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Electron microprobe analysis of phase segregation in the Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$

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Aged specimens of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ were examined by means of the ARL scanning electron microprobe quantometer. The process of segregation of the components was observed and the precipitates were identified with the phases detected previously by means of X-ray diffraction. The observed evolution of microstructures and the results of X-ray diffraction and magnetometric measurements were the basis of the description of the process of the decomposition of β-phase of the system Cu–Mn–Al at temperatures below 973 K. Considerable difference between the microstructures of the alloy annealed below and above 700 K confirmed the previously indicated existence of a critical point localized between 673 and 723 K.

1. Introduction

The results of the X-ray and magnetometric investigations of the decomposition process of the β-phase in the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ were the subject of our previous papers [1, 2]. It was indicated, in agreement with other results [3–13], that the β-phase is metastable at temperatures below 973 K and decomposes into three phases of the types β-Mn, γ-Cu_9Al_4 and T-Cu_3Mn_2Al, the structures of which were described previously. Among other facts it was indicated that the decomposition of the β-phase proceeded quite differently at temperatures below and above a critical point localized between 673 and 723 K. Furthermore, preliminary observations of the microstructures of the alloy, by means of an optical microscope, indicated that heterogeneous precipitation on the grain boundaries occurred during the early stages of the decomposition at 733 K. Thus, it seemed to be interesting to research the influence of the annealing temperature on the microstructure of the alloy and on the alloying components' segregation and to investigate the temperature dependence of the degree of supersaturation of the solid solution Cu_2MnAl.

In this paper the results of systematic electron microprobe analysis of the annealed samples of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ are presented.

2. Specimens and experimental details

The process of the production of the alloy of the stoichiometric composition Cu_2MnAl was described in the previous papers. The specimens examined by means of electron microprobe analysis were plates 1 mm thick spark eroded from the ingot. They were sealed in vacuum in quartz ampoules and after homogenization at 1123 K were annealed at temperatures between 423 and 973 K and quenched in water. Similarly, as previously [1, 2], the samples were annealed isothermally at 633, 733 and at 833 K and isochronally for 24 h at 50 degree temperature intervals between 423 and 973 K. After the thermal treatment the surfaces of the plates were polished mechanically. The observation of the microstructures and of the segregation of the alloying components was carried out by means of the ARL scanning electron microprobe quantometer. The accelerating voltage and the sample current were equal to 20 kV and 7 μA, respectively,

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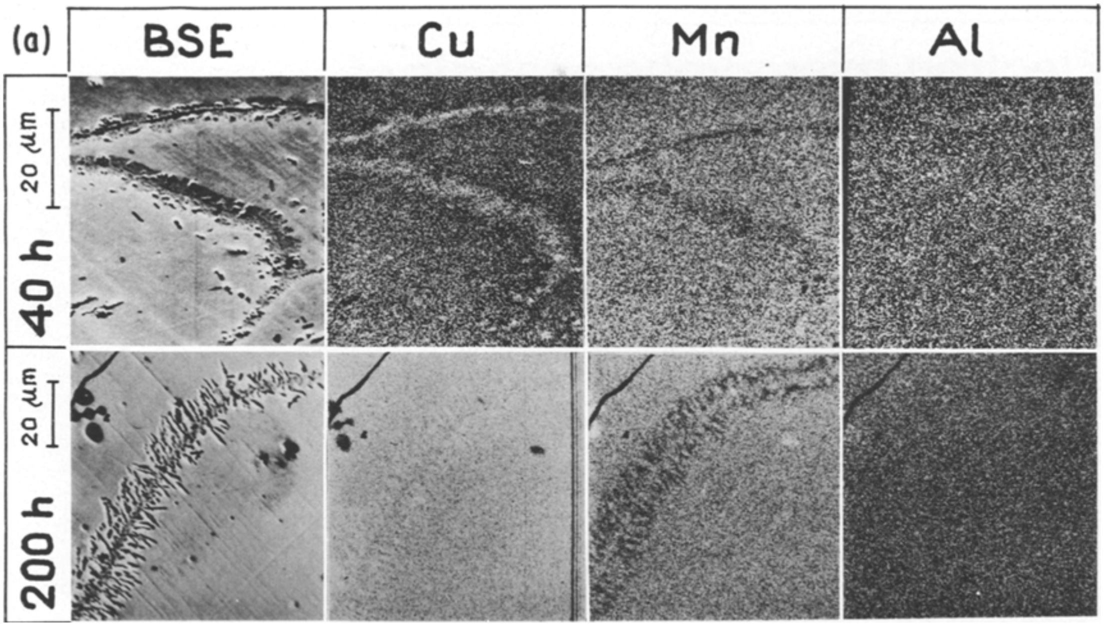


