

Spinodal decomposition in Co-3wt% Ti-1wt%Fe and Co-3 wt % Ti-2 wt % Fe alloys

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The transformation on ageing Co-3 wt % Ti-1 wt % Fe and Co-3 wt % Ti-2 wt % Fe alloys has been followed by transmission electron microscopy and diffraction to establish that the solid solutions undergo spinodal decomposition at 823 and 973 K. The microstructural evolution has been correlated with the observed variations in hardness and yield strength. The coarsening of the modulations on ageing is seen to follow $\lambda^3 - \lambda_0^3 = Kt$ kinetic law. After long periods of ageing a discontinuous coarsening process sets in.

1. Introduction

Precipitation in cobalt-rich cobalt-titanium alloys was first studied by Fountain and co-workers [1, 2] and by Bibring and Manenc [3]. The precipitation was preceded by composition fluctuations along the $\langle 100 \rangle$ directions which could be detected by the appearance of satellites in single-crystal oscillation patterns [2] and side bands in powder patterns [3]. The precipitating phase was γ -Co₃Ti with the $L1_2$ -Cu₃Au structure. The γ -phase had a cuboidal morphology as shown by a study of extracted particles and also replica electron microscopy [1, 2]. Longer ageing was associated with a coarsening of the γ cuboids. The decomposition was also studied by following the changes in hardness and electrical resistivity on ageing of Co-6 wt % Ti and Co-9 wt % Ti alloys [2]. Results of both indicated a two-stage decomposition. The first stage was interpreted to correspond with the precipitation of very thin platelets followed by their impingement in the second stage. This interpretation is, however, not in conformity with the observation of the cuboidal morphology. Blaise *et al.* [4] have recently confirmed the precipitating phase to be Co₃Ti with the $L1_2$ structure by TEM and have shown it to be stable up to high temperatures.

Chuistov and co-workers [5-7] in a study of a Co-7.45 wt % Ti alloy by X-ray and electron metallography, however, came to the conclusion

that in the very initial stages of decomposition, Guinier-Preston type zones form randomly and subsequently align along $\langle 100 \rangle$ directions due to elastic interaction. Zakharova and Vasil'yeva [8] supported this sequence of the precipitation process for a Co-10 at % Ti alloy. These authors, however, do not appear to have studied the decomposition at the very early stages in sufficient detail to justify their claim.

Thompson and Edington [9] have conducted a TEM study of a Co-10 at % Ti alloy and shown the existence of a periodically modulated structure. By the choice of different ageing temperatures, they also deduced the coherent phase-boundary temperature for this alloy to be about 870°C.

Davies and Ralph [10], in a field-ion microscopic investigation of the early stages of decomposition of a Co-10 at % Ti alloy, have shown that the periodicity of the precipitates is present at very short ageing times and agrees with that deduced from X-ray diffraction suggesting a spinodal mode of transformation.

The binary cobalt-rich Co-Fe alloys are stable as solid solutions; however, the ternary cobalt-rich Co-Ti-Fe alloys are amenable to a precipitation-hardening treatment [11]. An impressive study of Co-12 wt % Fe-6 wt % Ti has been carried out recently by Shilling and Soffa [12]. These workers have correlated the microstructural development of the alloy with changes in its magnetic properties.

