



Cu_xY compounds as thin films: crystallographic and compositional analyses of copper rich phases

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Abstract

This study which relates the interdiffusions of Y films deposited onto Cu substrate, is devoted to the Cu-rich phases formed at temperatures higher than 553 K. The same experimental procedures (concentration profiles, X-ray and electron diffraction patterns) as those mentioned in a preceding investigation, were used to characterize the compounds formed throughout the thin layers. In samples deposited by flash evaporation the Cu₉Y₂, β-Cu₅Y and Cu₇Y compounds were detected in the course of successive annealings up to 1053 K. Moreover, electron diffraction patterns reveal that some particles scattered all over the sample are characterized by superlattice structures. From this study the formation of Cu₄Y for heavy rare earth elements has been excluded. In sputtered films the formation of yttrium hydrides or oxides (YH₂, Y₂O₃) strongly perturbs the Cu diffusion process. © 1998 Elsevier Science S.A.

Keywords: Y–Cu alloys; Y thin films; Interdiffusion; Concentration profiles; Compound formation

1. Introduction

In a previous paper [1] it was shown that the annealing of uncontaminated Cu–Y films in the temperature range 373–553 K led to the formation of three well characterized compounds: CuY, Cu₃Y₂ and Cu₂Y. In particular it was concluded that Cu₃Y₂ was a transitory phase, stable over a small temperature range, between the other two phases.

The purpose of this article is to investigate the formation of copper/yttrium compounds at temperatures higher than 553 K. Many Cu rich compounds, containing more than 66 at.% of Cu, are reported in the literature. Their nature is briefly discussed below.

The Cu₄Y stoichiometry reported elsewhere refers to a hexagonal structure with the CaCu₅ type. Chakrabarti and Laughlin [2] accept the existence of this phase at equilibrium. Domagala et al. [3] reported for the Cu₄Y compound a hexagonal lattice (H₁, without space group) with the following parameters:

$$a_{H_1} = 0.496 \text{ nm}, \quad \text{and} \quad c_{H_1} = 0.820 \text{ nm}.$$

However, Buschow et al. [4] claimed that such a hexagonal lattice (H₁) cannot be observed for a 4/1 stoichiometry, and Subramanian and Laughlin [5] showed clearly that for heavy rare earths (R) from Gd to Tm (included Y), the Cu₄R compound is not formed. This is probably why, in this context, Gschneidner [6] proposed a hexagonal structure with a slightly different stoichiometry such as Cu_{4.8}Y_{1.2}, which is not convincing in regard to Subramanian and Laughlin's conclusion [5]. In fact, it is likely that Cu₄Y does not form because the hexagonal structure of the CaCu₅ type reported here is that of a Cu₅Y compound (see below).

The Cu₉R₂ phase is only mentioned for Dy and Gd by Franceschi and coworkers [7,8]. They report that this compound, very stable thermodynamically, is characterized by a tetragonal structure (T₁) with the following parameters (for Cu₉Dy₂):

$$a_{T_1} = 0.4999 \text{ nm}, \quad \text{and} \quad c_{T_1} = 1.394 \text{ nm}.$$

Many authors claimed that β-Cu₅Y (high temperature

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form) is easily formed by rapid solidification [9–12]. It was observed for various R elements: Gd [10,11], Tb [4,11], Dy [4,7] and Ho [4,11,12]. For example Franceschi [7] and Carnasciali et al. [8] showed that β -R Cu₅ (R=Dy and Gd) were stable at high temperature, and indicated that they crystallized according to the CaCu₅ hexagonal structure (H₂), as reported by Dwight [12] (for β -Cu₅Dy) Buschow and van der Goot [11] (for β -Cu₅Y) with the following parameters:

$$a_{H_2} = 0.5005 \text{ nm}, \quad \text{and} \quad c_{H_2} = 0.4100 \text{ nm}.$$

Buschow and van der Goot [11] reported a Cu₇R phase (R=Gd, Tb, Dy and Y) characterized by a hexagonal lattice (H₃) whose parameters for Cu₇Y are:

$$a_{H_3} = 0.4940 \text{ nm}, \quad \text{and} \quad c_{H_3} = 0.4160 \text{ nm}.$$

These authors indicated that such a compound, unstable below 973 K, is formed with a structure closely related to the one of the CaCu₅ type. In the case of Cu₇Tb there are 22% of the Y sites substituted at random by pairs of Cu atoms resulting in the actual stoichiometry Cu_{5.44}Tb_{0.78}. Franceschi [7] observed that Cu₇Dy formed peritectically from the liquid and the solid phase β -Cu₅Y at about 1133 K and decomposed eutectically near 1058 K. He concluded that this phase is only formed over a small temperature range (~80–90°C) and cannot be stabilized at room temperature.

