

Structure Refinement of the S-Phase Precipitate MgCuAl_2

Birgit Heying, Rolf-Dieter Hoffmann, and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster,
Corrensstraße 36, D-48149 Münster, Germany

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **60b**, 491–494 (2005); received January 28, 2005

The technologically important S-phase precipitate MgCuAl_2 has been synthesized from the elements in a sealed tantalum tube in an induction furnace. The aluminide was investigated by powder and single crystal X-ray diffraction methods: *Cmcm*, $a = 401.19(9)$, $b = 926.5(2)$, $c = 712.4(1)$ pm, $wR2 = 0.0425$, 234 F^2 values, and 16 variable parameters. The new crystallographic data fully confirm the original work by Perlitz and Westgren [Ark. Kemi, Mineral. Geol. **16**, 1 (1943)], but the present structure refinement has led to a much higher precision. The crystal chemical peculiarities of MgCuAl_2 are briefly discussed.

Key words: Light Weight Alloy, Precipitation Hardening, Crystal Structure

Introduction

Binary CuAl_2 (θ -phase), the Zintl phase Mg_2Si , and the so-called S-phase MgCuAl_2 are important precipitates that form during the hardening process of modern light-weight aluminium and magnesium based alloys [1]. The structure of MgCuAl_2 was originally determined by Perlitz and Westgren in 1943 [2] from crystals that had grown in blowholes of an alloy with the starting composition 11 Mg : 35 Cu : 45 Al. Since that time, the aging and corrosion behavior [3–6] within the alloys, and the shape and growth mechanism of the S-phase precipitations was thoroughly studied [7]. The phase relationships in the Mg–Cu–Al system have competently been summarized by Prince and Effenberg [8].

Despite the broad technological use and extensive studies, the crystal structure, morphology, and the interface structure are still not well understood. A good literature overview on the various studies is given in [9]. The only X-ray single crystal study of MgCuAl_2 was based on Weissenberg film data [2]. All further investigations used X-ray powder data or electron microscopy [10–26]. Since, in an aluminium based matrix, the MgCuAl_2 precipitates have dimensions in the range of nanometers, such nanocrystals have repeatedly been investigated by transmission electron microscopy including nanodiffraction and high-resolution imaging [13–16, 18–20].

The space group symmetry and the magnesium/copper ordering of the MgCuAl_2 structure was repeatedly questioned in recent years [10–26, and ref. therein]. Especially the inverted Mg/Cu occupancy (with respect to the model derived by Perlitz and Westgren [2]) is doubtful from a crystal chemical point of view. We have recently reviewed the crystal chemistry of intermetallics with MgCuAl_2 type structure, including many aluminides, gallides, indides and thallides [27]. For more than 30 of these compounds the structures were successfully refined with the initial MgCuAl_2 model. To the best of our knowledge, the structure of the prototype MgCuAl_2 has never been refined from single crystal diffractometer data. Herein we report on the synthesis of a MgCuAl_2 bulk sample and a precise single crystal study which fully confirms the model derived by Perlitz and Westgren [2].

Experimental Section

Synthesis

Starting materials for the preparation of MgCuAl_2 were a magnesium rod (Johnson Matthey, \varnothing 16 mm, > 99.95%), a copper wire (Johnson Matthey, \varnothing 1 mm, > 99.9%), and an aluminium rod (VAW, > 99.9%). The three elements were weighed in the ideal 1:1:2 atomic ratio and sealed in a tantalum tube [28] under an argon pressure of *ca.* 600 mbar. The argon was previously purified over molecular sieves, silica gel, and titanium sponge (900 K). The tantalum tube was then placed in a water-cooled sample chamber [29] of

a high-frequency furnace (Hüttinger TIG 5/300) and first inductively heated at *ca.* 1200 K for 15 minutes under flowing argon and quenched by switching off the furnace. The tantalum tube was subsequently sealed in an evacuated silica ampoule and annealed at 820 K in a resistance furnace for 2 h and quenched in ice water. In the final step, this ampoule was heated to 460 K for 6 days and quenched by radiative heat loss on a sand bath. The silvery gray sample could readily be separated from the tantalum tube by mechanical fragmentation. No reaction with the container material was observed. Polycrystalline MgCuAl₂ is light gray. Single crystals exhibit metallic luster. Fine-grained powder is dark gray. MgCuAl₂ is stable in moist air over years.