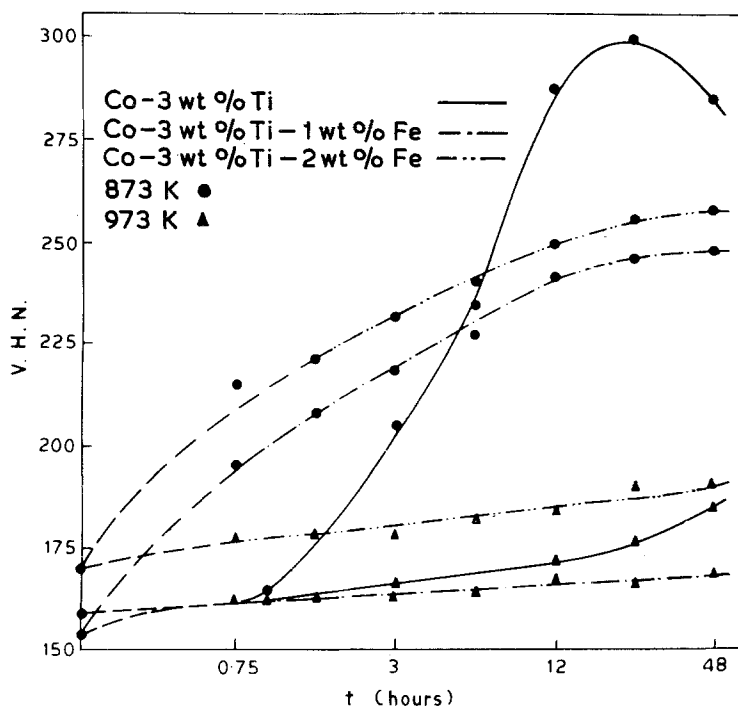


Figure 1 Isothermal hardness plots for Co-3 wt% Ti-1 wt% Fe and Co-3 wt% Ti-2 wt% Fe for ageing temperatures of 873 and 973 K.

They reported the precipitation of a metastable coherent or semicoherent γ' phase arranged in periodic arrays and giving rise to the usual satellites. However, the origin of the modulated structure was not explained.

The aim of the present investigation is to study dilute alloys so that the volume fraction of the precipitating phase is reduced and would enable a distinction to be made between the two possible mechanisms for the formation of the observed modulated structures [13, 14].

2. Experimental procedure

Alloys having the compositions Co-3 wt% Ti-1 wt% Fe and Co-3 wt% Ti-2 wt% Fe supplied by Cobalt Information Centre, Belgium in the form of 20 mm diameter rods of 150 mm length, were used in this investigation. Specimens for mechanical testing and microstructural observations were prepared by hot-forging followed by cold rolling with intermediate heating to about 1100 K, and quenching.

All the samples were solutionized at 1473 K for 1.5 h in vacuum-sealed silica tubes and then quenched in water. Subsequently, the samples were aged at 823, 873 and 973 K under vacuum for different times ranging from 1 min to 15 days.

The hardness values were found by using a Vickers hardness tester using a load of 30 kg. The tensile test samples were prepared according to the

dimensions used by earlier workers [15] and tested in an Instron TT-CM-L 5000 kg universal testing machine using a constant strain rate of $2.5 \times 10^{-3} \text{ sec}^{-1}$.

Thin foils for electron microscopic examination were prepared by utilizing a twin-jet polisher with a solution of 50% orthophosphoric acid in distilled water. The foils were examined at 100 kV in a Philips EM300 electron microscope.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows an isothermal hardness plot for Co-3 wt% Ti-1 wt% Fe and Co-3 wt% Ti-2 wt% Fe for ageing temperatures of 873 and 973 K. The as-quenched hardness values for the two ternary alloys are nearly equal to that for a binary Co-3 wt% Ti alloy. This is possible due to the atomic sizes of Co (1.252 Å) and Fe (1.274 Å) [16] being nearly equal and thus having a small solid solution strengthening effect.

As shown in Fig. 1, there is hardly any age-hardening response at 973 K for the ternary alloys. This is indicative of the solvus being close to these compositions in the ternary phase diagram at 973 K.

In contrast, there is a significant increase in the hardness on ageing at 873 K. The peak hardness values for both ternary alloys are lower than that for the binary alloy. As the strength of

TABLE I Yield strength (2% offset) for alloys aged at 873 K

Ageing time (h)	Yield strength (MPa)	
	Co-3 wt % Ti-1 wt % Fe	Co-3 wt % Ti-2 wt % Fe
0	197	216
0.75	296	374
6	424	384
24	433	473
96	443	482

alloys with periodic distribution of phases is strongly dependent on the variation of the lattice parameter in the matrix and precipitate [17, 18], it appears that iron influences this variation so as to reduce the strength.

