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Microstructural changes during ageing of Cu–2.5 wt % Ti

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Microstructural changes in Cu–2.5 wt% Ti during ageing at 573 and 773 K have been studied by transmission electron microscopy. Ageing times ranged from 60 sec to 200 h. Ordering of the β' precipitates was observed after very short ageing treatments at 773 K, and coarsening according to $t^{1/3}$ was also observed from very early times. The β' particles were observed to become increasingly aligned into rod-like groups along ⟨1 0 0⟩ as ageing progressed. These results permit a new interpretation of the strengthening mechanisms in this alloy.

1. Introduction

Alloys of copper containing up to 6 wt % titanium have been studied for some years (e.g. [1–5]). Above approximately 873 K these alloys form a single-phase solid solution which decomposes at lower temperatures. Microstructural investigations have established that on ageing between 573 and 773 K decomposition of the supersaturated solution generally proceeds as follows: (i) spinodal decomposition, with compositional fluctuations along the elastically soft ⟨1 0 0⟩ directions; (ii) ordering of the titanium-rich regions; (iii) formation of coherent metastable β' particles, which have a body-centred tetragonal ordered (D1a) structure; (iv) formation of the equilibrium second phase, β, by a cellular reaction.

The presence of β' particles may raise the yield stress of dilute copper-titanium alloys to one hundred times that of pure copper. This makes these alloys attractive for commercial applications and there have, therefore, been a number of investigations of their mechanical properties. One of the interesting features of these materials is that they may exhibit two peaks in strength during ageing [4, 6–8], as shown in Fig. 1 [6].

Several origins of this behaviour have been proposed. Firstly, it has been suggested that these alloys obey Cahn's theory of strengthening by spinodal decomposition [9]. Some investigators have attributed the first peak in strength to spinodal decomposition and the second peak to the growth of β' particles [4, 7, 10]. Kratochvil *et al.* [7] have attributed the strengthening to ordering of the developing precipitates and the drop in strength to the onset of coupled dislocation motion through the ordered structure. Greggi and Soffa [11] attribute the strengthening to coherency strains rather than ordering, and the drop in strength to a breakdown in regularity of the structure as the precipitates start to coarsen.

The aim of the present work was to distinguish between these various theories by characterizing the microstructural changes occurring during the early stages of ageing of a Cu–2.5 wt % Ti alloy and correlating the microstructure with previously measured mechanical properties [6].

2. Experimental procedure

The material chosen for this investigation was the alloy containing 2.5 wt % Ti previously studied by Thompson and Williams [6]. Considerable information on the mechanical properties of this material has been obtained [6, 12], in particular the yield strength measurements shown in Fig. 1. Two peaks in strength were observed for both ageing temperatures investigated, 573 and 773 K.

The general features of the precipitation reaction were studied by Thompson and Williams [6]. Water quenching from the solution temperature does not suppress spinodal decomposition, so that the as-quenched material contains composition fluctuations [13]. On ageing at 573 K the strength rises slightly during the first ten minutes and then remains constant for ageing times of up to an hour, which suggests that true spinodal decomposition, associated with a constant wavelength, is completed within 10 min. This is in agreement with the observation of Mencl and Vostry [13] that in Cu–1.6 wt % Ti spinodal decomposition is completed in less than 30 min at 573 K.

On continued ageing the microstructure goes through the sequence of changes described above until the strength declines after the second peak due to the formation of the β phase [3, 4, 6, 14, 15]. However, the precise points at which the changes (i)–(iv) occur have not been determined. In the present investigation the microstructures produced during the early stages of the reaction, particularly those associated with the first strength peak, were examined by transmission

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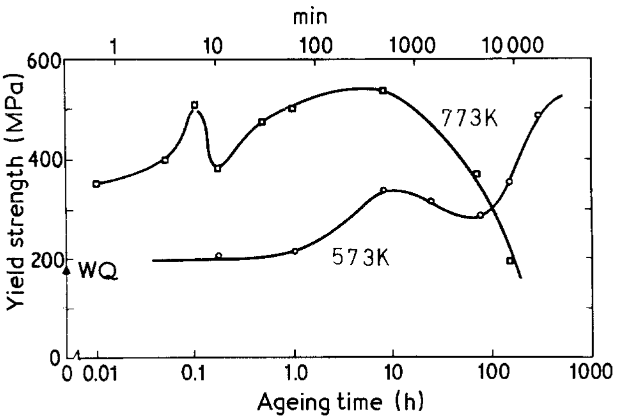

Figure 1 Yield strength of Cu–2.5 wt % Ti as a function of ageing time at 773 and 573 K (from [6]).

electron microscopy (TEM). Of particular interest were the wavelength, λ, of the composition fluctuations, the size, shape and spacing of the β' particles and the time at which reflections from the β' superlattice could first be detected.

