Transactions on Engineering Sciences vol 2, © 1993 WIT Press, www.witpress.com, ISSN 1743-3533

A spinodal Cu-Ni-Cr alloy

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ABSTRACT

The Cu-Ni binary system is considered to be an ideal isomorphous system. However, the addition of a ternary alloying element such as Fe, Sn, or Cr is known to introduce miscibility gaps which make these alloys susceptible to heat treatment and change the properties of the binary alloys. Use is widely made of Cu-Ni-Fe alloys as magnetic materials, and Cu-Ni-Sn alloys, after appropriate heat treatment, possess very high elastic limits and are therefore attractive as spring materials. An application of Cu-Ni-Cr alloys is for condenser tubes in sea atmospheres. In this work, Cu-30wtNi-2.5wtCr alloy has been prepared by melting under vacuum and then homogenised. After that, it is heat treated in the range of 300-800^{o}C, and the microstructure and strength of the alloy has been changed via spinodal decomposition. The best temperature and time are found for the optimum mechanical properties. It is seen that this optimum strength is very much bigger than the conventional Cu-30wtNi binary alloy due to periodic spinodal structure.

INTRODUCTION

The heat treatment that will result in spinodal decomposition of a hypothetical alloy of composition C_0 (Fig.1) is as follows: 1.Homogenise at a temperature above the miscibility gap, such as T_1, so that only statistical variations in composition exist within the specimen. 2.Cool rapidly to a temperature within the spinodal, such as T_0, and hold at that temperature, or continuously cool the specimen from T_1 to room temperature, T_R [1]. The decomposition-product phases have the same structure but are different in composition, while in the case of precipitation the precipitate phase has a different structure and composition from that of the matrix. The chief advantage of the products having the same structure is that microstructure is uniform. Therefore no local anodes or cathodes (e.g. as in grain boundary precipitates) to worsen corrosion resistance.

Decomposition of supersaturated solid solutions within the spinodal region of the equilibrium diagram produces composition fluctuations in the elastically soft directions in the crystal [2]. Satellite reflections are produced in the direction of the composition fluctuation with contributions from both the scattering factor variation [3] and the lattice parameter variation [4-5]. In addition, wavelength (interparticle spacing) is constant in the early stages of ageing and this is the second characteristic of spinodal decomposition.

The miscibility gap in the Cu-Ni-Cr system was first reported by Meijering et al.[6-7] by means of metallographic and X-ray diffraction methods at 930^{o}C an isothermal section was determined (Fig. 2). In this work, two face centred cubic phases rich in copper and nickel and one body centred cubic phase rich in chromium were found to exist, although the binary copper-nickel alloys show complete miscibility. Investigations have been carried out on some Cu-Ni-Cr alloys in the composition range close to the copper-rich end of the miscibility gap with the primary aim of developing a substitute for the conventional 70 Cu-30 Ni alloy with higher strength for applications in a marine atmosphere. These studies have led to considerable ambiguity regarding the nature of decomposition in alloys in this region of the miscibility gap. Badia et al.[8] investigated the mechanical properties and microstructure of a series of Cu-Ni-Cr alloys containing 20-54 wt % Ni and up to 4 wt% Cr and found that the maximum strengthening was obtained from alloys containing 30 wt% Ni and over 2 wt% Cr. These authors reported the formation of side bands in quenched and aged alloys and confirmed the presence of a modulated microstructure by electron microscopy. They found that precipitation of an almost pure chromium phase took place in the as-quenched specimens.

Wu and Thomas [9] investigated Cu-28 wt Ni-2.8 wt Cr alloy by tensile testing. The yield stress increased in the early stages of ageing due to spinodal decomposition and then it decreased after long time ageing at high temperatures (Fig. 3, Table 1). After long time ageing at high temperatures, coherent structure was replaced by incoherent structure due to dislocation.