Although peak hardness is achieved in about 24 h for all alloys, the detailed kinetics is also different for the binary and ternary alloys at 873 K. The rate of increase of hardness for the ternary alloys is nearly constant up to the peak which is rather flat. In fact, significant over-ageing was not observed even when measurements were extended for ageing up to 30 days. On the other hand, the binary alloy exhibited a very slight increase in the hardness reflecting slow initial decomposition followed by rapid attainment of the peak and over-ageing. This difference in behaviour can arise due to various factors as discussed by Cahn [19].

Microstructural evidence shows that the loss in hardness on over-ageing is associated primarily with a coarsening of the periodically modulated structure and in the case of the ternary alloys with discontinuous coarsening.

The variation of yield strength with time on ageing at 873 K is given in Table I. The behaviour of the yield strength is similar to that of hardness and can be explained on the same basis. Dahlgren [18] has related the increase in the yield strength, $\Delta\sigma$, with the difference, Δa , in the lattice parameters of the two phases through

$$\Delta\sigma = (\bar{m}/3\sqrt{6})(C_{11} + C_{12} - 2C_{12}^2/C_{11})(\Delta a/a),$$

where \bar{m} is the Taylor factor (= 3.06), C_{ij} are single-crystal elastic stiffness constants and a is the average lattice parameter. In view of the fact that neither the elastic stiffness constants nor the difference in the lattice parameters are available for these alloys, we have used the elastic data for nickel and the observed $\Delta\sigma$ values to estimate Δa which turns out to be about 10^{-3} nm. This appears to be a reasonable value.

3.2. Microstructural evolution

A microstructure typical of the as-quenched alloys as revealed by transmission electron microscopy is shown in Fig. 2. A very slight amount of decomposition is evident in some regions. Thus the quenching rate is just insufficient to completely suppress initiation of decomposition. Considerable faulting is, however, evident and is indicative of the allotropic transformation temperature from the fcc to the hcp phase being above room temperature as expected [20].

On ageing Co-3 wt % Ti-2 wt % Fe at 873 K for short times, a modulated microstructure results (Fig. 3). The micrographs show a wavy contrast perpendicular to the operating vector namely $[200]$. It follows that the contrast arises due to matrix strain with a displacement vector along the $\langle 100 \rangle$ matrix directions. The decomposition is accompanied by the formation of satellites flanking the matrix reflections as shown in the inset. A pair of satellites form around $h00$ reflections along the $[100]^*$ direction while two pairs form around $hk0$ reflections along $[100]^*$ and $[010]^*$. The microstructures and the diffraction patterns thus arise due to the formation of a tri-axially modulated

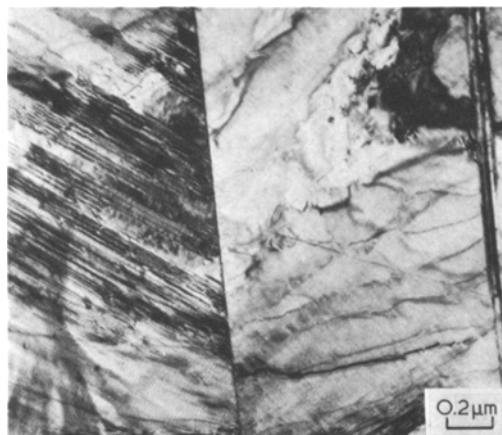


Figure 2 Micrograph of Co-3 wt % Ti-2 wt % Fe in as-quenched condition.