Disc-shaped specimens for TEM examination were cut from the tensile specimens used by Thompson and Williams. The samples were sealed in silica tubes under a partial pressure of argon, solution treated at 875° C for 1 h and water quenched. The disc specimens were then aged at 573 or 758 K whereas the tensile specimens had been aged at 573 or 773 K. Calculations of the time required to reach a comparable point on the strength curve at temperatures of 758 and 773 K, based on the apparent activation energy derived by Thompson and Williams [16], indicate that this difference in the higher ageing temperature of the specimens should not be significant. However, it should be noted that the particle distributions observed after ageing at 758 K will be slightly finer, and the reaction slower, than for ageing at 773 K. After ageing the samples were water quenched again, the silica tubes being broken under water. Ageing treatments of up to 1 h were carried out in a fluidized bed while a furnace was used for longer treatments.

The heat-treated discs were thinned for TEM examination in a Fischione twin jet electropolisher using a solution of 30% nitric acid in methanol at 233 K. The specimens were examined in a Philips EM400T electron microscope. Particle sizes and spacings were measured from bright-field images in [1 0 0] orientation using standard techniques [17]. The presence of order in the developing precipitates was determined by overexposing diffraction patterns taken with the specimen in [1 0 0] orientation. At this orientation two variants of the D1a superlattice give rise to diffraction spots at 1/5.420 positions [18].