Chou et al.[10] investigated Cu-31.6 wt Ni-1.7 wt Cr alloy by tensile testing and transmission electron microscopy. The homogenised and quenched alloy showed ~130MPa yield stress. The yield stress increased quickly during the early stages of ageing and reached ~260MPa at 650°C after 2 hours ageing. If we compare Chou et al. and Wu and Thomas' results, we can see that Wu and Thomas' results show better mechanical properties. Probably this is due to more chromium content in Wu and Thomas' alloy.

Rao and co-workers [11] have investigated the transformation characteristics of a Cu-27 wt% Ni-2 wt% Cr alloy which lies just outside the miscibility gap and also correlated microstructure and mechanical properties. They have investigated this alloy by means of tensile testing, X-ray diffraction and TEM between 773-1073K ageing temperatures and concluded from morphological features that the coherent spinodal was at 946K. In addition, yield stress increment on ageing was found to follow monotonically coherency strain and to be independent of the wavelength of composition modulation. In figure 4, yield stress, strain amplitude and wavelength versus time are shown at 500°C. It can be seen from this figure that if ageing time increases strain amplitude and yield stress increase and reach the maximum value. After that strain amplitude remains constant. If we compare strain amplitude (ε) with wavelength (λ), we can see that during the early stages of ageing wavelength remains constant, but strain amplitude increases. In the later stages of ageing, wavelength increases inspite of constant strain amplitude on the maximum value. From these results, it is understood that if particles reach to the equilibrium state, coarsening of the particles starts.

The purpose of this work is to substitute of Cu-30Ni alloy with a Cu-Ni-Cr alloy which has better mechanical properties and coherent microstructure and also find out suitable heat treatment and time to get this coherent microstructure.

EXPERIMENTAL PROCEDURE

The alloys of nominal compositions Cu-30 wt% Ni-2.5 wt% Cr were prepared by melting pure copper (99.999%), nickel (99.9%) and chromium (99.9%) in a vacuum arc furnace. Chemical analysis of the alloys by X-ray energy dispersive analysis showed the actual compositions to be as tabulated below:
Cu: 65.6 wt %, Ni: 31.7 wt %, Cr: 2.7 wt %.

After casting and checking the composition, the cast buttons were cut to 2mm thickness using an oil lubricated carborundum slitting wheel. The slices were degreased, coated with alumina powder in order to be a barrier to contact between the discs and sealed into quartz capsules. The capsules were evacuated prior to sealing, flushing with high purity argon twice and finally filled with argon to a pressure of 0.25 atm. and sealed. After homogenisation, they were fast quenched by breaking the tubes in iced water.

Heat treatments were carried out in a vertical tube furnace. The temperature within the hot zone of the furnace was controlled to an accuracy of ± 5°C. Ageing times from 5 minutes to 3 weeks were employed and after the ageing all specimens were fast quenched into iced water.

The 2 mm thick slices were ground to 0.3 mm thickness on 1200 grit SiC paper; and then 3 mm discs were cut by a spark erosion machine. Then thinning was done by jet polishing in a Struers Tenupol unit operating at 19V with a current density of 2.0 A/cm^2 and a temperature of -30°C, using a solution of 25% nitric acid in methanol.

Foils were examined in both a JEOL TEM 120CX operating at 100 kV and a JEOL TEM 2000 FX operating a 200 kV. Chemical analysis of the phases was carried out by X-ray energy dispersive analysis in the 2000FX using a Be holder to eliminate the possibility of a spurious Cu signal being generated.

A Philips PW 1710 X-ray diffractometer equipped with a graphite diffracted beam monochrometer, a Cu anode tube, and a step scan mode was used to observe the sidebands. X-ray diffraction analysis was carried out under the following conditions:- X-ray; CuKα, radiation, voltage, 40kV current, 40 mA scanning speed, $1/4^{0}$ min^{-1}.

RESULTS AND DISCUSSION

1. Obtained Structures:

In the TEM micrographs of as-quenched samples, the periodic structure was not clearly seen in that alloy. No clear periodicity but bend contours in [100] directions are seen to be mottled.