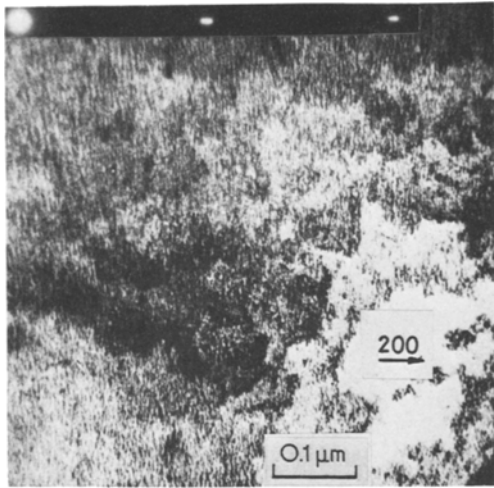


Figure 3 Micrograph of Co-3 wt % Ti-2 wt % Fe aged at 873 K for 1 h: dark-field using 200 reflection and small angle diffraction pattern showing satellites around 200 spot shown as inset.

structure with the modulation being along the cube directions [21]. Such modulations are expected to occur along the elastically soft directions ([100] or [111] in cubic crystals) in alloys undergoing spinodal decomposition [19].

Although, it is desirable to follow the microstructural sequence method of Laughlin and Cahn [22] for proving spinodal decomposition, it was not possible to utilize this method in the present investigations owing to considerable faulting being present in the initial stages of ageing and also the faintness of the satellites and modulations. However, periodicity and alignment along the elastically

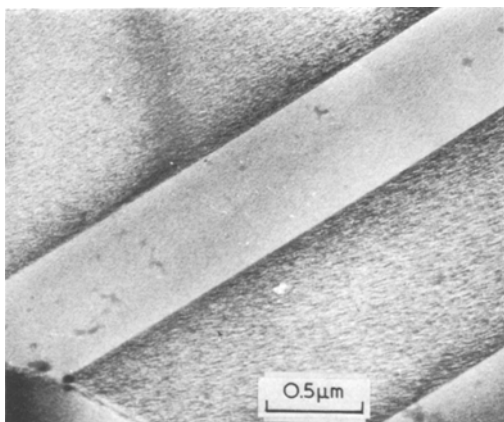


Figure 4 Micrograph of Co-3 wt % Ti-2 wt % Fe aged at 873 K for 15 min showing a modulated structure. Note that the twin boundary does not affect the structure except for a change in the direction of the modulations.

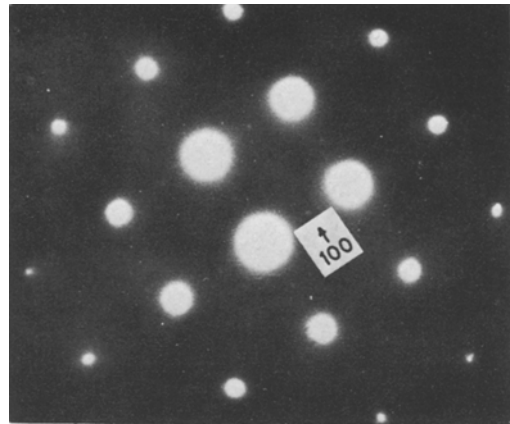


Figure 5 Small angle diffraction pattern from Co-3 wt % Ti-2 wt % Fe aged at 873 K for 1 h showing superlattice spots from ordered precipitate.

soft directions from the earliest stages of transformation, as shown in Fig. 4, is strong evidence for spinodal decomposition. It may be added that periodicity and alignment without spinodal decomposition can occur only at a late stage in the transformation [14]. An interesting feature of Fig. 4 is that the modulations are not affected by twin boundaries, as expected.

Superlattice reflections from the precipitating ternary variant of the Co_3Ti phase were first observed, as shown in Fig. 5, after ageing for 1 h at 873 K in the Co-3 wt % Ti-2 wt % Fe alloy. As the volume fraction of the precipitating phase is small for this alloy composition, the superlattice reflections are always rather weak. Under these circumstances, it is not possible to conclude whether or not the superlattice spots were present for even shorter ageing times and consequently to infer whether the observed homogeneous transformation proceeds through the mechanism of spinodal clustering followed by ordering or of continuous ordering [23]. Shilling and Soffa [12], however, have noted the simultaneous appearance of the satellites and the superlattice reflections and concluded that the formation of the precipitate phase can be described by "a periodic model incorporating a rectangular concentration profile".