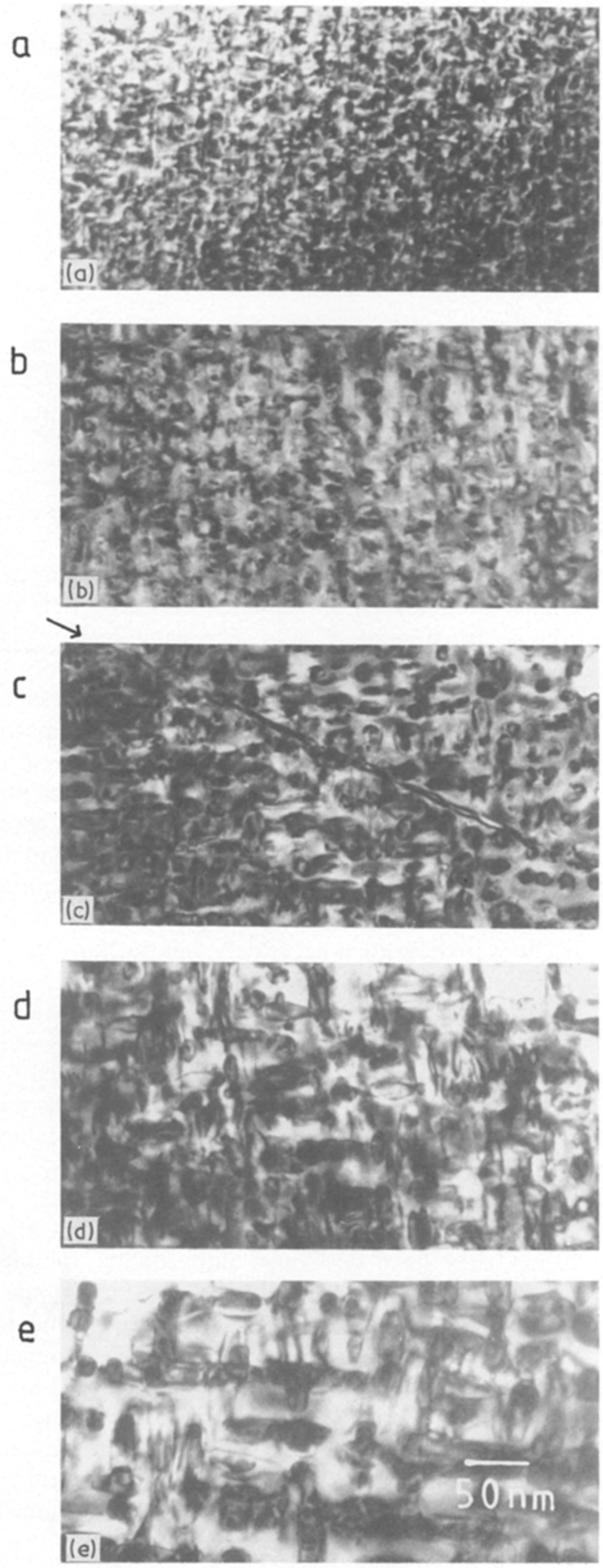

Figure 2 Bright-field images of Cu–2.5 wt % Ti aged at 758 K (a) 2 min, (b) 5 min, (c) 10 min, (d) 45 min, (e) 90 min. Incident beam direction [1 0 0]. The position of a twin boundary in (c) is indicated.

3. TEM observations

3.1. Ageing at 758 K

Bright-field images of specimens annealed at 758 K for various times are shown in Fig. 2. All these images were obtained with the incident beam parallel to [100]. Well defined images of particles are observed after even the shortest ageing time of 2 min, which corresponds to a point well before the first peak strength shown in Fig. 1. The particles grow as ageing proceeds, the mean particle diameter being proportional to $t^{1/3}$ as expected for a diffusion controlled process. The measured average particle diameter as a function of ageing time is shown in Fig. 3. The spacing, λ, between the particles was of the same magnitude as the particle diameter at all ageing times. A similar $t^{1/3}$ dependence

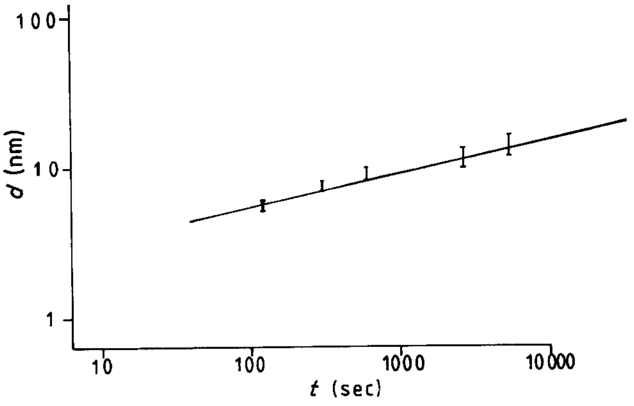

Figure 3 Average particle diameter as a function of ageing time at 758 K.

of particle size on ageing time has been observed in other dilute copper–titanium alloys [4, 5, 19].

Measurements of the area fraction of the micrographs occupied by precipitates indicated that the volume fraction of β' was increasing with ageing time. The area fraction of precipitate could only be measured in very thin regions of the specimens because of the occurrence of strain contrast in the matrix around the particles. The electropolish was found to remove the matrix slightly more quickly that the precipitates, so that in the thinnest regions of the specimens the precipitates were not totally embedded in the matrix and there was very little strain contrast around them. This made it possible to measure the sizes of the particles in these areas accurately, but the thin regions were not extensive enough to allow accurate measurements of the volume fraction of precipitate. Dark-field images formed from β' superlattice reflections were used to measure particle sizes in specimens aged for longer than 30 min [6]. The values obtained in this way differed by less than 10% from the values obtained from bright-field images of the same specimens.

At ageing times of up to 5 min the precipitates appear to be roughly ellipsoidal in shape, but after 10 min they have developed into slightly rounded cuboids with projected aspect ratios in the image plane of less than 2. Thereafter they retain their cuboidal shape as they grow. The way in which the alignment of the precipitates increases with ageing time is most noticeable. In specimens aged for 2 min only occasional pairs of particles can be seen which have lined up face to face, but as ageing proceeds the particles arrange themselves into rows and after 10 min clear channels have developed between the rows. After 45 min the rows of precipitates have become rod-like groups along $\langle 100 \rangle$, as reported by other investigators [1, 20], and except in the thinnest regions of the specimens the individual β' particles within the groups cannot be distinguished in bright-field images because of the strong strain-field contrast.