Figure 1 Back scattered electrons (BSE) images of microstructures and X-ray ($K\alpha$) mappings of copper, manganese and aluminium of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ annealed isothermally at 633 K (a), 733 K (b) and 833 K (c).

the LiF, germanium and RAP crystals were used in the X-ray spectrometers. The computer program Magic IV was used for the calculation of the absorption, fluorescence, backscattering and stopping power correction factors [14] to the results of the quantitative analysis of the precipitates. The final relative errors of the estimated weight percentages of the elements did not exceed 5%.

3. Results

3.1. Isothermally annealed specimens

3.1.1. Specimens annealed at 633 K (Fig. 1a)

After 40 h ageing, the precipitates were situated on the grain boundaries. The matrix was homogeneous and its composition was nearly stoichiometric (Cu 61.9 wt %, Mn 24.3 wt %, Al 13.8 wt %). The dark Mn-rich precipitates were situated in a Mn-depleted region of the composition approximating Cu_9Al_4 (Cu 83.7 wt %, Mn 1.7 wt %, Al 13.8 wt %). In the range of grain boundaries, the precipitates of the composition approximating Cu_3Mn_2Al were also detected, however, the precise analysis of the precipitates was impossible due to the limited resolution of the microprobe.

After 200 h ageing, the heterogeneous precipitates on the grain boundaries were much more evolved. Needle-like ones of the composition approximating Cu_9Al_4 growing into the grains were separated by the regions of the composition approximating Cu_3Mn_2Al. Among the needle-like precipitates the dark Mn-rich particles were localized. The matrix was homogeneous of nearly stoichiometric composition Cu 60.9 wt %, Mn 26.8 wt %, Al 13.0 wt %.

3.1.2. Specimens annealed at 733 K (Fig. 1b)

Formation of the precipitates on the grain boundaries was detected after 1 h of annealing. The precipitates were Mn-depleted, however, the presence of very fine Mn-rich ones could not be excluded because of the limited resolution of the apparatus. The matrix was of nearly stoichiometric composition. After 4 h ageing, the process of precipitation was much more advanced and the precipitates of characteristic "jagged" shapes formed, here and there, a dense network. The precipitates consisted of regions of compositions approximating Cu_9Al_4 and Cu_3Mn_2Al and also contained Mn-rich particles (shown in the photographs as dark dots). In the range of the dense network of the precipitates, the matrix was depleted of manganese and its composition approximated Cu_9Al_4.

After 40 h annealing, the whole matrix was homogeneous and its composition was Cu 83.9 wt %, Mn 1.8 wt %, Al 13.1 wt %, i.e. $Cu_9Mn_{0.22}Al_{3.27}$.