If we look at the microstructures of short time aged samples at 300-400^{O}C, we can only see mottling; however, clear periodic structures are observed above 500^{O}C (Figure 5). Furthermore, no heterogeneous nucleation and grain boundary particles have been observed in short time aged samples, in addition sidebands are observed on both sides of X-ray diffraction peaks.

After long time ageing, the microstructures were clearly periodic showing Cu-rich and Cu-poor regions (Figure 6). In bright field images, bright regions correspond to the Cu-rich phase and dark regions correspond to the Cu-poor phase (as determined by X-ray EDS) since the copper rich regions preferentially thin in the electrolyte used. Both phases contain all three alloying elements and no "pure chromium" phase was observed, contrary to a previous report [8].

The coherent structure was destroyed after long time ageing at high temperatures due to dislocations, grain boundary precipitation and discontinuous precipitation (Figure 6b). Therefore a decrease tendation was seen in the hardness curves (Figure 7). The fcc and periodic structures in <100> directions were seen in Figure 6a.

2. Coarsening Behaviour:

In the early stages of ageing, the wavelength was showing a constant value (Figure 8); however after long time ageing a particle coarsening behaviour was obtained. The coarsening equation was developed by Lifshitz-Sloyozov-Wagner [12-13] and lot of researchers [10-11] found coarsening gradient as 1/3 similar to present results. Figure 9 reflects this case. In this figure, in spite of some deviation from the common gradient a general agreement to 1/3 gradient is observed.

3. Age Hardening:

In the early stages of ageing, hardness values increase quickly due to spinodal decomposition, they remain stable for a while at maximum hardness values and then decrease gradually due to particle coarsening. In this work, the presented hardness values were obtained from the aged samples in the range of 300-800^{O}C.

In the studied alloy, despite the continuous hardness increases on the aged samples at 300-600^{O}C, the gradual hardness decreases were observed after long time ageing at higher temperatures (700-800^{O}C) (Figure 7). The peak hardness was obtained at 600^{O}C after 3 weeks ageing in the present alloy. However, this value does not reflect the maximum hardness value, because the hardness was increasing continuously and the ageing time was not enough to obtain the maximum hardness value. In the range of 700-800^{O}C, the hardness values decreased gradually after 2 hours ageing and the reason of this hardness decreasing was due to the coarsening of the fcc particles. The present work and Wu and Thomas' [9] results are in agreement because in both works the highest strength was obtained at 600^{O}C and it is about ~460MPa. This value is about three times bigger than the classical Cu-30Ni alloy's strength (~130MPa). Therefore, instead of using classical Cu-30Ni alloy in marine atmosphere, a little chromium content (Cu-30Ni-2.5Cr) will give a much better mechanical strength and completely coherent microstructure after suitable heat treatment at a certain temperature (homogenisation + spinodal temperature at 600°C).

CONCLUSIONS

1. If Cu-30Ni-2.5Cr alloy is solution treated at 950°C and aged at 300-600°C, it decomposes via spinodal decomposition and 700-800°C are outside the spinodal.
2. The alloy showed morphological features such as aligned precipitates and absence of preferential precipitations at microstructural inhomogeneities.
3. The highest strength was obtained at 600°C for the present alloy, therefore this temperature is the ideal temperature for the heat treatment of Cu-30Ni-2.5Cr condenser tube material in sea atmosphere and as a result a three times more mechanical strength than Cu-30Ni classical alloy is obtained.
4. In the present alloy, only fcc particles are obtained.

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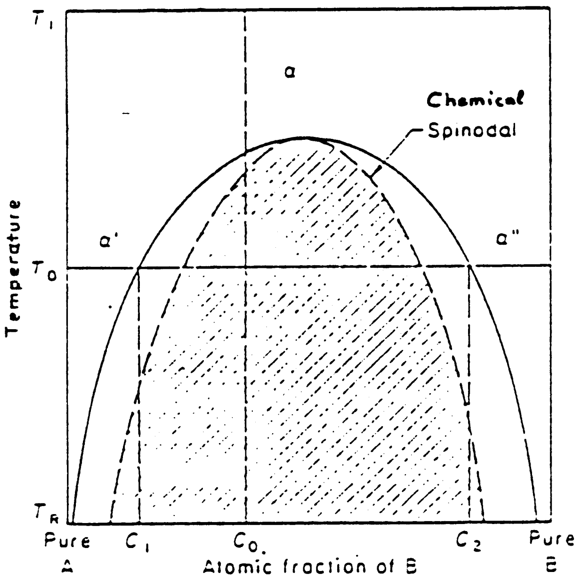

