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X-RAY DIFFRACTION STUDY OF MASSIVE AND MARTENSITIC PHASES IN EUTECTOID Cu-Ga ALLOY RAPIDLY QUENCHED FROM THE MELT

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The structure of liquid-quenched Cu-Ga eutectoid alloy was examined by means of X-ray diffraction and compared with published results obtained on samples, quenched from the high-temperature β-phase region. Phases detected in liquid-quenched samples were found to be substantially the same as those occurring during quenching of solid alloys from the β-phase region. However, the massive transformation was not suppressed during the liquid quenching procedure as it occurs in the case of rapid quenching of samples from the solid β-phase region. Diffraction patterns of martensitic phases were indexed and unit cell lattice parameters proposed. The relationship between the martensitic phases and the equilibrium ζ-phase is discussed.

1. *Introduction*

The Cu-Ga system in the region of the eutectoid belongs to the systems which have a bcc β-phase stable over a wide range of concentrations at high temperatures. Spencer and Mack[1)] were the first to report that the Cu-Ga β-phase could not be retained on quenching to room temperature, but that a closepacked hexagonal ζ-phase supersaturated with Ga up to the eutectoid composition appears (now referred to as the massive ζ_m structure). Spencer and Mack also pointed out that in »drastically« quenched samples a martensite reaction occurs, but no detailed study was made.

The paper of Massalski[2] may be considered as a pioneering work on the subject and since then many papers (important ones are Refs. 3—12), have been devoted to the mode and morphology of massive or martensitic transformations in the Cu-Ga system in the region of the eutectoid. The results from these investigations can be summarized as follows:

The Cu-rich portion of the Cu-Ga equilibrium diagram is given in Fig. 1.[10,11], where ζ is the equilibrium hcp phase with lattice parameters $a = 0.2599$ and $c = 0.4244$ nm for 21.5at.%Ga[3]. Fig. 1. shows the equilibrium phases and approximate temperatures at which the massive and martensitic structural changes take place. The composition studied in this work is indicated by means of an arrow on the abscissa.

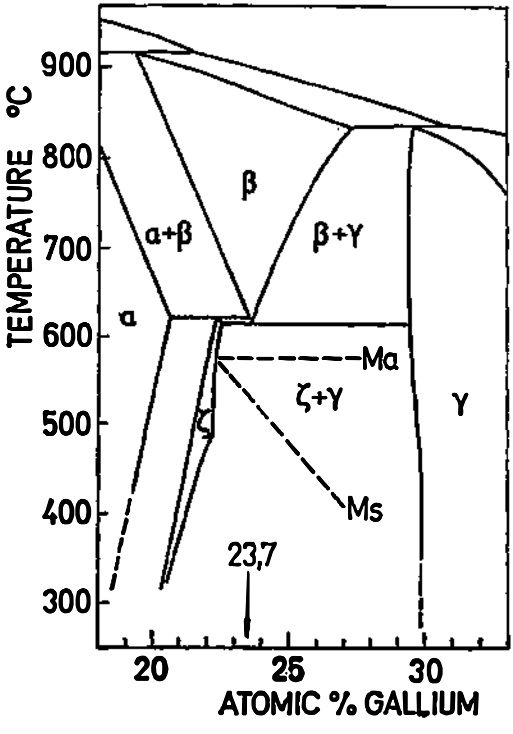

Figure 1. Part of the Cu-Ga phase diagram[10,11] showing the temperatures and compositions at which the different structural changes take place. M_a and M_s are approximate massive and martensite transformation temperatures, respectively. The composition of the currently studied alloy is shown by an arrow.

When quenching from the β-region, the mode and morphology of the transformation of the β-phase have been shown to be composition and quenching rate dependent[10]. In samples containing 23.7at.%Ga (the eutectoid composition), quenched at cooling rate of up to 5000 °C/s, the massive phase ζ_m has been detected, while at a rate of 6000 °C/s a martensite phase appears in addition to the ζ_m-massive phase. At cooling rate of 20000 °C/s and up to the maximum cooling rate used in the respective experiment (25000 °C/s), the massive transformations becomes suppressed and the samples become fully transformed into martensite.

That two types of martensite may appear in the Cu-Ga eutectoid alloys was first reported by Saburi and Wayman4) (they denoted them β_1' and β') and Delaey and Warlimont5) who denoted them β_1'' and γ_1'.

Saburi and Wayman4) succeeded in indexing the β_1' diffraction patterns according to an orthorhombic unit cell whose *c* dimension contain eighteen stacking layers, as proposed by Nishiyama and Kajiwara13). The β' martensite was also found to have an orthorhombic unit cell but with nine stacking layers along the *c*-axis.