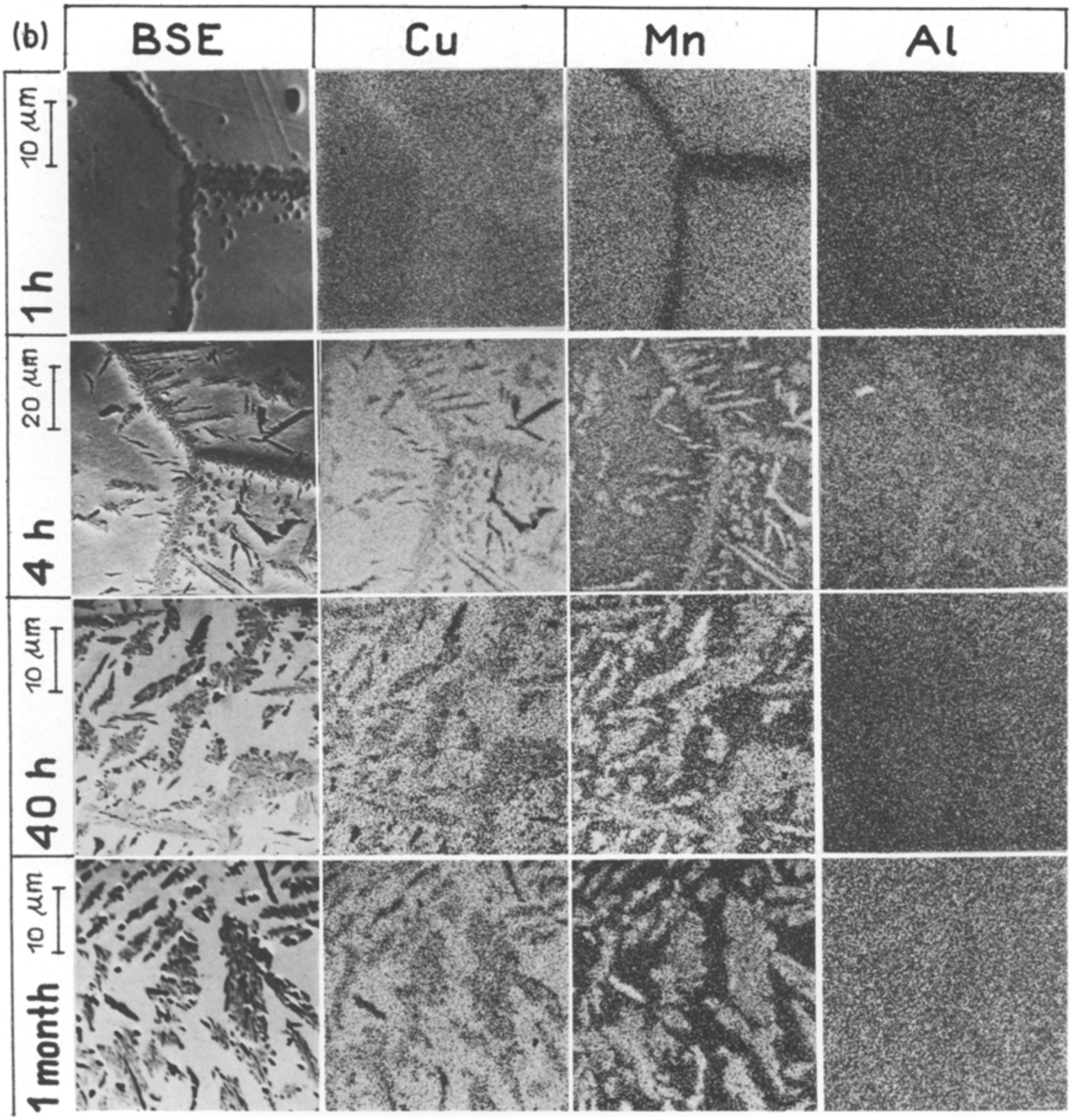


Figure 1 Continued.

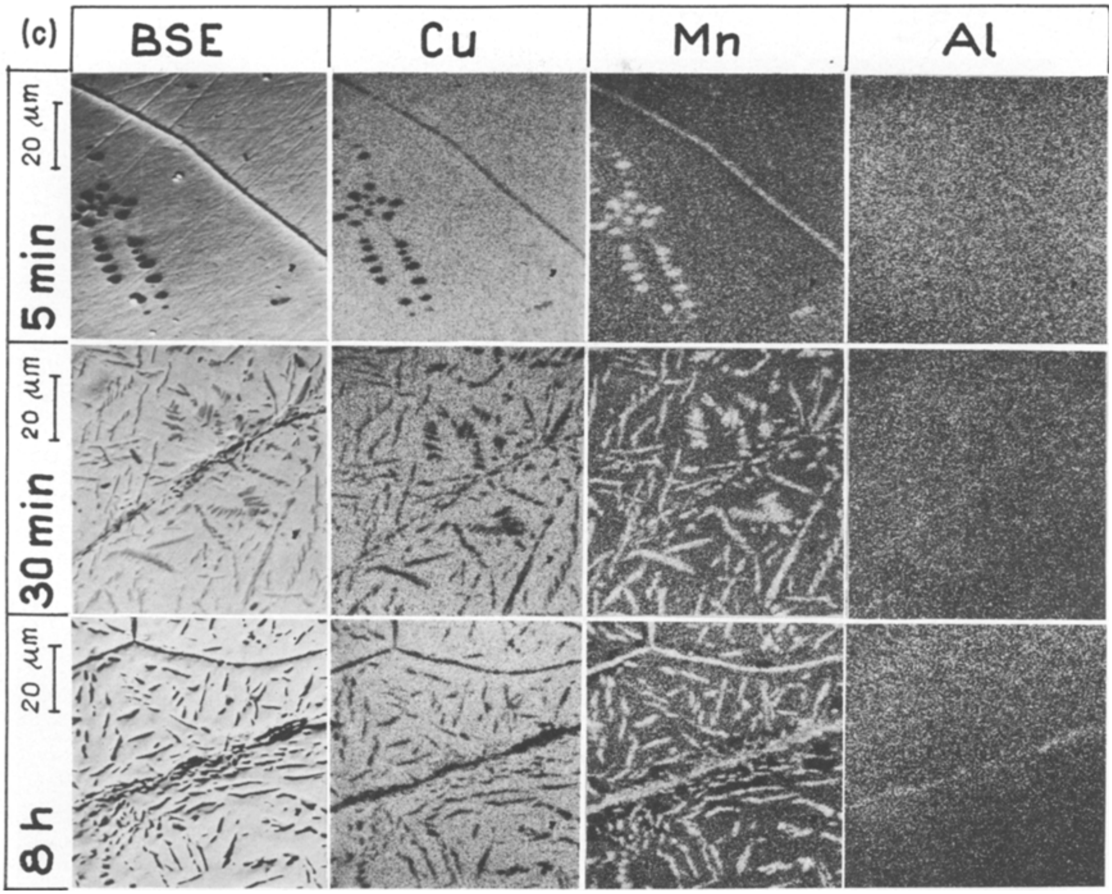
The "jagged"-shaped precipitates were of similar microstructure as they were after 4 h of ageing. After 1 month of ageing a similar type of microstructure was observed.