Another phase Cu₆Y cannot be formed beyond R=Tb [5] while Cu₉Y was only observed by electron diffraction as a metastable orthorhombic compound [12]. Lastly, the α -Cu₅Y (low temperature face centered cubic form) was observed by numerous researchers [5].

In our case, it was possible from a great number of samples (more than 80) to determine the formation of well-known phases as those mentioned above and to characterize by transmission electron microscopy (TEM) various other ones; so-called “exotic phases”. These being only present in some crystallites embedded in the matrix, it was difficult to analyze them. However, it was sometimes possible to establish correlations between the unit-cell parameters of these “exotic phases” and those of the well-known ones.

2. Experimental

The formation of Cu rich compounds has been studied in the temperature range 748–1053 K in films whose thickness was varying from 120 to 180 nm. The annealing at high temperature of a deposit formed at room temperature always leads to the contamination of Y, even under cryogenic vacuum conditions (~10⁻⁷ Pa). Then, after deposition, a low temperature interdiffusion (440 K, 2 h) is allowed to take place in order to form the CuY phase.

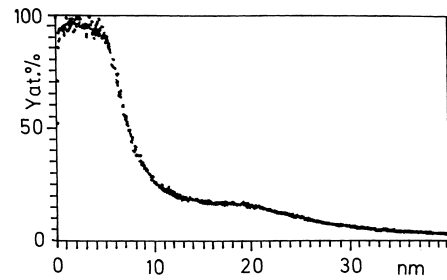


Fig. 1. Y concentration profile of a Cu–Y film annealed 1 min at 883 K, showing the formation of the β -Cu₅Y phase (evaporated Y film, 15 nm thick).

Subsequently a high-temperature thermal treatment is carried out. In most cases such a procedure protects Y metal against contamination. However, X-ray diffraction patterns (XDP) and electron diffraction patterns (EDP) sometimes show the formation of Y compounds such as YH₂ and Y₂O₃ after heating beyond 553 K. As previously, Y films were deposited either by flash evaporation or sputtering [1].

Concentration profiles were recorded with the STIMS method mentioned in Ref. [1]. That allows mainly to fix the temperature range in which a phase is likely to be formed. For example, a phase with 16–17 at.% Y is formed at the interface with Cu after annealing at 883 K during 1 min (Fig. 1). XDP allows it to confirm that this phase corresponds to β -Cu₅Y. But, due to the fast diffusion of Cu along Y grain boundaries, there is not always a clear spatial separation between phases of slightly different concentrations as in the case of diffusion throughout a single crystal [14]. This is why at the front of the phase formed in Fig. 1, there is a continuous gradient of Y concentrations instead of a series of plateaux corresponding to well-separated phases [15]. However, bulk diffusion is becoming competitive at higher temperatures, as the spatial separation between phases becomes sharper. So, for a sample annealed for 2 h at 923 K, two distinct phases with Y concentrations of 16.7 and 12.5 at.% are visible in Fig. 2. They correspond to the β -Cu₅Y and Cu₇Y compounds, respectively.

3. Results

3.1. Y film depositions at high evaporation rates

3.1.1. The Cu₉Y₂ compounds

This compound is easily formed in films annealed for a few hours at 748 K. The XDP (Fig. 3) clearly shows the presence of a basal tetragonal (T₂) unit-cell from the indexation of 14 diffraction lines. The lattice parameters are calculated according to the sin² θ method:

$$a_{T_2} = 0.502 \pm 0.002 \text{ nm}, \quad \text{and} \quad c_{T_2} = 1.398 \pm 0.004 \text{ nm}.$$

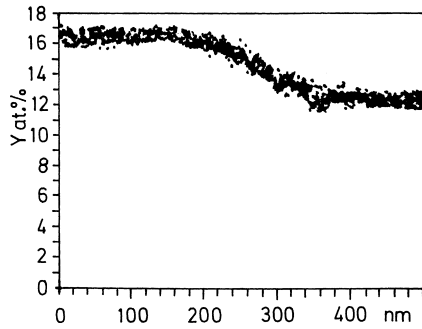


Fig. 2. Y concentration profile of a Cu–Y film annealed 2 h at 923 K showing the juxtaposition of the β -Cu₅Y phase (Y concentration 16.7 at.%) with the Cu₇Y phase (Y concentration 12.5 at.%) (evaporated Y film, 180 nm thick).

These values are in good agreement with those reported by Franceschi [7] for Cu₉Dy₂ as mentioned above (unit-cell T₁).

From the indexation of the crystallographic planes it is possible to determine the following selection rules:

$$hk0: h + k = 2n; 0k\ell: \ell = 2n; h00: k = 2n.$$

Such rules should be consistent with the space group $n\bar{3}10$ ($P4/ncc$). One must add that the grains did not present any preferential orientation and that this sample was very slightly contaminated by Y₂O₃ and YH₂. Moreover a small amount of Y metal can also be detected.