The MgCuAl₂ single crystal investigated on the imaging plate diffractometer and the bulk sample were analyzed by an EDX measurement using a LEICA 420 I scanning electron microscope with MgO, copper, and Al₂O₃ as standards. No impurity elements were detected. The analyses, 24 ± 2 at.-% Mg : 25 ± 2 at.-% Cu : 51 ± 2 at.-% Al, are in good agreement with the ideal composition of 1:1:2.

X-ray film data and structure refinement

MgCuAl₂ was characterized through a Guinier powder pattern using Cu-K_{α1} radiation and α-quartz (*a* = 491.30, *c* = 540.46 pm) as an internal standard. The Guinier camera was equipped with an image plate system (Fujifilm BAS-1800). To ensure correct indexing, the experimental powder pattern was compared to a calculated one [30] using the atomic parameters of the structure refinement. The orthorhombic lattice parameters (Table 1) were obtained by least-squares fits of the Guinier data.

Irregularly-shaped single crystals were selected from the annealed sample and first examined on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature on a Stoe IPDS-II diffractometer with graphite monochromatized Mo-K_α radiation. A numerical absorption correction was applied to the data. All relevant crystallographic data for the data collection and evaluation are listed in Table 2.

Analysis of the data set was consistent with space group *Cmcm*. The atomic positions initially determined by Perlitz and Westgren [2] were taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on *F*_o²) [31] with anisotropic atomic displacement parameters for all sites. The occupancy parameters were refined in a separate series of least-squares cycles in order to check for the correct composition. They are 102.9(16)% for Mg, 98.9(11)% for Cu, and 99.6(12)% for Al. Thus, all sites were fully occupied within one (Cu, Al) and two (Mg) standard deviations. In the last cycles, ideal occupan-

Table 1. Lattice parameters of orthorhombic MgCuAl₂.

<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)	Reference
400	923	714	0.2636	[2]
401.19(9)	926.5(2)	712.4(1)	0.2648	this work
403(1)	930(13)	708(10)	0.2654	[9, 16]
400	461	718	0.1324	[14]
404	918	713	0.2644	[19] ^a
401	925	714	0.2648	[22]
400	927	714	0.2648	[25]

^a Data after an aging time of 576 h at 460 K.

Table 2. Crystal data and structure refinement for MgCuAl₂.

Empirical formula	MgCuAl ₂
Formula weight [g/mol]	141.81
Unit cell dimensions	Table 1
Pearson symbol	oC16
Structure type	MgCuAl ₂
Space group	<i>Cmcm</i>
Formula units per cell	<i>Z</i> = 4
Calculated density [g/cm ³]	3.56
Crystal size [μm ³]	10 × 20 × 50
Transmission ratio (max/min)	1.19
Absorption coefficient [mm ⁻¹]	8.8
<i>F</i> (000)	268
Detector distance [mm]	40
Exposure time [min]	4
<i>ω</i> Range; increment [°]	0–180, 1.0
Integration parameters A, B, EMS	14.0, 3.9, 0.026
<i>θ</i> Range for data collection [°]	5 to 30
Range in <i>hkl</i>	±5, ±12, ±10
Total no. of reflections	1343
Independent reflections	234 (<i>R</i> _{int} = 0.0911)
Reflections with <i>I</i> > 2σ(<i>I</i>)	186 (<i>R</i> _{sigma} = 0.0724)
Data / parameters	234 / 16
Goodness-of-fit on <i>F</i> ²	0.918
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0328; <i>wR</i> 2 = 0.0391
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0575; <i>wR</i> 2 = 0.0425
Extinction coefficient	0.009(1)
Largest diff. peak and hole [e/Å ³]	0.93 and –0.93