3.1.3. Specimen annealed at 733 and at 473 K

In order to investigate how the low temperature transition occurring in the partially decomposed alloy at 473 K [1, 2] influenced its microstructure the specimen annealed for 40 h at 733 K was additionally aged for 1 week at 473 K. It was observed that while in general, the microstructure of the alloy was the same as before the additional annealing, the formation of regions of the compositions approximating Cu_2MnAl occurred in the range of the Mn-depleted matrix surrounding the "jagged"-shaped precipitates. The photographs are not presented due to too weak a contrast of the new precipitates, the existence of which, however, was ascertained by the quantitative analysis.

3.1.4. Specimens annealed at 833 K (Fig. 1c)

After 5 min ageing, the Mn-rich precipitates were localized on the grain boundaries but already



after 15 min they were distributed also inside the grains. Although, in general, the matrix was of nearly stoichiometric composition, very thin zones of different compositions surrounded the Mn-rich precipitates. Particularly, in the range of big clusters of Mn-rich particles the regions of the composition approximating Cu_9Al_4 were detected.

3.2. Isochronally annealed specimens (Fig. 2)

No precipitation was detected in the samples annealed at temperatures below 623 K. At 623 and at 673 K the process occurred on grain boundaries but the precipitates were much more evolved after ageing at 673 K. In both cases the quantitative analysis gave the same results as it did in the case of the samples aged at 633 K. Especially, the stoichiometry of the matrix should be emphasized.

The increase of the annealing temperature from 673 up to 723 K caused the marked change in the type of microstructure. At 723 K its development was similar as it was at 733 K.

Further elevation of the annealing temperature was followed by a continuous decay of the "jagged"-shaped precipitates. A few of them, surrounded by Mn-depleted regions of the composition approximating Cu_9Al_4, were observed at 773 and at 823 K. On the other hand, at temperatures above 723 K the manganese precipitation dominated more and more and it was the most intensive at 873 K. At higher temperatures the precipitation process in the alloy decayed continuously.

In all specimens the Mn-rich precipitates contained about 20 wt % aluminium, the matrix was stoichiometric and homogeneous although the precipitates were surrounded by zones of other compositions.