Fig. 1 Schematic phase diagram of a binary alloy system that contains a miscibility gap in the solid state. An equilibrium structure for alloy C_0 at temperature. T_0 would contain two α phases, of compositions C_1 and C_2. The shaded region is the temperature-composition range within which spinodal decomposition can occur [1].

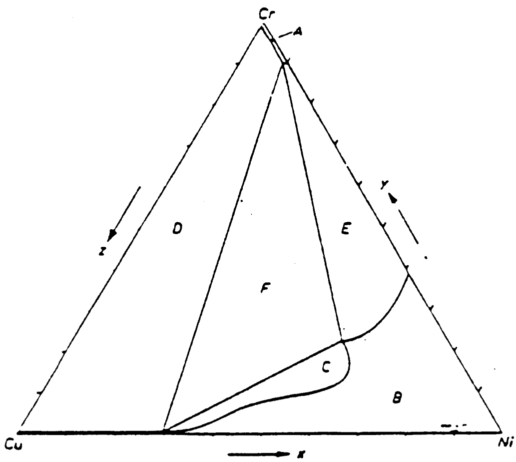

Fig. 2 Cu-Ni-Cr phase diagram at 930°C, experimental [6]. Atomic concentrations. A: homogeneous bcc; B: homogeneous fcc; C: 2 fcc phases; D: bcc+Cu-rich phase; E: bcc+Ni-rich fcc; F: bcc+2 fcc phases.

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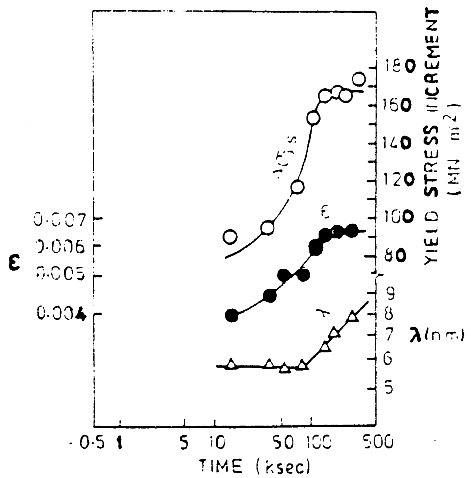

Fig. 3 Plot of yield stress vs log (ageing time) for alloys aged at 600 and 700°C [9].

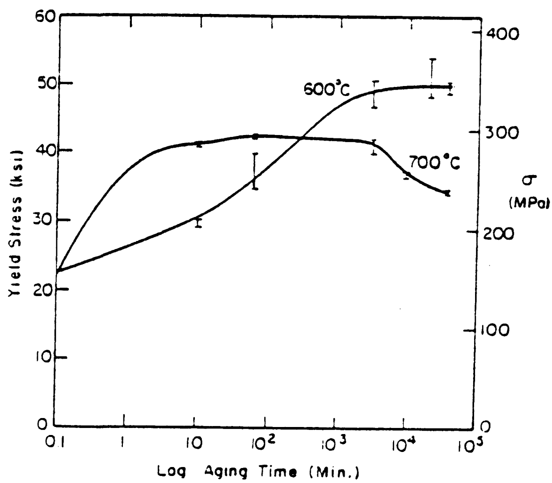

Fig. 4 Variation of wavelength, strain amplitude and yield stress increment with ageing time at 500°C [11].