EDP taken in different areas of different samples revealed the presence of various kinds of rings and spots. Some of the ring patterns were so complex that it was not possible to identify them correctly. However some spot patterns are representative of grains that are scattered within the matrix of the film (Fig. 4 a,b). They were indexed according to a (3×3×1) superlattice (SL) of the Cu₉Y₂ phase. They could be characterized by a tetragonal unit-cell (TSL) with the following parameters:

$$a_{\text{TSL}} = 1.520 \pm 0.005 \text{ nm}, \quad \text{and} \quad c_{\text{TSL}} = 1.450 \pm 0.005 \text{ nm}.$$

They are dimensionally related to those of the (T₂) structure as:

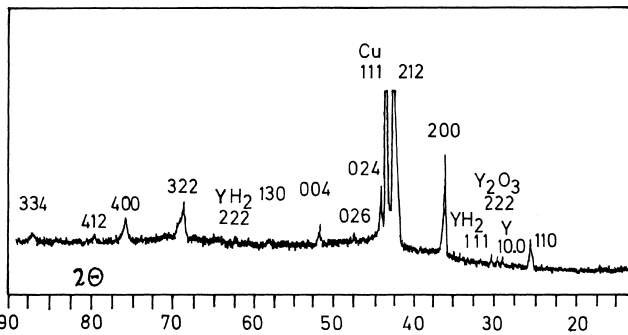
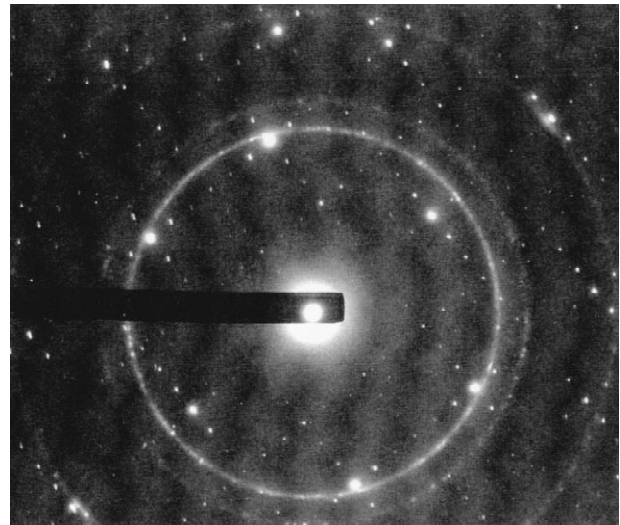
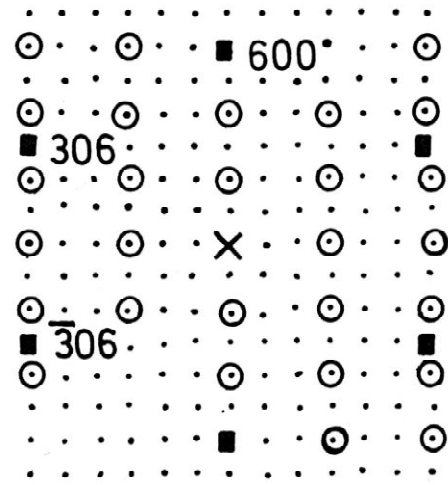


Fig. 3. XDP of the Cu₉Y₂ phase obtained from a Cu–Y film annealed 6 h at 748 K (evaporated Y film, 120 nm thick). Very small amounts of Y, YH₂ and Y₂O₃ are detected in the pattern.



(a)



(b)

Fig. 4. EDP of the superlattice (3×3×1) of the Cu₉Y₂ phase (T_{SL}, T₂ rotation). (a) Pattern photography. (b) Partial indexation (zone axis [010]). ● Cu₉Y₂ spots; ○ Cu₉Y₂ spots (3×3×1); ■ Cu₉Y₂ intense spots of the superlattice.

$$a_{\text{TSL}} = 3.03 a_{\text{T}_2} \quad \text{and} \quad c_{\text{TSL}} = 1.04 c_{\text{T}_2}.$$

3.1.2. The β -Cu₅Y phase

In the case of films slightly contaminated during preparation, the β -Cu₅Y phase appears at 873 K after 1–2 h of annealing. In this way the sample is ill-crystallized but, increasing the temperature up to 943 K, makes the grains to grow (without preferential orientation). At last, this phase becomes preponderant.