Superlattice reflections from the β' precipitates are present from the earliest times, as shown in Fig. 4. This is a [1 0 0] diffraction pattern showing distinct superlattice spots which was taken from a specimen aged only 2 min at 758 K, which is well before the first peak in strength. However, although superlattice spots could be seen clearly in over-exposed diffraction patterns they were insufficiently intense for dark-field images of the precipitates to be formed from them for ageing times shorter than 45 min.

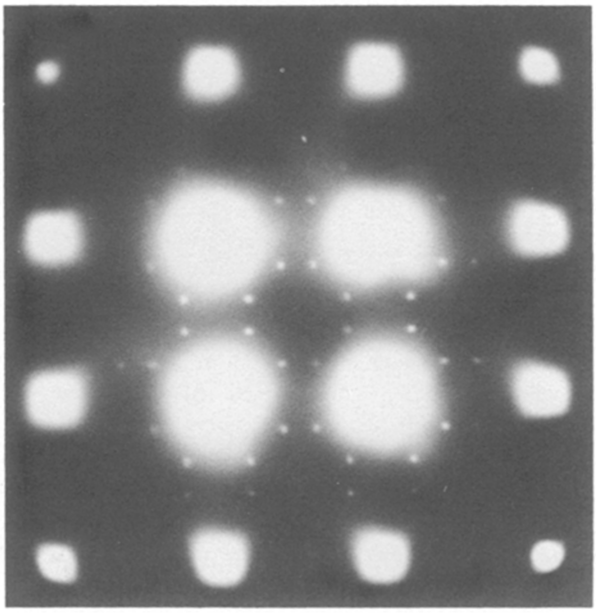

Figure 4 Electron diffraction pattern of Cu–2.5 wt % Ti aged for 2 min at 758 K, showing strong β' superlattice reflections. Incident beam direction [1 0 0].

Cellular colonies of the equilibrium phases were observed at many grain boundaries in specimens aged for 45 min and occasionally in specimens aged for only 10 min [6]. Specimens aged for 10 min sometimes displayed preferential formation of β' at grain boundaries, as can be seen at the twin boundary in Fig. 2c. Sometimes this was accompanied by a precipitate-free zone around the boundary. However, this was never observed in specimens aged for less than 10 min, so it may be attributed to preferential growth at the boundary rather than to preferential nucleation there.

3.2. Ageing at 573 K

Specimens aged at 573 K were observed to have a modulated structure which produced satellite reflections near the 200 diffraction spots and gave a striated appearance to images taken with $g = 200$. Well defined particles were not observed after even the longest ageing time of 204 h. Attempts were made to measure the average wavelength of the compositional modulations, λ, from bright-field images taken under two-beam conditions with $g = 200$ [2, 19]. However, the spacings of the intensity variations in the images were found to be random. Examination of the edges of very thin specimens indicated that λ was of the order of 2 nm. This very short wavelength means that even in thin specimens the electron beam is traversing several modulations as it passes through the material, so that the final image intensity is not related in a simple manner to λ. Thus it was not possible to determine λ from the images or even to determine whether it was changing as a function of ageing time.

Attempts were also made to measure λ from the position of the 200 satellite spots in electron diffraction patterns, but the satellites were found to be too close to the main spot for accurate measurement.

Superlattice reflections were not observed from any of the specimens examined.

4. Discussion

These observations of the microstructure of Cu–2.5 wt % Ti allow us to discuss possible strengthening mechanisms. It is apparent that none of the theories which have previously been proposed is entirely consistent with the observations.

Firstly, in the case of material aged at 758 K well defined, ordered β' particles are present and are undergoing coarsening well before the first peak in strength. Therefore the first strength peak cannot be due to spinodal decomposition, as has been suggested [4, 7]. Spinodal decomposition remains a possible origin of the first strength peak in material aged at 573 K since we were unable to determine whether or not the structure is coarsening at this stage of the ageing sequence. However, spinodal decomposition would be expected to occur from the very beginning of ageing, since it does not involve nucleation, and thus the strength would be expected to rise immediately, reaching a constant value when decomposition is complete. If such behaviour occurs on ageing at 573 K it is completed during the first ten minutes of ageing and the strength then remains constant for ageing times of up to an hour. Therefore it seems that spinodal decomposition is complete well before the first strength peak. This is in agreement with the conclusions of previous workers [13].