4. Discussion

The results of the electron microprobe analysis

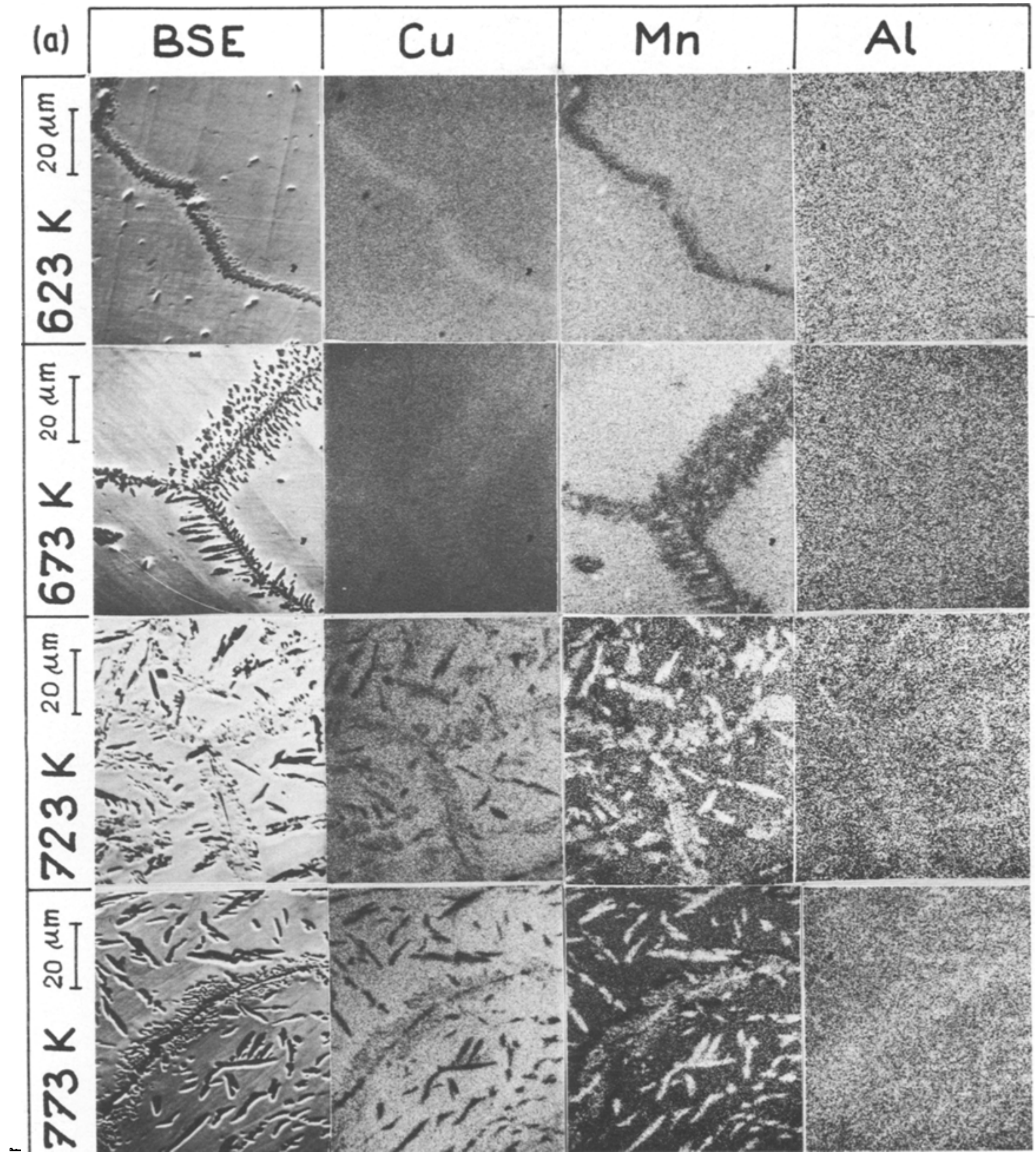


Figure 2 (a and b) Back scattered electrons (BSE) images of microstructures and X-ray ($K\alpha$) mappings of copper, manganese and aluminium of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ annealed isochronally for 24 h at marked temperatures.

together with those of X-ray diffraction and magnetometry [1, 2] allowed a more precise description of the decomposition process of the β-phase in the stoichiometric alloy Cu_2MnAl. All the experimental results obtained up to the present ascertained the existence of the critical point localized between 673 and 723 K dividing the temperature range of metastability of the β-phase into two regions characterized by different kinetics of the process of β-phase decomposition. On the basis of the observations of the evolution of microstructures of the alloy it might be concluded that the decomposition of the β-phase at temperatures of both regions proceeded as follows.