If the preparation is performed under a cryogenic vacuum, the film is very clean, i.e. without any amount of YH₂ or Y₂O₃, and the β -Cu₅Y phase is formed at 833 K after 5 h annealing. In this case the grains exhibit a preferential orientation with their compact planes (00 ℓ) nearly parallel to the substrate. This allows one to calculate

the hexagonal unit-cell (H_3) parameters which are closed to those given by Buschow and van der Goot [11]:

$$a_{H_3} = 0.498 \pm 0.001 \text{ nm}, \quad \text{and} \quad c_{H_3} = 0.410 \pm 0.001 \text{ nm}.$$

They are dimensionally related to the basal structure (T_2) of Cu_9Y_2 as:

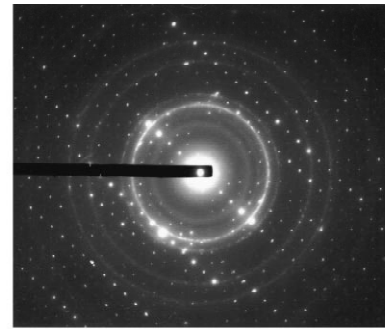
$$a_{H_3} = a_{T_2} \quad \text{and} \quad 2\sqrt{3}c_{H_3} \cong c_{T_2}.$$

Moreover, the space group $P6/mmm$ [5], not characterized by formal selection rules, seems to be very appropriate.

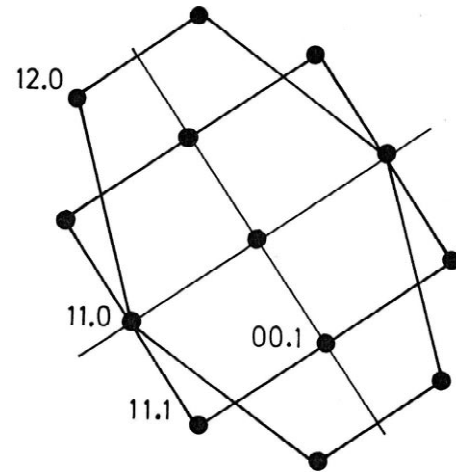
On the other hand, some films do not present a preferential orientation even after annealing at 903 K (Fig. 5).

It could be concluded that this compound is certainly $\beta\text{-Cu}_5\text{Y}$, not Cu_4Y . The latter must be firmly rejected because in a thin layer it is not conceivable that, having formed the Cu_9Y_2 compound at 748 K, a Cu demixing occurs to create a less Cu-rich phase at a higher temperature. In fact, as the temperature is rising, the Cu diffusion flux originating from the substrate is enhanced, which prevents such a demixing process occurring. It is most unlikely that at 943 K better crystallinity is obtained and that at higher temperatures (1053 K) the amorphous state develops. Two preferential orientations as $(\bar{1}10)$ and (00.2) are respectively observed. For such temperatures it is possible that a partial melting occurs due to the eutectic (see Fig. 11 of Ref. [1]).

On the other hand, TEM observations have allowed the indexation of specific spot pattern configurations of crystals scattered over all the $\beta\text{-Cu}_5\text{Y}$ matrix. Taking the Cu rings as a reference, the first system (Fig. 6a and b) can be



(a)



(b)

Fig. 6. EDP of the “ $\gamma\text{-Cu}_5\text{Y}$ ” superlattice ($4 \times 4 \times 3$) (H_4 notation). (a) Pattern photography. (b) Partial indexation (zones axes $[1\bar{1}.0]$ and $[00.1]$).

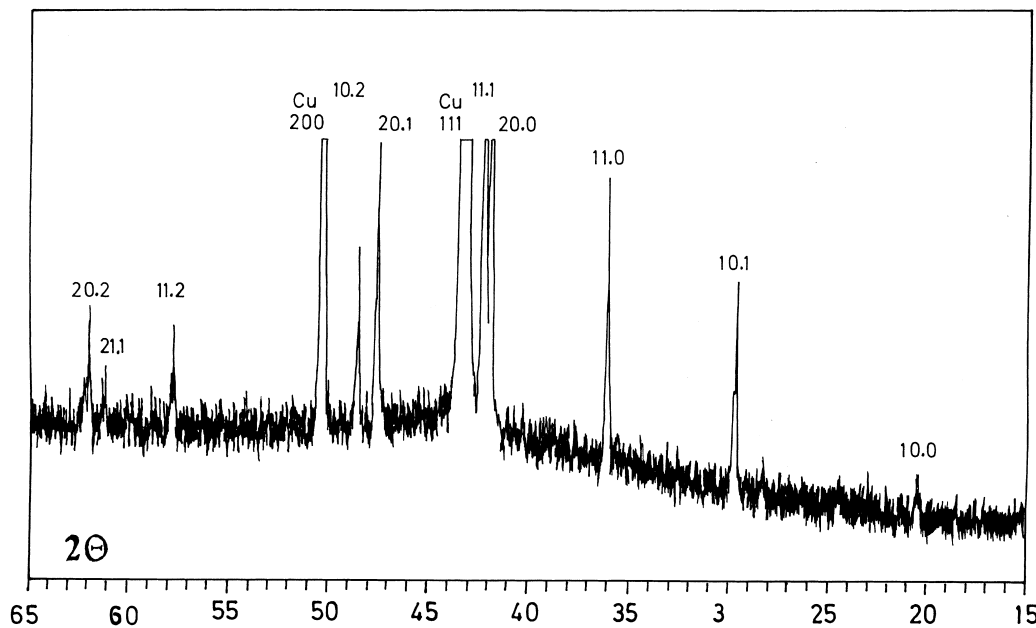


Fig. 5. XDP of the $\beta\text{-Cu}_5\text{Y}$ compound obtained in a Cu–Y film annealed 4 h at 903 K (evaporated Y film, 150 nm thick).