A similar ageing response is observed at 823 K also. The kinetics of the process is considerably slower due to the lower temperature.

During continued ageing a coarsening of the periodic microstructure occurred (Fig. 6). These micrographs also illustrate two interesting features. Fig. 6a shows that the modulated structure extends up to the grain boundary as expected during a

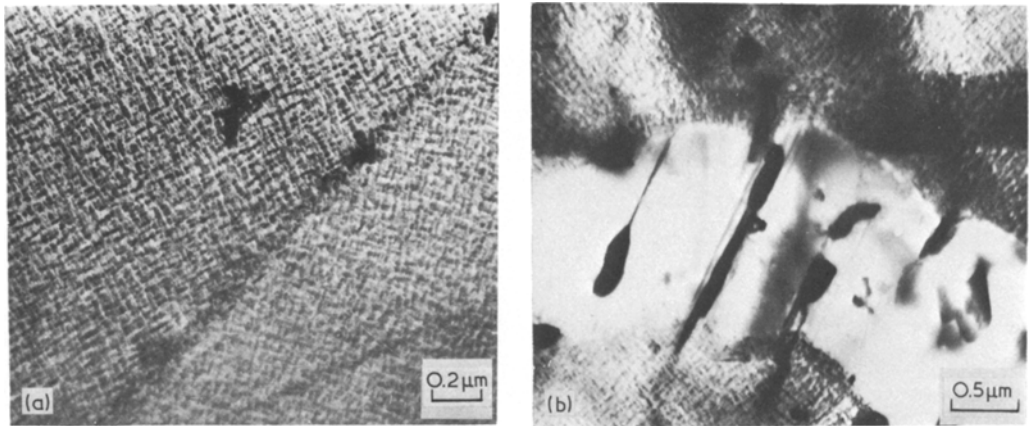


Figure 6 Micrographs of Co-3 wt% Ti-2 wt% Fe aged at 873 K for 96 h: (a) spinodal decomposition unaffected by grain boundary; (b) discontinuous coarsening at grain boundary.

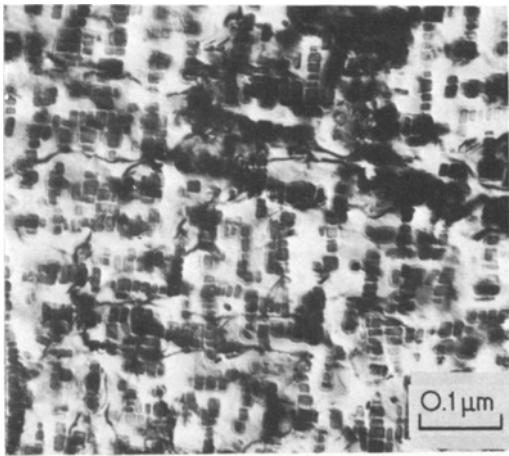


Figure 7 Bright-field micrograph illustrating formation of cuboids after breakdown of modulations in Co-3 wt% Ti-2 wt% Fe aged at 873 K for 360 h.

spinodal transformation. Fig. 6b shows that after a certain ageing time, discontinuous coarsening starts at some locations on the grain boundary. Details of the discontinuous coarsening will be published separately.

As pointed out by Saunderson *et al.* [24], a second stage of coarsening follows during which a slow breakdown of the modulated microstructure to yield a particulate morphology occurs. The particles are cuboidal in shape (Fig. 7). As shown by the dark-field micrograph (Fig. 8a), the cuboids are generally arranged in rows, the length of the row being much greater than the width. The diffraction pattern (Fig. 8b) shows that the precipitates have the ordered $L1_2$ structure.