(a) Below the critical point the phases γ-, T- and β-Mn precipitated on the grain boundaries and the elevation of the annealing temperature up to

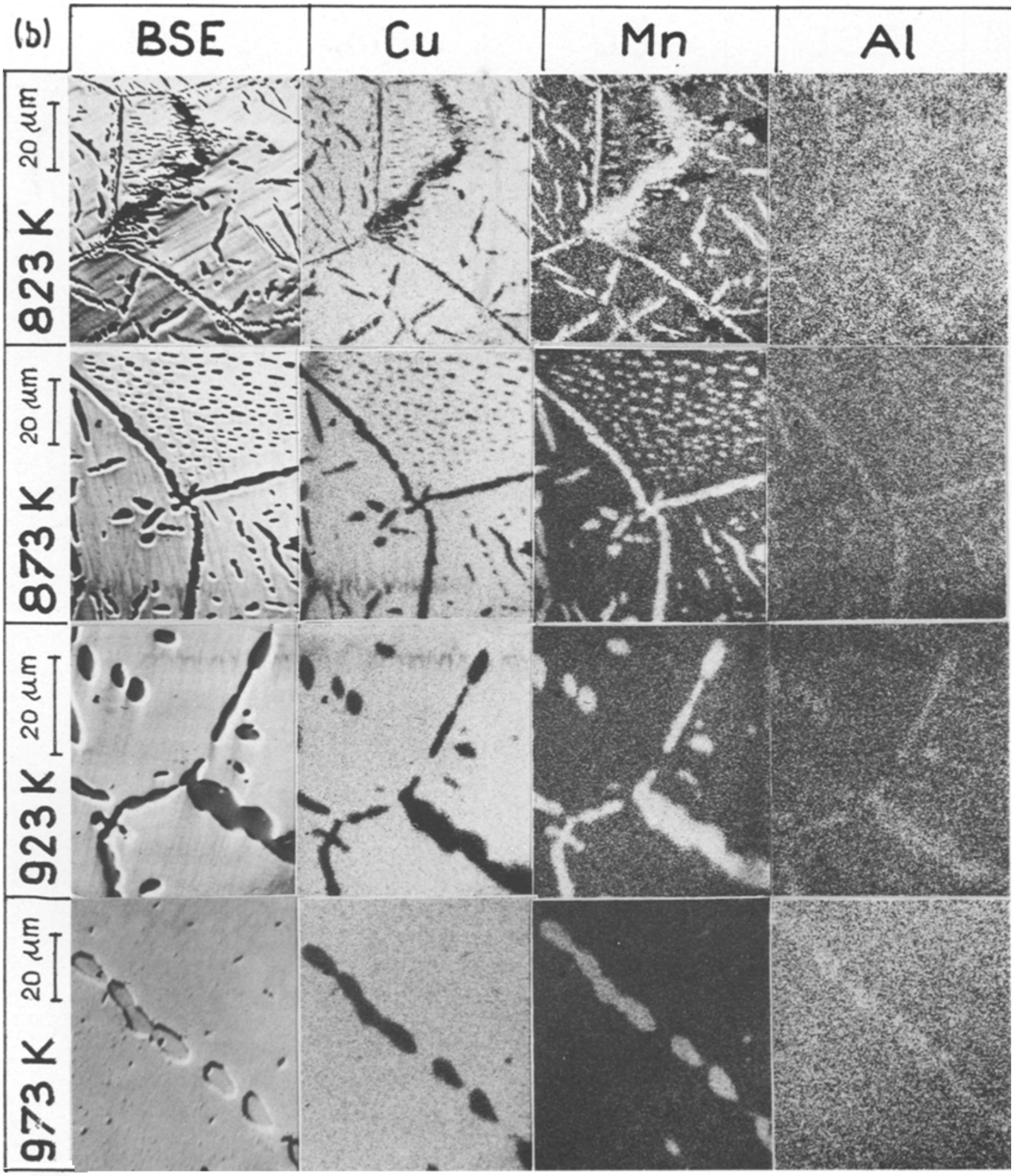


Figure 2 Continued.

the critical point caused only the increase of the rate of the process. The arrangement of the precipitates might suggest that they originated from cells being the product of discontinuous precipitation which might occur during the early stages of decomposition. However, this supposition requires further investigation by means of transmission electron microscopy (TEM). This is already in progress.

(b) During the initial stage of the process, at temperatures just above the critical point, heterogeneous precipitation of the γ-phase on the grain boundaries occurred. However, the simultaneous formation of very fine Mn-rich precipitates was probable as the presence of the β-Mn phase in powder samples was detected by X-ray diffraction already after 30 min at 733 K. The Mn-enrichment of the "jagged"-shaped precipitates after 4 h at 733 K resulted probably from the growth and coalescence of Mn-rich particles proceeding at the cost of Mn-depletion of the matrix and stimulating the growth of the γ-phase precipitates.