indexed according to a hexagonal system (H_4) with the following parameters:

$$a_{H_4} = 2.003 \pm 0.005 \text{ nm}, \quad \text{and} \quad c_{H_4} = 1.240 \pm 0.004 \text{ nm}.$$

which are dimensionally related to the parameters of the β - Cu_5Y compound:

$$a_{H_4} = 4a_{H_3} \quad \text{and} \quad c_{H_4} = 3c_{H_3}.$$

This can be envisaged as a $(4 \times 4 \times 3)$ superlattice composed of a unit cell with 48Y and 240Cu ($\text{Cu}_{240}\text{Y}_{48}$), i.e. the 48-fold of the β - Cu_5Y cell. This phase is denoted as “ γ - Cu_5Y ”.

Another hexagonal $(4 \times 4 \times 3)$ SL (H_5) (Fig. 7) with unit-cell of parameters:

$$a_{H_5} = 1.960 \pm 0.005 \text{ nm}, \quad \text{and} \quad c_{H_5} = 1.270 \pm 0.004 \text{ nm},$$

was also observed. Compared to (H_4) it represents a small volume contraction ($\sim 2\%$) which induces little perturbation for the atomic arrangement.

Other EDP show the presence of unknown phases. For instance, as reported in Fig. 8a and b, large crystals give rise to two different spot networks. They were tentatively indexed according to another hexagonal unit-cell (H_6) with parameters:

$$a_{H_6} = 1.225 \pm 0.004 \text{ nm}, \quad \text{and} \quad c_{H_6} = 1.005 \pm 0.004,$$

and an f.c.c. lattice with:

$$a_F = 0.433 \pm 0.002 \text{ nm}.$$

It should be noticed that the a_F parameter is almost equal to the a_o one of the orthorhombic Cu_2Y phase. (One must exclude the formation of Cu_2O which crystallizes according to a primitive cubic cell). In the same way the c_{H_6}

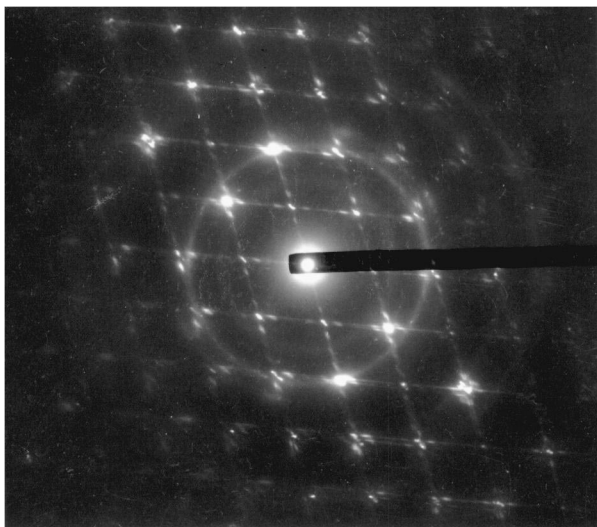


Fig. 7. EDP of a slightly different superlattice $(4 \times 4 \times 3)$ of the β - Cu_5Y phase (H_5 notation).

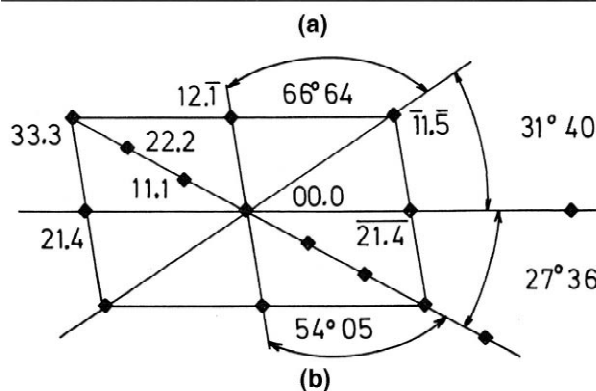


Fig. 8. Complex EDP exhibiting the coexistence of several phases. One of them (H_6 notation) corresponds to the intense spots. (a) Pattern photography. (b) Partial indexing (zones axis $[\bar{3}2.1]$).

parameter is also dimensionally related to the b_o one of Cu_2Y [1] by $c_{H_6} \sim 1.5 b_o$.