Table 3. Atomic coordinates and anisotropic displacement parameters (pm²) for MgCuAl₂. *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. *U*₁₂ = *U*₁₃ = 0. The atomic coordinates originally determined by Perlitz and Westgren [2] are listed in italics for comparison.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Mg	4 <i>c</i>	0	0.0651(3)	1/4	95(12)	80(12)	154(13)	0	109(6)
			0.072						
Cu	4 <i>c</i>	0	0.7801(1)	1/4	46(5)	68(4)	56(5)	0	57(3)
			0.778						
Al	8 <i>f</i>	0	0.3558(2)	0.0556(2)	77(8)	76(8)	55(8)	–5(7)	70(4)
			0.356	0.056					

cies were again assumed. A final difference Fourier synthesis revealed no significant residual peaks (see Table 2). The positional parameters and interatomic distances are listed in

Table 4. Interatomic distances (pm) of MgCuAl₂ (standard deviations in parentheses), calculated with the powder lattice parameters. The distances calculated from the Perlitz-Westgren [2] data are listed for comparison.

This work			Perlitz-Westgren [2]
Mg:	1	Cu	264.1(3)
	2	Cu	282.7(2)
	2	Al	302.8(3)
	4	Al	305.0(1)
	4	Al	311.5(2)
Cu:	2	Mg	376.1(2)
	2	Al	251.5(2)
	4	Al	253.6(1)
	1	Mg	264.1(3)
	2	Mg	282.7(2)
Al:	1	Cu	251.5(2)
	2	Cu	253.6(1)
	1	Al	277.0(3)
	1	Al	278.8(3)
	2	Al	291.4(2)
	1	Mg	302.8(3)
	2	Mg	305.0(1)
	2	Mg	311.5(2)

Tables 3 and 4. Further details on the structure refinement are available.

Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-415062.

Discussion

The present structure refinement of the technologically important S-phase precipitate MgCuAl₂ fully confirms the initial work by Perlitz and Westgren [2], however, the diffractometer data are more precise than

the Weissenberg film data. The largest difference between the two structure refinements concerns the magnesium position (Table 3). Consequently, the Mg–Cu, Mg–Al, and Mg–Mg distances differ by up to 7 pm.

The copper atoms in MgCuAl₂ have six aluminium neighbors at Cu–Al distances ranging from 252 to 254 pm, close to the sum of the covalent radii [32] of 242 pm. Similar Cu–Al distances occur in the θ -phase of CuAl₂ (259 pm) [33] and in Mg₂Cu₆Al₅ (249–265 pm) [34]. The Mg–Al distances range from 303 to 312 pm, similar to those in ϵ -Mg₂₃Al₃₀ [35] and β -Mg₂Al₃ [36]. The aluminium atoms build up a three-dimensional network of distorted tetrahedra at Al–Al distances from 279 to 291 pm, close to the Al–Al distance of 286 pm in *fcc* aluminium [37]. In contrast, the magnesium atoms are well separated from each other at 376 pm, much longer than the average Mg–Mg distance of 320 pm in *hcp* magnesium [37].

The MgCuAl₂ type intermetallics have repeatedly been described as transition metal filled versions of the Zintl phases with CaIn₂ structure [27]. Such a substructure is not known for the magnesium-aluminium system. Binary MgAl₂ [38] adopts the tetragonal HfGa₂ type structure, where the aluminium atoms form a square-planar network and zig-zag chains [39]. For a detailed discussion of the crystal chemistry and chemical bonding in MgCuAl₂ type intermetallics we refer to a recent review article [27].

Acknowledgements

We thank H.-J. Göcke for the work at the scanning electron microscope. This work was financially supported by the Deutsche Forschungsgemeinschaft.