The fact that the regions of the compositon approximating Cu_3Mn_2Al were contained in the "jagged"-shaped precipitates after 40 h as well as after 1 month at 733 K suggested that those regions might be identified with the transient $\beta_{\|}$-phase detected by X-ray diffraction at 733 K and transforming into the T-phase after about 200 h ageing [1].

Thus, the following stages of the process at temperatures just above the critical point might be distinguished:

1. heterogeneous precipitation of the γ- and β-Mn phases,
2. formation of "jagged"-shaped precipitates containing β-Mn and the transient $\beta_{\|}$-phases,
3. diffusion controlled growth of the β-Mn precipitates and the evolution of the γ-phase regions,
4. slow transformation of the $\beta_{\|}$-phase into the T-phase.

Such detailed information concerning the decomposition of the β-phase were not available in the case of higher annealing temperatures since the rate of the initial stage of the process increased rapidly when the ageing temperature was elevated [1]. However, on the basis of Fig. 1c it might be supposed that the process of precipitation always started on the grain boundaries. The arrangement of the Mn-rich precipitates observed at temperatures above 723 K might result either from the formation of a Widmanstätten structure or from the rapid spinodal decomposition. This is the subject of further TEM investigations. The relatively high weight percentage of aluminium in the Mn-rich particles is in agreement with the fact that at temperatures at which the alloy was annealed the β-Mn compositional range reached up to the content of about 20 wt% Al [15].

The heterogeneous precipitation in the alloys Cu–Mn–Al was observed also by other authors [5–7, 12, 13]. Detailed investigations of non-stoichiometric alloys were performed by Yamane *et al.* [13]. In the case of the alloy $Cu_{2.05}Mn_{0.92}Al$ aged at 673 and at 873 K, they observed microstructures nearly similar to those presented in Fig. 2.

Generally, the presented results were in agreement with those obtained by means of other experimental methods. The observed migration of the manganese atoms confirmed the previously made supposition about its great importance in the whole process of decomposition. Particularly, it was very interesting to register the rearrangement of manganese at 473 K leading to the restoration of the ferromagnetic properties in the partially decomposed alloy [1, 2].

However, the comparison of the results of electron microprobe analysis with the results of X-ray diffraction investigations requires special comment.

The best agreement between the results of both methods was achieved in the case of the identification of the precipitating phases. In general, the observed precipitates could always be identified with respective phases detected by X-ray diffraction. The discrepancies between the results concerned mainly the advancement of the decomposition process after a certain thermal treatment of the alloy. It was suggested that the process was much more rapid in powder samples especially at temperatures below the critical point (e.g. X-ray diffraction indicated complete decay of the β-phase in the powder sample after 200 h at 633 K [1]). Two factors might be the origin of the above effect:

1. limited depth of X-ray penetration,
2. increase of the grain boundary area in the alloy by the reduction of the material into powder.

The problem of the first fact has already been discussed [16]. However, the diameters of the grains in the examined powder did not exceed $100\,\mu m$ so it might be expected that the whole volumes of the majority of grains situated on the surfaces of the samples were penetrated by X-rays. Besides, if the decomposition of β-phase occurred only in the surface layers of the grains the changes of the magnetic properties of the alloy would have been much weaker than those measured [1, 2]. However, as the surfaces of grains were probably always the sites of heterogeneous nucleation of the precipitates surrounded by zones of the non-stoichiometric matrix, the effect of the diffraction of the majority of the registered intensity of X-rays by surface layers of the grains might be the origin of the observed reduction in the lattice parameter of β-phase [1, 2].

The influence of the second factor was probably much more important since the theoretical considerations of heterogeneous transformations indicated that the rate of such processes is strongly sensitive to the changes of the area of nucleation sites [17]. The successful growth of a single crystal of the alloy Cu_2MnAl (see e.g. [18]) confirmed additionally to the above suggestion as the growth would have been impossible if the decomposition of the β-phase in the originating single crystal occurred so rapidly as it did in the powder samples.

Thus, it became clear that the decomposition of the β-phase in the temperature range of its metastability may be damped by reducing the number or the area of nucleation sites. The practical conclusion is that the best way to avoid the effects of the decomposition is to use single crystals in the investigations of the β-phase properties.

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