A coarsening of the cuboids occurs in the third stage. As shown in Fig. 9, the kinetics governing

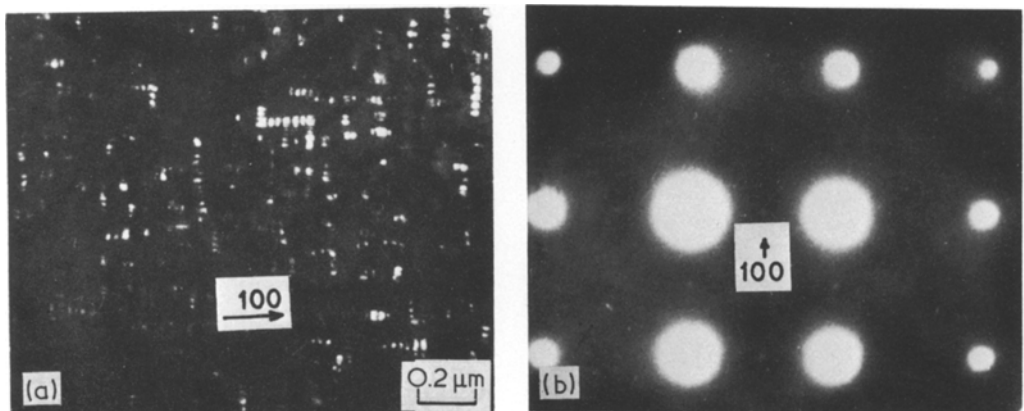


Figure 8 (a) Dark-field micrograph from 001 superlattice reflection for Co-3 wt% Ti-2 wt% Fe aged at 873 K for 360 h. (b) small angle diffraction pattern.

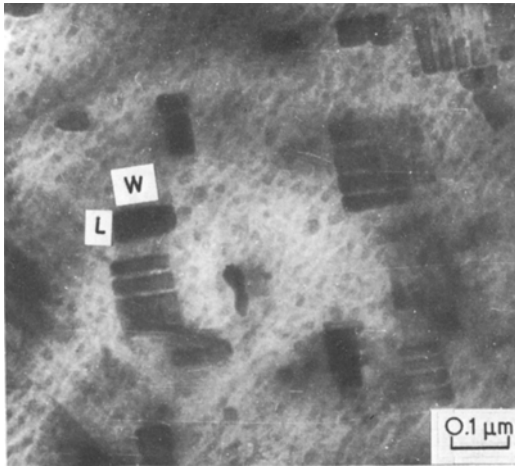


Figure 9 Micrograph of Co-3 wt% Ti-2 wt% Fe aged at 973 K for 48 h showing coarsening of cuboids to yield rectangular particles.

the coarsening of the width appears much faster than that for the length of individual particles along a row with the result that the particles no longer appear as squares but rather as rectangles in a two-dimensional projection. It may be noted that the length of the particle has been defined as the dimension of the particle along a row of particles (Fig. 9). A quantitative representation of this is shown in Fig. 10 for ageing at 873 K. The dimension a corresponds either to the length or width of the particles, as illustrated in Fig. 9.