3.1.3. The Cu_7Y phase

This compound is obtained after 4 h annealing at 903 K. At a higher temperature (953 K) the film is well crystallized, and characterized by large grains (50–100 μm) without any preferential orientation (Fig. 9). No other phase is present in the sample. From the exact positioning of 13 diffraction lines, it was possible to determine that the Cu_7Y phase crystallizes according to a hexagonal lattice (H_7) with the following parameters:

$$a_{H_7} = 0.499 \pm 0.002 \text{ nm} \quad \text{and} \quad c_{H_7} = 0.420 \pm 0.002 \text{ nm}.$$

These parameters are close to those reported by Buschow and van der Goot [11]. The crystallographic plane indexation leads to the following selection rules: $h k \ell: \ell = 2n$, and $00 \ell: \ell = 2n$, which is in concord with the space group $n^\circ 173 (P6_3)$.

It was mentioned [7,11] that the Cu_7Dy compound was only formed within a small temperature range (80–90°C)

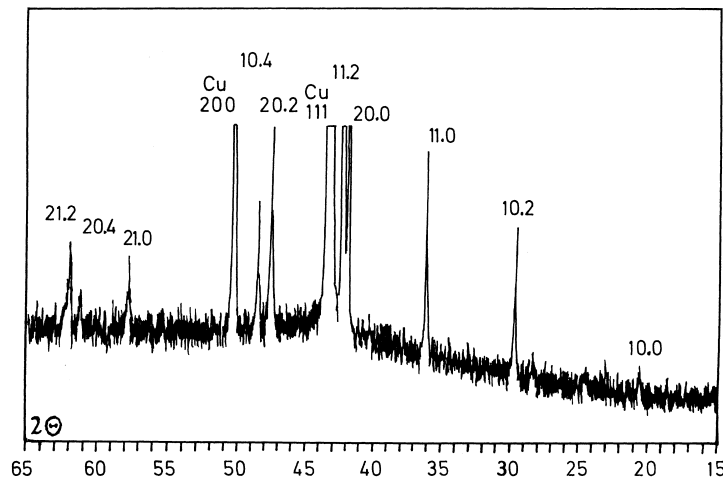


Fig. 9. XDP of the Cu_7Y compound obtained in a Cu–Y film annealed 2 h at 953 K (evaporated Y film, 150 nm thick).

and cannot be stabilized at room temperature. This appears not to be the case in thin films. Indeed, it is well known that it is often possible to “freeze-in” high-temperature and/or high-pressure phases in thin layers. Therefore the stabilization of the Cu_7Y compound at room temperature is

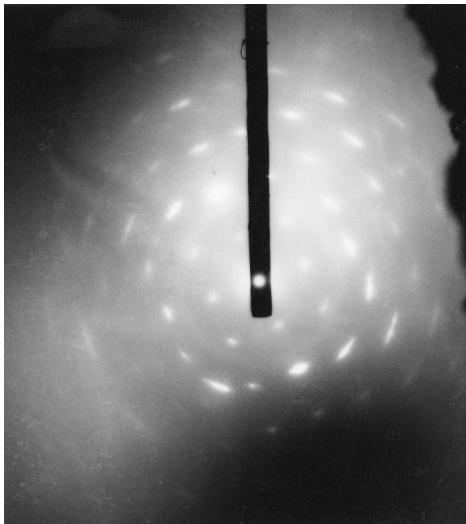


Fig. 10. EDP of an unknown cubic centered phase with (C_1 notation) $a_c = 0.700$ nm (zone axis $[1\bar{1}0]$).

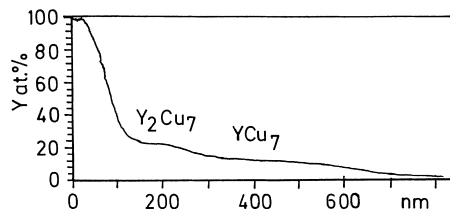


Fig. 11. Y concentration profile of a sample prepared by sputtering (Y deposition temperature 873 K, thickness 220 nm, annealing 0.5 h at 873 K) showing the formation of two juxtaposed phases attributed to Cu_7Y_2 (Y concentration 23 at.%) and Cu_7Y (Y concentration 12.5 at.%) compounds.

not surprising because of the thin film form a single phase. After heating at 1003 K, XDP show that the diffraction lines are enlarged and rounded at the top. This induces an ill-crystalline state (as in the case of $\beta\text{-Cu}_5\text{Y}$), moreover the grains become mainly oriented according to their compact plane (00.2). Finally, such a degradation has not allowed the observation of the metastable Cu_9Y compound, detected previously near 1300 K [13].