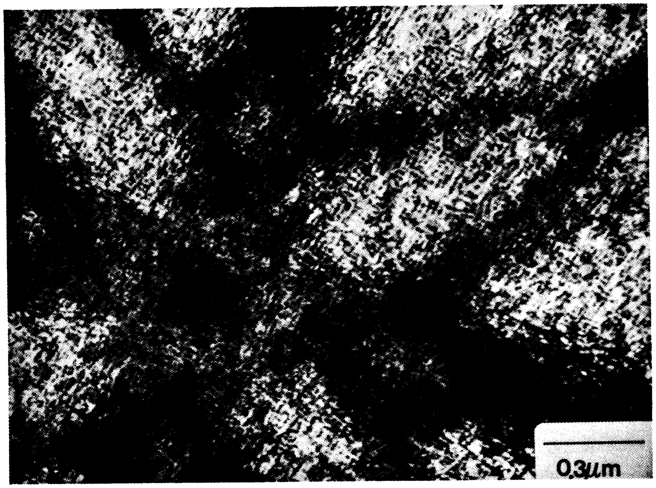

Fig. 5 Bend contours and periodic structure in the 2.5Cr alloy after 1 day ageing at 500°C, $\lambda \sim 200$Å.

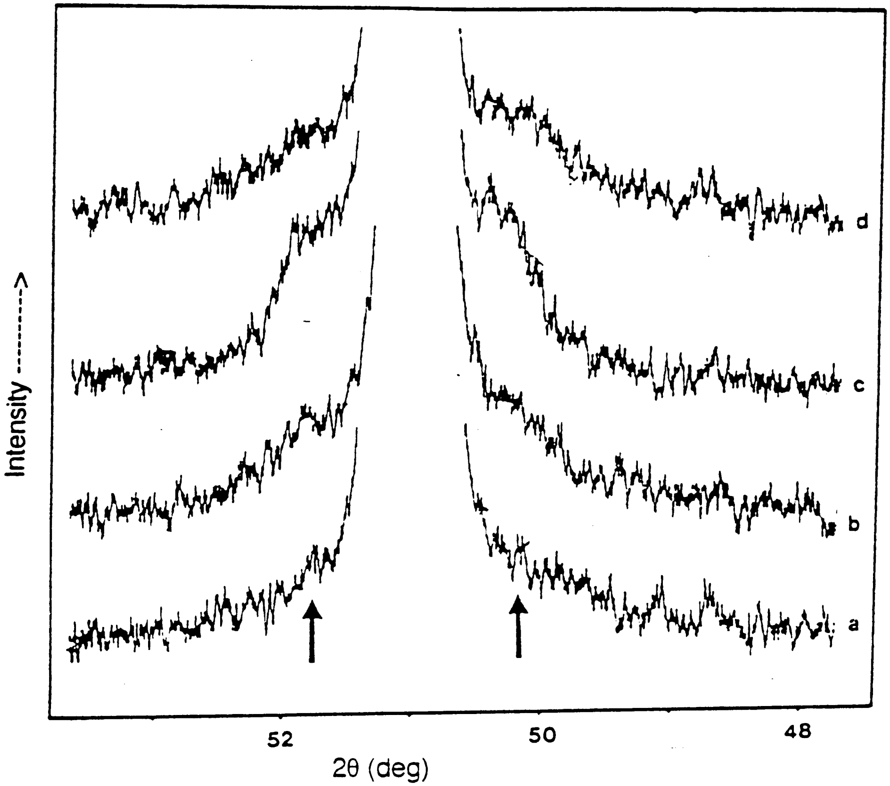

Fig. 6 Sidebands in the X-ray diffraction patterns of spinodal 2.5Cr alloy in (200) planes, due to the lattice parameter variation and the scattering factor variation: a) 2 hours aged at 300°C, b) 1 week aged at 400°C, c) 1 week aged at 500°C, d) 20 minutes aged at 600°C.