If spinodal decomposition is complete before the strength of the material begins to rise to its first peak value the two observed strength peaks must be due to the β' particles. It is probable that the precipitates predominantly strengthen the material by a combination of order strengthening and coherency strain strengthening [21]. In systems strengthened by coherent particles strengthening due to these mechanisms will be proportional to the square root of particle diameter. Both contributions to the strength should therefore increase as the particles grow, assuming that the misfit and antiphase boundary energy remain sensibly constant.

Measurements of the ratio of the yield stress at 77 K to that at room temperature [16] suggest that in material aged into the second strength peak order strengthening is dominant, since the yield strength ratio does not show the temperature dependence of the elastic modulus expected for coherency strain strengthening [21]. The present investigation has shown that order strengthening alone cannot cause the first peak in strength for material aged at 573 K, since no superlattice reflections were detected until well into the second peak. Thus for material aged at this temperature it is not possible to attribute the drop in strength at intermediate ageing times to the onset of coupled dislocation motion [7]. However, order strengthening may contribute to the first strength peak at the higher ageing temperature.

It can be seen from the contrast of TEM images that the β' particles are surrounded by considerable strain fields, and hence coherency strain strengthening is possible for all ageing times at both temperatures. It is likely to be most important as a strengthening mechanism in Cu–Ti alloys for short ageing times before ordering has become well developed. It now remains for us to consider whether the observed reductions in strength at intermediate ageing times could be caused by a decrease in coherency strain. Perhaps the most obvious way in which coherency strains could be reduced would be by loss of coherency of the β' particles. However, TEM showed no evidence for the presence of misfit dislocations and it is extremely unlikely that such small particles, less than 5 nm in diameter in the case of material aged at 573 K, would become incoherent [21]. Also at all ageing times the β' particles were observed to be aligned along the matrix $\langle 1\,0\,0 \rangle$ directions, which are the elastically soft directions in copper. This highly aligned microstructure indicates that coherency strains are present and are controlling the arrangement of the precipitates.

Another origin of the reduction in coherency strain is suggested by the micrographs shown in Fig. 2. Early in the ageing process the precipitates become cuboids on $\{1\,0\,0\}$, but as ageing proceeds the β' particles become aligned with one another, eventually forming long, rod-like groups of particles with clear channels between them [22]. This increase in the regularity of the precipitate distribution is most noticeable on comparing Figs 2a and 2e. The alignment of coherent precipitates during growth has been observed in other alloy systems (e.g. [23]) and is known to be caused by elastic interactions between the precipitates. In the case of β' in copper–titanium alloys the fully ordered precipitates are body-centred tetragonal with approximately zero misfit along the c axis and a misfit of 2% parallel to the a and b axes [1]. It is therefore energetically unfavourable for two β' particles with parallel c axes to grow side by side, since their overlapping strain fields are of the same sign, and most favourable for them to grow nose to tail. During coarsening, precipitates in favourable positions will grow at the expense of those in unfavourable positions, and this effect produces the rod-like groups of particles with c axes parallel to the length of the rod which are observed.

The exact form of the strain fields around the β' particles is expected to be complex. The strain fields around single ellipsoidal [24] and cuboidal [25] inclusions have been calculated. However, in the copper–titanium system a large number of closely spaced, elastically anisotropic particles are interacting with one another in an elastically anisotropic matrix, and as precipitation proceeds the number, size, shape, volume fraction, chemical composition and, as tetragonality develops, the geometrical form of the misfit between the particles and the matrix are all continually changing. For a complete theory of the strength changes in this alloy all these factors would have to be considered, but at the present state of development of particle-hardening theory we only feel justified in proposing a qualitative model.

We therefore propose that the reduction in internal strain which leads to the drop in strength at intermediate ageing times occurs when the coarsening β' precipitates become large enough to interact elastically with one another and begin to form aligned groups.