3.2. Y films deposited by sputtering

Due to the low Y deposition rate (3.3 nm min^{-1}) samples prepared by sputtering always contained oxides (Y_2O_3) and hydrides (YH_2) when annealed beyond 550 K, even under a cryogenic vacuum. Thus, up to 800 K, it was not possible to determine a well-defined sequence of compound formation as a function of the annealing temperature, nor to take advantage of XDP since the grain size was so small that diffraction patterns were badly defined [1]. The only result of importance was that after the formation of Cu_2Y , the Cu_9Y_2 compound, which is easily formed in evaporated layers, was never observed in sputtered samples.

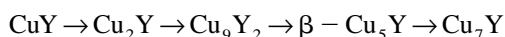
At about 800 K, the strong Cu diffusion led to a better crystallization with the formation of the $\beta\text{-Cu}_5\text{Y}$ phase. But, on the other hand, EDP showed that crystals of unexpected phases were scattered all over the sample. For instance, a body centered cubic (C_1) phase with $a_1 \cong 0.700 \pm 0.0003$ nm was identified (Fig. 10). Such a lattice parameter is equal to that of the $\alpha\text{-Cu}_5\text{Y}$ form. But, as the latter is face centered cubic, the two compounds cannot be compared. Other structure types were considered and the corresponding lattice parameters were tentatively calculated as f.c.c. type (C_{F2}) with $a_{F2} \cong 0.685 \pm 0.0003$ nm and tetragonal type (T_3) with $a_{T3} \cong 0.430 \pm 0.0002$ nm and $c_{T3} \cong 0.685 \pm 0.0003$ nm. The parameters are dimensionally related to those of the Cu_2Y compound as: $a'_F = c'_T = 2b_o$.

and $a'_T = a_o$ (a_o and b_o being the parameters of the orthorhombic cell [1]).

When raising the temperature above 800 K, more concentrated Cu phases appeared as can be seen in Fig. 11. But due to the strong contamination, there is a lack of reproducibility, so concentration profiles appear less convincing. After annealing at 1023 K, the films are totally oxidized as they have become transparent.

4. Discussion and conclusion

The eutectic melting point curves reported in Fig. 11 in Ref. [1] and the Cu–Dy compound phase diagram [5] justify the fact that the Cu_xY_z compound series (from CuY to Cu_9Y) was never correctly established on a macroscopic scale. However, as for Cu–Dy, the sequence:



is obtained in thin layers prepared by evaporation and Cu diffusion under cryogenic vacuum ($\sim 10^{-7}$ Pa). It is important to notice that the existence of the Cu_3Y , Cu_4Y and Cu_6Y compounds, which is a matter of controversy in macroscopic materials, did not form in thin layers. This is not surprising because Cu_3R , Cu_4R and Cu_6R belong to light rare earths (La to Sm). Moreover it is not conceivable that in the course of the copper diffusion across the thin

layer, the Cu_9Y compound demixes to form a less Cu rich phase.

On the other hand, the formation of various phases only observed by TEM is not surprising. Indeed, it is not unusual that, on a mesoscopic level, some grains have particular structural characteristics inside the matrix. These specificities are often observed in binary materials. They originate either from areas not in thermodynamic equilibrium or from diffusion in inhomogeneous materials. Another hypothesis is that a local high thermic gradient induced at the electron beam impact can produce phase transitions. This is sometimes the case for the formation of superlattices.

Compounds prepared by diffusion in sputtered Y films often consist of very small grains and sometimes they are nearly amorphous. XDP are less suited for determining their crystalline structure. Moreover, the presence of Y oxides and hydrides (Y_2O_3 and YH_2 and sometimes $\text{YN}_{1-x}\text{O}_x$) even under cryogenic vacuum depositions can strongly perturb the diffusion process and the thermodynamic kinetics. In this way, the formation of metastable compounds is expected. This is probably the reason for the unusual unit-cells observed from EDP.

As a conclusion, it is often difficult to interpret correctly the phase diagram pertaining to thin layers because it depends strongly on the sample preparation and thermal diffusion conditions. This is particularly true for R elements whose chemical activity is very sensitive to temperature, pressure, residual gases (hydrogen, oxygen, nitro-