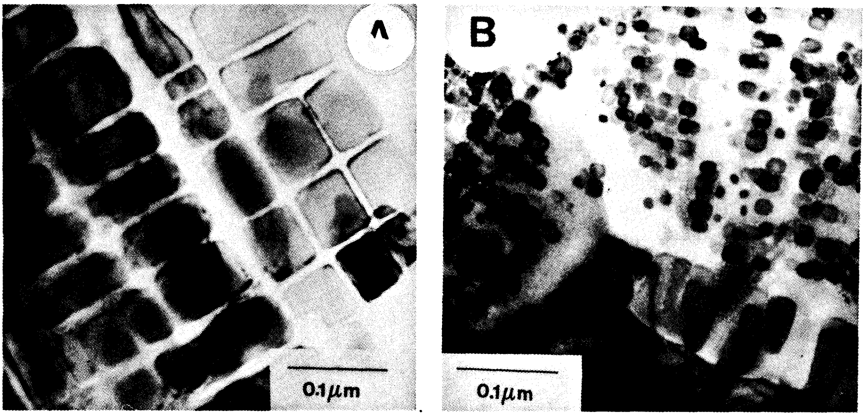

Fig. 7 More clear periodic structure (A) and discontinuous precipitation (B) after long time ageing. (A: 3 weeks aged at 700°C, B: 3 weeks aged at 600°C).

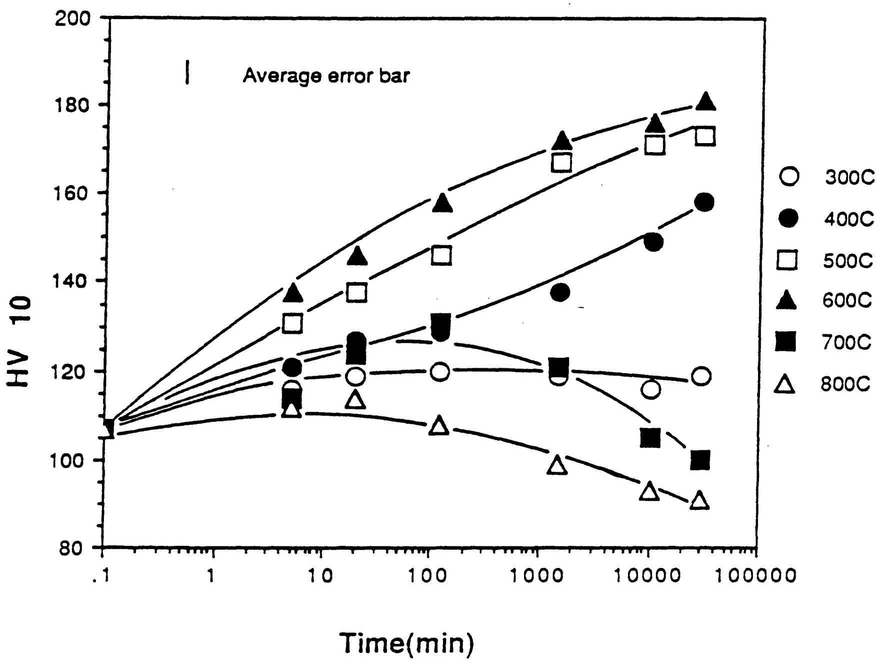

Fig. 8 The relationship between hardness and time during ageing in the range of 300-800°C in various times for the 2.5Cr alloy.