A quantitative estimate of the coarsening with

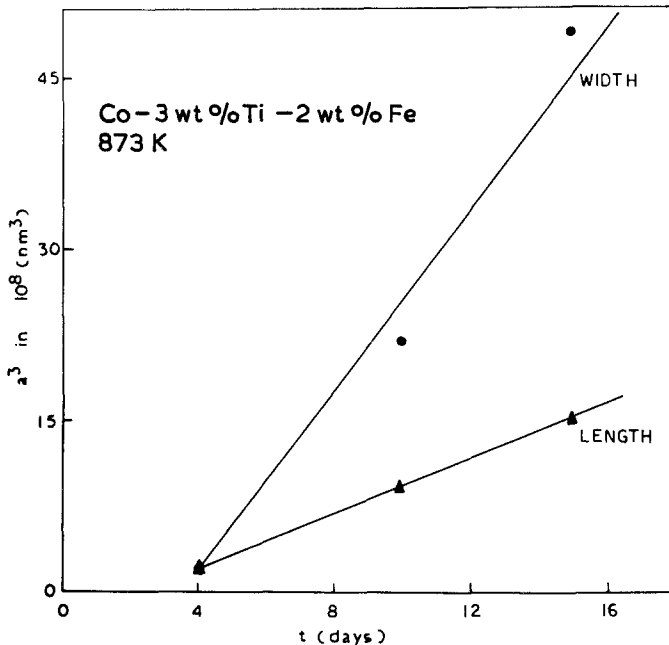


Figure 10 Plot of cube of length and width of particles against time for Co-3 wt% Ti-2 wt% Fe aged at 873 K.

ageing time, t (before the breakdown of the modulated microstructure), is provided by measurement of the wavelength, λ , of the modulations. A plot of λ^3 versus t is shown in Fig. 11. A linear relationship is obtained at both the ageing temperatures indicating that the kinetics of the coarsening can be represented by $\lambda^3 - \lambda_0^3 = Kt$, where λ_0 is the wavelength at the initiation of coarsening and K is a rate constant. A plot of $\log(KT/c)$ against $(1/T)$ then yields the activation energy. Using the data of Fountain and Forceng [1] for c , we obtain an activation energy of 515 kJ mol^{-1} . Comparison with activation energy of self-diffusion in Co and also those of diffusion of Fe and Ti in Co [25] shows that the present value, although of the same order of magnitude, is rather high.

4. Conclusions

(1) Transmission electron microscopy and diffraction has revealed the formation of modulated microstructures and associated satellites in Co-3 wt% Ti-1 wt% Fe and Co-3 wt% Ti-2 wt% Fe alloys. The microstructural changes lend strong support to the concept of spinodal decomposition of these alloys in the range 823 to 973 K.

(2) The mechanical strengthening arising from the modulated microstructures can be traced to the differences in lattice parameters of the co-existing phases.

(3) The kinetics of coarsening of the modula-

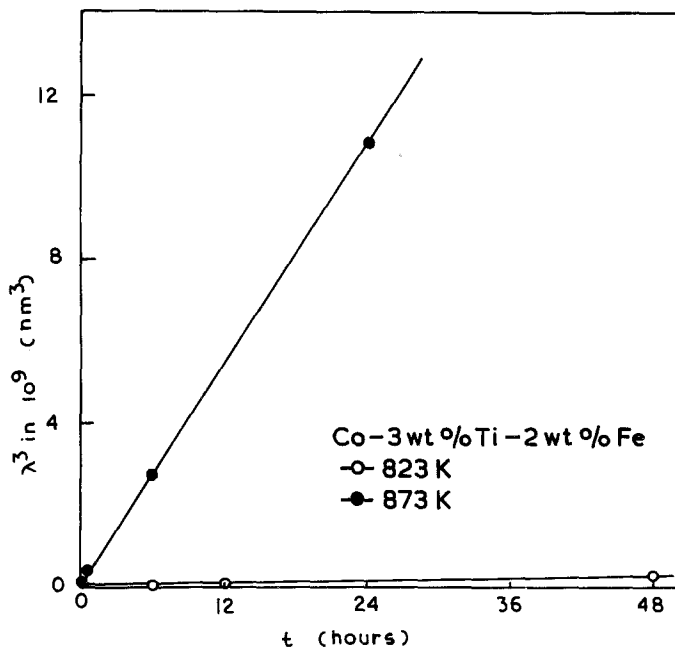


Figure 11 Plot of cube wavelength of modulation against time for Co-3 wt % Ti-2 wt % Fe aged at 823 and 873 K.

tions obeys the $\lambda^3 - \lambda_0^3 = Kt$ relationship with an activation energy value of 515 kJ mol $^{-1}$.

(4) After long ageing, a discontinuous reaction sets in, leading to selective coarsening of precipitates near grain boundaries.

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