Table 1
Crystallographic data of the Cu–Y alloys

Cu_xY phases	Lattice designation	a (nm)	b (nm)	c (nm)	Ratio between parameters	Volume (nm^3)
CuY	C_P	0.3480	0.3480	0.3480		0.0421
Cu_2Y	O_1	0.4305	.6800	0.7315		0.2141 ($\sim 5 V_{\text{CuY}}$)
Cu_9Y_2 (“ Cu_9Y_2 ”) isolated crystals	T_P (T_2) T_{SL} (T_2) ($3 \times 3 \times 1$)	0.5020 1.5200	0.5020 1.5200	1.3980 1.4500	$a \sim \sqrt{2}a_{\text{uY}} \sim 1.5b_{\text{Cu}_2\text{Y}}$ $a_{\text{SL}} \sim 3a_{\text{Cu}_9\text{Y}_2}$ $c_{\text{SL}} \sim a_{\text{Cu}_9\text{Y}_2}$	0.3523 3.3500 ($\sim 9.5 V_{\text{Cu}_9\text{Y}_2}$)
$\beta\text{-Cu}_5$	H (H_5)	0.4980	0.4980	0.4100	$a = a_{\text{Cu}_9\text{Y}_2}$ $2\sqrt{3} = c_{\text{Cu}_9\text{Y}_2}$	
(“ $\gamma\text{-Cu}_5$ ”) $_{\text{SL}}$ isolated crystals	H_{SL} (H_4) ($4 \times 4 \times 3$)	2.0030	2.0030	1.2400	$a = 4a_{\beta}$ $c = 3c_{\beta}$	12.9250 ($\sim 48 V_{\beta}$)
(“ Cu_5Y ”) $_{\text{SL}}$ isolated crystals	H_{SL} (H_5) ($4 \times 4 \times 3$)	1.9600	1.9600	1.270	$a = 4a_{\beta}$ $c = 3c_{\beta}$	12.6750
(“ Cu_5Y ”) $_{\text{SL}}$ isolated crystals	H (H_6)	1.2250	1.2250	1.0050	$c \sim 1.5b_{\text{Cu}_9\text{Y}}$ $\sim 2a_{\text{Cu}_9\text{Y}_2}$	3.3930 ($\sim 10 V_{\text{Cu}_9\text{Y}_2}$)
Cu_7Y	H (H_7)	0.4990	0.4990	0.4200	$a = a_{\beta} = a_{\text{Cu}_9\text{Y}}$.2718 ($\sim V_{\beta}$)
Unknown composition	C_1	0.7000	0.7000	0.7000	$a = a_{\alpha\text{-CuY(aF)}}$	0.3430
Unknown composition	C_{F1}	0.433	0.433	0.433	$a = a_{\text{Cu}_2\text{Y}}$	0.0812
Unknown composition	C_{F2}	0.685	0.685	0.685	$a = b_{\text{Cu}_2\text{Y}}$	0.3214
Unknown composition	T_3	0.430	0.430	0.685	$a = ac_{F1}, b = ac_{F2}$	0.1267

C: cubic; T: tetragonal; H: hexagonal; P: primitive; I: centered; F: face centered; SL: superlattice.

gen, water vapor) and other chemical reactants. Therefore, extreme precautions must be taken in the preparation of samples.

A large overview of the various compounds obtained in the course of our works (see also Ref. [1]) is given in Table 1. This table shows that the main phases are formed according to a well-established sequence. These phases have been observed from XDP. The other phases and their structures were only determined from EDP. Therefore the nature of some compounds is only speculative, particularly for H_5 and H_6 lattices. In this way one must notice that at the mesoscopic scale numerous unknown compositionally different phases are formed.

References

- [1] J.M. Engels, M. Gasgnier G. Blaise, *J. Alloys Comp.* see preceding article in this issue.
- [2] D.J. Chakrabarti, D.E. Laughlin, in: J.F. Smith (Ed.), *Bulletin Alloy Phase Diagrams (The copper rare-earth systems)*, vol. 2, 1981, p. 315.
- [3] R.F. Domagala, J.J. Rausch, D.W. Leivnson, *Trans. Am. Soc. Metals* 20 (1970) 309.
- [4] K.H.J. Buschow, A.S. van der Goot, J. Birkhan, *J. Less-Common Metals* 19 (1969) 433.
- [5] P.R. Subramanian, D.E. Laughlin, in: J.F. Smith (Ed.), *Bulletin Alloy Phase Diagrams (The copper rare-earth systems)*, vol. 9, No. 3a, 1988, pp. 316–434.
- [6] K.A. Gschneidner Jr., *Rare Earth Alloys*, Van Nostrand, Princeton NJ, 1961, pp. 155, 388.
- [7] E. Franceschi, *J. Less-Common Metals* 87 (1982) 249.
- [8] M.M. Carnasciali, S. Cirafici, E. Franceschi, *J. Less-Common Metals* 92 (1983) 143.
- [9] K. Jansson, M. Nygren, *J. Less-Common Metals* 128 (1987) 319.
- [10] J.H. Wernick, S. Geller, *Acta Crystallogr.* 12 (1959) 662.
- [11] K.H.J. Buschow, A.S. van der Goot, *Acta Crystallogr.* B27 (1971) 1085.
- [12] A.E. Dwight, *Trans. Am. Soc. Metals* 53 (1961) 479.
- [13] X. Zhang, P.M. Kelly, A. Atrens, *Acta Metall. Mater.* 41 (1993) 2877.
- [14] R.J. Tarento, G. Blaise, *Acta Metall.* 36 (1988) 655.
- [15] R.J. Tarento, G. Blaise, *Acta Metall.* 37 (1989) 2305.