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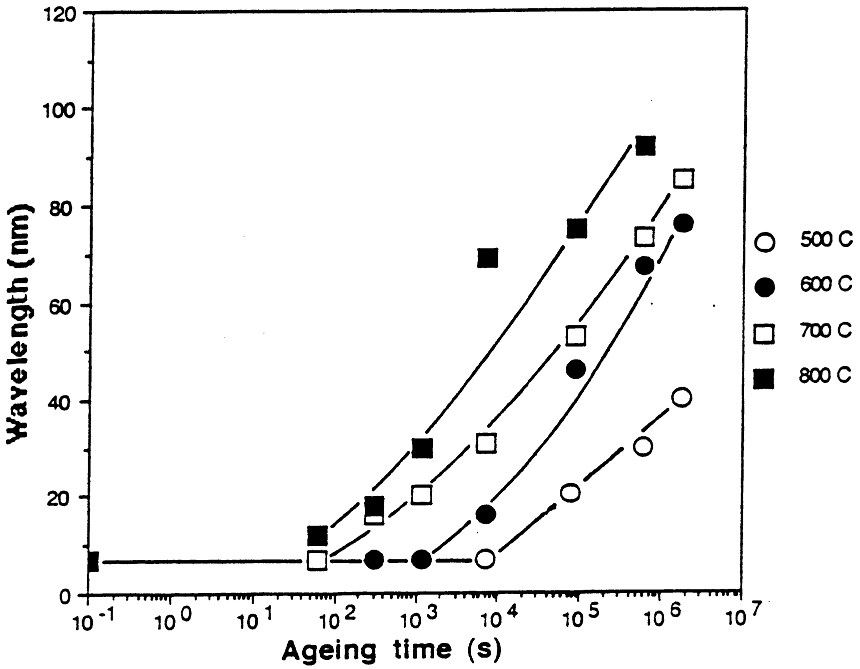

Fig. 9 The graphs of wavelength versus ageing time for all alloys during the early and later stages, showing a constant wavelength during the early ageing times.

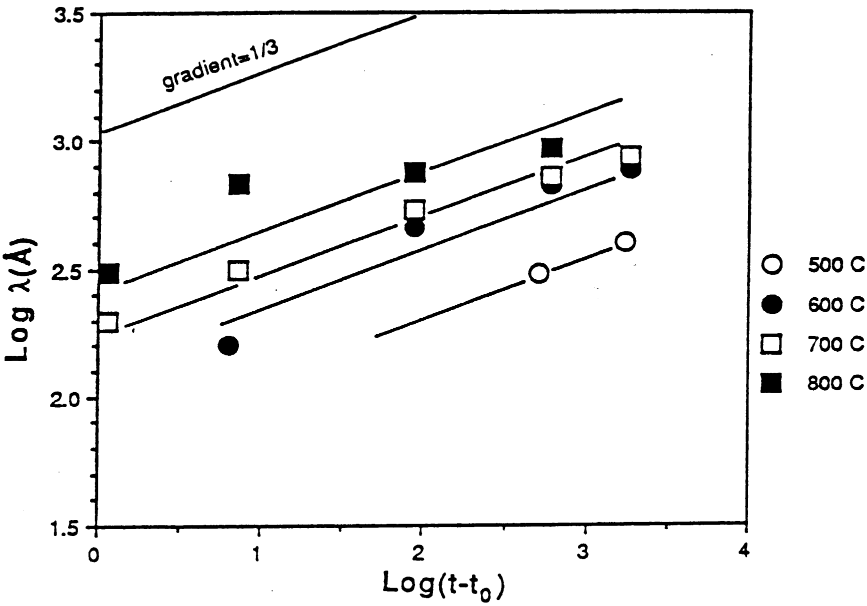

Fig. 10 The relationship between wavelength versus coarsening time at different temperatures for the 2.5Cr alloy.

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(a) 700°C

Aging time	As Quenched	10 min.	1 h.	50 h	166 h.	616 h.
Yield stress (KSI)	22.5	41.1	42.3	42.1	36.3	34.6
(MPA)	155.	283.	291.	290.	250.	238.
Ultimate tensile stress (KSI)	51.0	56.8	64.4	61.2	53.2	56.7
(MPA)	352.	391.	444.	422.	367.	391.
Elongation	32%	22%	18%	13%	18%	

(b) 600°C

Aging time	As Quenched	10 min	1 h	50 h.	340 h	616 h
Yield stress (KSI)	22.5	29.6	37.9	48.6	51.4	49.6
(MPA)	155.	204.	261.	335.	354.	342.
Ultimate tensile stress (KSI)	51.0	57.4	58.3	61.1	66.5	65.3
(MPA)	352.	396.	402.	421.	459.	450.
Elongation	32%	25%	16%	8%	8%	7%

Table 1 Tensile test results of the material at 700 and 600°C [9].