The order strengthening term presumably increases continuously as the precipitates grow so that the reduction in strength due to the decrease in coherency strain is only temporary. In more dilute copper–titanium alloys, in which the volume fraction of β' precipitate will be smaller, the elastic interactions between individual β' particles will be weaker. We would, therefore, expect that more dilute alloys will show a less pronounced drop in strength and that below a critical titanium concentration no intermediate decrease in strength will occur. Such an effect has been reported [20].

5. Conclusion

This investigation has shown that previous theories of the origin of the double peak in strength in copper–titanium alloys are not correct. In Cu–2.5 wt % Ti the first peak in strength is not due to spinodal decomposition but instead is due to β' particles. At 758 K well defined, ordered β' particles are formed before the first peak in strength, while at 573 K ordering does not occur until the beginning of the second peak. TEM observations suggest that the strength declines from its first peak value because of a reduction in the level of coherency strain in the material, which is caused by the alignment of the growing precipitates.

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References

1. T. HAKKARAINEN, DTech thesis, Helsinki University of Technology (1971).
2. J. A. CORNIE, A. DATTA and W. A. SOFFA, *Metall. Trans.* **4** (1973) 727.
3. D. E. LAUGHLIN and J. W. CAHN, *Acta Metall.* **23** (1975) 329.
4. A. DATTA and W. A. SOFFA, *ibid.* **24** (1976) 987.
5. R. WAGNER, "Strength of Metals and Alloys" (proc. ICSMA 5) Vol. 1, edited by P. Haasen, V. Gerold and G. Kostorz (Pergamon, New York, 1980) p. 645.
6. A. W. THOMPSON and J. C. WILLIAMS, *Metall. Trans.* **15A** (1984) 931.
7. P. KRATOCHVIL, M. SAXLOVA and J. PESICKA, in "Strength of Metals and Alloys" (proc. ICSMA 5), Vol. 2, edited by P. Haasen, V. Gerold and G. Kostorz (Pergamon, New York, 1980) p. 687.
8. V. I. DOTSENKO, P. KRATOCHVIL, J. PESICKA and B. WIELKE, *Czech J. Phys.* **B31** (1981) 209.
9. J. W. CAHN, *Acta Metall.* **11** (1963) 1275.
10. L. H. SCHWARTZ and J. T. PLEWES, *ibid.* **22** (1974) 911.
11. J. GREGGI and W. A. SOFFA, *Scripta Metall.* **14** (1980) 649.
12. A. W. THOMPSON and A. PORTER, *Scripta Metall.* **18** (1984) 1185.
13. J. MENCL and P. VOSTRY, *Czech J. Phys.* **B31** (1981) 221.
14. R. C. ECOB, J. V. BEE and B. RALPH, *Met. Trans.* **A11** (1980) 1407.
15. H. T. MICHELS, L. B. CADOFF and E. LEVINE, *ibid.* **3** (1972) 667.
16. A. W. THOMPSON and J. C. WILLIAMS, in "Deformation of Multi-phase and Particle containing Materials", (Proc. 4th Riso symposium), edited by N. Hansen (Riso National Laboratory, Roskilde, Denmark, 1983) p. 551.
17. E. E. UNDERWOOD, "Quantitative Stereology" Addison-Wesley, Reading MA (1970) Chap. 6.
18. D. E. LAUGHLIN and J. W. CAHN, *Met. Trans.* **5** (1974) 972.
19. P. CIZINSKY and J. PESICKA, *Czech J. Phys.* **B31** (1981) 752.
20. M. SAXLOVA and J. BALIK, *ibid.* **B31** (1981) 215.
21. L. M. BROWN and R. K. HAM, "Strengthening Methods in Crystals" (edited by A. Kelly and R. B. Nicholson) Elsevier, London (1971) p. 9.
22. P. E. DONOVAN, *J. Mater. Sci. Lett.* **4** (1985) 1337.
23. A. J. ARDELL, R. B. NICHOLSON and J. D. ESHELBY, *Acta Metall.* **14** (1966) 1295.
24. J. D. ESHELBY, *Proc. R. Soc.* **252A** (1959) 561.
25. T. MURA, "Micromechanics of Defects in Solids", Nijhoff, Dordrecht (1982).

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