Delaey and Warlimont5) concluded that both, the β_1'' and the γ_1' martensite, have orthorhombic cells (β'': 22 stacking layers in c direction; γ_1': no details). In later publications Delaey and Warlimont6,7) confirmed the simultaneous appearance of two martensite phases in Cu-Ga eutectoid, but they published no new crystallographic data.

Since the cooling rate is obviously one of the factors most influencing the formation of microstructure, we decided to apply the method of rapid quenching from the melt (cooling rates of up to 10^6 °C/s and even more can be achieved14)) to see if it is possible to quench-in the β-phase at room temperature, and if not what would be the influence of rapid quenching from the melt on the appearance of massive and martensitic phases in the Cu-Ga system.

2. *Experimental procedure*

Two master alloys were splat quenched using the two piston15) and the piston-and-anvil quenching techniques16) (the composition of the master alloy was rechecked on as quenched samples by means of chemical methods and found to be 23.7at.%Ga).

The as-quenched samples were examined by X-ray diffraction using Siemens Bohlin and Guinier de Wolf focusing cameras, a 114.6 mm diam Debye-Scherrer camera, and CuK$_\alpha$ and CoK$_\alpha$ radiations. The *d*-values of pure copper were used as internal standard.

3. *Results*

The results show that three metastable phases appeared in quenched samples: the massive ζ_m-phase and two martensitic phases (we denoted them MI and MII). We examined 29 as-quenched samples, the thickness of which varied from 20 to 130 μm. There was no unique distribution of metastable phases in the as quenched samples. There were samples which contained MI, MII or ζ_m-phases, then samples which contained different proportions of all three phases, and samples containing only two of them. The most frequent phase distribution was an approximately equal amount of the ζ_m and MI phases together with small quantities of the MII phase. Samples containing more of the MII phase appeared very rarely. We could not establish any correlation between the distribution of phases in the samples and the thickness of the samples (thinner samples should be better quenched[14]).

On X-ray diffraction patterns, it was possible to distinguish the lines belonging to the ζ_m, MI and MII phase. We succeeded in indexing the obtained MI and MII X-ray diffraction patterns on the basis of two hexagonal unit cells whose c dimensions contained nine stacking layers (MII phase), and eighteen stacking layers (MI phase) along the *c*-axis. The measured and calculated *d*-values of the MI and MII phases are given in Table 1., with approximative relative intensities estimated from diffraction patterns.

TABLE 1.

MI phase				MII phase			
hkl	d_{cal} (nm)	d_{obs} (nm)	*I*	*hkl*	d_{cal} (nm)	d_{obs} (nm)	*I*
100	0.2253	0.225_2	m	100	0.2243	0.224_0	mb
102	0.2237	0.223_7	m	009	0.2122	0.212_0	s
0018	0.2122	0.212_0	s	104	0.2030	0.203_0	ms
0019	0.2010	0.200_7	ms	105	0.1934	0.195_5	m
109	0.1990	0.199_0	m	108	0.1634	0.163_0	mw
1018	0.1545	0.154_2	mb	0013	0.1470	0.147_0	mw
0031	0.1317	0.131_0	mw	1012	0.1298	0.129_4	mb
1024	0.1298	0.129_4	m	110	0.1295		
0032	0.1194	0.119_5	mw	1013	0.1228	0.122_0	m
1029	0.1137	0.113_0	w	115	0.1226		
205	0.1114	0.111_5	w	1014	0.1165	0.117_1	m
1030	0.1108	0.110_3	w	0017	0.1123	0.112_6	vw
207	0.1103			200	0.1122		
0035	0.1091	0.109_0	w	1015	0.1107	0.110_8	mb
1119	0.1092			119	0.1105		
207	0.1096			204	0.1092	0.109_0	vw
1031	0.1081	0.108_0	vw	205	0.1076	0.108_4	vw
2010	0.1884			0018	0.1061	0.106_0	w
0036	0.1061	0.106_0	w	0019	0.1005	0.100_9	vvw
2012	0.1062			1017	0.1005		
0038	0.1005	0.100_0	vw	1112	0.1005		
1034	0.1007			1113	0.0971	0.097_9	vvw
1124	0.1007						
2017	0.1007						

vs very strong s strong ms medium strong m medium b broad
mw medium weak w weak vw very weak vvw very very weak

Observed and calculated *d*-spacings for MI and MII phases in rapidly quenched Cu-23.7at.%Ga alloy.

Hexagonal unit cells: $a\,(\mathrm{MI}) = 0.260_1$ nm $a\,(\mathrm{MII}) = 0.259_0$ nm
$c\,(\mathrm{MI}) = 3.819_6$ nm $c\,(\mathrm{MII}) = 1.909_8$ nm

After annealing the quenched samples for 30 min at 630 °C/s and subsequent furnace cooling, in all examined samples equilibrium ζ- and γ-phases appeared as the only constituents.

