *Phys. Rev. B*, *30* (1984) 2524.
11 Y. Aoki, T. Nakamichi and M. Yamamoto, *Phys. Status Solidi B*, *53* (1972) K137.
12 H. R. Khan and O. Loebich, *Physica C*, *153–155* (1988) 433–434.
13 K. Yasohama and N. Usui, *Jpn. J. Appl. Phys.*, *7* (1968) 1128.