- [1] J. R. Davis, Aluminium and Aluminium Alloys, ASM Speciality Handbook, ASM International, Materials Park, OH (1993).
- [2] H. Perlitz, A. Westgren, Ark. Kemi, Mineral. Geol. **16**, 1 (1943). [3]
- [3] R. G. Buchheit, L. P. Montes, M. A. Martinez, J. Michael, P. F. Hlava, J. Electrochem. Soc. **146**, 4424 (1999).
- [4] R. R. Leard, R. G. Buchheit, Electrochem. Soc. Proceedings **24**, 310 (2002).
- [5] M. Kendig, S. Jeanjaquet, R. Buchheit, H. Guan, R. Leard, Electrochem. Soc. Proceedings **23**, 1 (2000).
- [6] R. G. Buchheit, Mater. Sci. Forum, Vols. **331–337**, 1641 (2000).
- [7] There are 263 entries for the formula MgCuAl₂ in the SciFinder Scholar version 2005: <http://www.cas.org/SCIFINDER/SCHOLAR/>.
- [8] A. Prince, G. Effenberg, Aluminium–Copper–Magnesium, in G. Petzow, G. Effenberg (eds): Ternary Alloys, ASM International, Vol. 4, p. 547–566, VCH, Weinheim (1991).
- [9] V. Radmilovic, R. Kilaas, U. Dahmen, G. J. Shiflet, Acta Mater. **47**, 3987 (1999).
- [10] F. Laves, H. Witte, Metallwirtschaft **15**, 15 (1936).
- [11] H. Nishimura, Mem. Colloid Eng. Kyoto, Imp. Univ. **10**, 18 (1937).
- [12] L. F. Mondolfo, Aluminium Alloys–Structure and Properties, p. 497, Butterworths, London (1976).
- [13] F. Cuisiat, P. Duval, R. Graf, Scr. Metallurg. **18**, 1051 (1984).
- [14] J. Yan, L. Chunzhi, Y. Minggao, J. Mater. Sci. Lett. **9**, 421 (1990).
- [15] J. I. Pérez-Landazábal, M. L. Nó, G. Madariaga, J. San Juan, J. Mater. Res. **12**, 577 (1997).

- [16] R. Kilaas, V. Radmilovic, *Ultramicroscopy* **88**, 63 (2001).
- [17] M. Jaime Vasquez, G.P. Halada, C.R. Clayton, P.I. Gouma, *Thin Solid Films* **458**, 37 (2004).
- [18] M. A. Al-Khafaji, W.M. Rainforth, L.M. Rylands, H. Jones, *Inst. Phys. Conf. Ser.* **161**, 279 (1999).
- [19] A. K. Gupta, P. Gaunt, M. C. Chaturvedi, *Philos. Mag. A* **55**, 375 (1987).
- [20] R. Kilaas, V. Radmilovic, U. Dahmen, *Mater. Res. Soc. Symp. Proc. Vol.* **589**, 273 (2001).
- [21] G. Phragmén, *J. Inst. Metals* **77**, 489 (1959); cited in *Metallurgical Abstracts* **17**, 910 (1950).
- [22] A. Biris, M. Bogdan, E. Indrea, D. Lupu, *Lucr. Simp. Natl. Fiz. Solidului*, pp. 310–312 (1978); conference report written in romanian.
- [23] N. S. Brommelle, H. W. L. Phillips, *J. Inst. Met.* **75**, 529 (1949).
- [24] I. Obinata, K. Mutuzaki, *Nippon Kinzoku Gakkai-Schi* **5**, 121 (1941).
- [25] M. S. Mirgalovskaya, E. S. Makarov, *Izv. Sek. Fiz.-Khim. Anal.* **18**, 117 (1949).
- [26] V. G. Kuznetsov, L. N. Guseva, *Izv. Akad. Nauk SSSR, Ser. Khim.* **6**, 905 (1940).
- [27] R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, *Z. Kristallogr.*, submitted.
- [28] R. Pöttgen, Th. Gulden, A. Simon, *GIT-Laborfachzeitschrift* **43**, 133 (1999).
- [29] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **624**, 1727 (1998).
- [30] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
- [31] G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
- [32] J. Emsley, *The Elements*, Oxford University Press, Oxford (1999).
- [33] A. Meetsma, J. L. de Boer, S. van Smaalen, *J. Solid State Chem.* **83**, 370 (1989).
- [34] S. Samson, *Acta Chem. Scand.* **3**, 809 (1949).
- [35] S. Samson, K. Gordon, *Acta Crystallogr.* **B24**, 1004 (1968).
- [36] S. Samson, *Acta Crystallogr.* **19**, 401 (1965).
- [37] J. Donohue, *The Structures of the Elements*, Wiley, New York (1974).
- [38] Ch. Suryanarayana, S. K. Tiwari, T. R. Anantharaman, *Z. Metallkd.* **69**, 155 (1978).
- [39] M. F. Zumdick, G. A. Landrum, R. Dronskowski, R.-D. Hoffmann, R. Pöttgen, *J. Solid State Chem.* **150**, 19 (2000).