The lattice parameters of the quenched-in hcp massive ζ_m-phase and the equilibrium ζ-phase which appeared after the annealing of the samples containing metastable ζ_m, MI or MII phases, were calculated using the diffraction patterns obtained in a 114.6 diam Debye-Scherrer camera. We obtained $a(\zeta_m) = 0.2604_2$ nm, $c(\zeta_m) = 0.4240_8$ nm for the quenched samples and $a(\zeta) = 0.2592_7$ nm, $c(\zeta) = 0.4241_8$ nm for annealed samples. The results are in agreement with published values[2,3].

The unit cells of the MII and MI phases are related to the ζ-phase as: $a(\mathrm{MII}) = a(\zeta)$, $c(\mathrm{MII}) = 9 \cdot d_{002}(\zeta)$ and $a(\mathrm{MI}) = a(\zeta)$, $c(\mathrm{MI}) = 18 \cdot d_{002}(\zeta)$. On the basis of these relationships we concluded that the MI and MII phases detected in our quenched samples may be consistent with the β_1'- and β'-martensite phases described by Saburi and Wayman[4].

4. *Discussion*

Our results show that using the liquid quenching technique we did not succeed in quenching-in the high temperature β-phase as well.

The quenching experiments from the high temperature β-phase region showed that the appearance of massive and martensitic phases is highly dependent on the quenching rate[10], and that the massive transformation can be suppressed by rapid quenching (quenching at cooling rates between 20000 and 25000 °C/s)[10].

Our experiments in which massive and martensitic phases appeared as single phase samples or several phase samples in quenching from the liquid state at a rate of about 10^6 °C/s indicate that using liquid-quenching methods the phase transformation process should be quite different in comparison with quenching from a solid β-phase.

The very important appearance of the massive ζ_m-phase indicates that the first phase which nucleates from melt in a cooling process is the ζ_m-phase which is then quenched-in to room temperature. However, the appearance of martensite phases indicates that the β-phase could also nucleate and then transform into martensite phases during the cooling of the solid. The fact that both the ζ_m- and the β-phase may have been generated simultaneously during the solidification process indicates that the respective free energies of the ζ_m- and β-phases must be nearly the same (the same statement about free energies may also apply to the MI and MII martensite phases). We suppose that the diversity of phase contents in the samples obtained in the same quenching experiment may be due to the variations in the quenching rate, which may be independent of sample thickness (the piston-and-anvil and the two-piston techniques are more or less »hit and miss« methods[14,17]).

5. *Conclusions*

A Cu-Ga alloy with an eutectic composition was submitted to rapid quenching from the melt and it was found that the equilibrium high-temperature β-phase cannot be quenched-in to room temperature by applying this method, either.

The massive phase was not suppressed by rapid quenching from the melt as it is by rapid quenching from the high-temperature β-phase region.

Three phases, the massive ζ_m-phase and two martensitic phases (we denoted them MI and MII), appeared in as-quenched samples. A possible explanation of this feature is given.

The diffraction patterns of the MI and MII phases were indexed and unit cell parameters determined. Both had a hexagonal unit cell with nine (MII) and eighteen (MI) stacking layers along the c-axis. A simple relationship between unit cells of massive ζ_m and MI and MII phases was established.

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ISPITIVANJE POMOĆU RENDGENSKE DIFRAKCIJE MASIVNIH I MARTENZITNIH STRUKTURA U UZORCIMA Cu-Ga SLITINE EUTEKTIČKE KONCENTRACIJE VRLO BRZO KALJENE IZ TEKUĆEG STANJA

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Pomoću rendgenske difrakcije ispitivali smo strukturu Cu-Ga slitine eutektičke koncentracije vrlo brzo kaljene iz tekućeg stanja i usporedili sa objavljenim rezultatima dobivenim na uzorcima kaljenih iz područja ravnotežne visokotemperaturne β-faze. Nađeno je da se faze u uzorcima koji su kaljeni iz tekućeg stanja, ne razlikuju bitno u usporedbi sa uzorcima kaljenim iz čvrstog stanja iz područja visoko temperaturne β-faze. Međutim u slučaju kaljenja iz tekućeg stanja dolazi do pojave masivne transformacije za razliku od kaljenja iz čvrste faze gdje je masivna transformacija spriječena. Rendgenogrami martenzitnih faza su indeksirani i izračunate pripadne konstante jediničnih ćelija. Uočena je kristalografska povezanost između martenzitnih faza i ravnotežne ζ-faze.