A SMALL ANGLE NEUTRON SCATTERING STUDY OF PHASE SEPARATION KINETICS IN ITS EARLY STAGES IN Cu-0.9 at% Ti

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Abstrak

STUDI SANS PADA KINETIKA SEPARASI FASA DALAM PADUAN LOGAM Cu-0,9 at % Ti. Telah dilakukan investigasi separasi fasa dalam paduan logam Cu-0,9at%Ti dengan menggunakan metode hamburan neutron sudut kecil dan sudut besar. Suhu *aging* yang dipilih untuk perlakuan panasnya adalah 573 K. Suatu skala dispersi halus dari fasa kedua Cu_4 Ti di dalam matriks pada paduan logam tembaga titanium, yang terakumulasi selama tahap-tahap awal dalam separasi fasa kinetiknya, dapat menjadi faktor penguat yang signifikan terhadap paduan logam tembaga-titanium. Kandungan titanium tang rendah, yaitu hanya sebesar 0,9at% saja, sengaja dipilih agar diperoleh kebolehjadian yang lebih besar untuk dapat berlangsungnya proses separasi fasa pada tahap-tahap awal. Suhu *aging* yang rendah juga dipilih dengan alasan yang sama, karena dapat berlangsungnya proses separasi fasa tahap awal merupakan faktor penentu untuk memperoleh sifat-sifat paduan logam yang lebih baik. Perangkat hamburan neutron sudut kecil dipilih sebagai alat ukur dalam investigasi ini oleh karena kemampuannya untuk menyajikan hasil analisis struktural dari ketidaklarutan paduan, baik pada tahap-tahap awal ketika fluktuasi komposisinya masih kecil, maupun pada tahap lanjut dalam proses separasi fasa. Tahap lanjut ini juga perlu diamati, agar dapat dipastikan batas yang jelas antara tahap awal dan tahap lanjut dalam suatu proses separasi fasa.

Abstract :

Phase separation kinetics in supersaturated Cu-0.9at% Ti alloys after isothermal heat treatment at 300 °C (573 K) are investigated by small and wide angle neutron scattering. A fine scale dispersion of the second phase Cu4Ti within a copper-titanium solid sulution, which is accumulated during the very early stage of phase separation, can lead to significant strengthening. Up to the present, no investigation have covered these very early stages in copper titanium alloys. The low titanium content of 0.9 at% was chosen in order to have a better possibility to study the phase separation process in its early stages. The chosen low aging

temperature leads to slow decomposition kinetics and, hence, is favourable to investigate early stage decomposition. Small angle neutron scattering (SANS) is used in this work because of its ability to provide access to structural analysis of unmixing alloys, in both the early stages where the composition fluctuation can be small in spatial extension and in amplitude, and in the later stages of decomposition. These later stages are needed to be covered, in order to assess the transition from earlier stages to the later stages of phase separation.

Keywords : Cu-0.9at% Ti alloys, phase separation, early stages, SANS.

1. Introduction

An addition of a few percent titanium to the copper matrix is well known to enhance its strength substantially, which is rendered possible by both solid solution and, in particular, age hardening. Without any addition of other metallic elements, pure copper is a good conductor and can easily be plastically formed at room temperature, but it suffers from a lack of strength. A fine scale dispersion of second phase precipitates within the matrix of a copper-titanium alloy can lead to significant strengthening. This commonly results from the decomposition of the solid solution during cooling from the single phase state at high temperature into the two-phase state at lower temperatures. For reasons of entropy, the single phase state a of a solid solution with a certain composition is thermodynamically stable only at elevated temperature. At lower temperatures the free energy of a binary system is lowered through phase separation or decomposition of a phase into two phases α and β.

One of the interesting and attractive properties af highly supersaturated Cu-Tirtamarta alloys develop from the formation of periodic precipate microstructures during aging, givinr rise to satellites around the main Bragg's Peaks [1]. Those Cu-Ti alloys thus belong to a class of alloys, which are termed "sidebands" alloys.

Decomposition of supersaturated metastable solid solution is initiated via formation of stable nuclei of the second phase, then proceeds to a more or less pronounced growth regime, and finally ends in a coarsening reaction of precipatates. In the 'classical' picture of decomposition of a metastable supersaturated solution, during nucleation and growth of stable nuclei the matrix becomes depleted from solute atoms. This leads to an increase for the critical size R^* of the nuclei, and consequently result in a strong decrease of nucleation rate. The coarsening reaction starts when the supersaturation of the matrix has been reduced so much that the crical radius R^* becomes larger than the radius R of the smaller precipitates within the size distribution. The latter then start to redissolve [2-4].

In an isothermal precipitation reaction, the kinetics are qualitatively characterized by an early stage during which the number density N_v of precipitates increases with time t. If the particles are assumed to be spherically shaped solute rich clusters, a size distribution g (R (t)) with a mean radius $\overline{R}$ is formed. During the early stages, $\overline{R}$ increases and the supersaturation decreases. A small reduction of supersaturation is sufficient to terminate the nucleation of new particles; this state of phase separation is indicated by the maximum of N_v (t). For any homogeneous precipitation reaction, in the earliest stages of the reaction, the precipitate phase β is still coherent with the parent phase α. In the Cu-Ti system the evolving β - Cu_4Ti precipitates are coherent with the parent phase α ; however, the β - particles are associated with significant coherency stresses which give rise to the strengthening of the two phase alloy.

2. Experimental

2.1. Preparation of samples

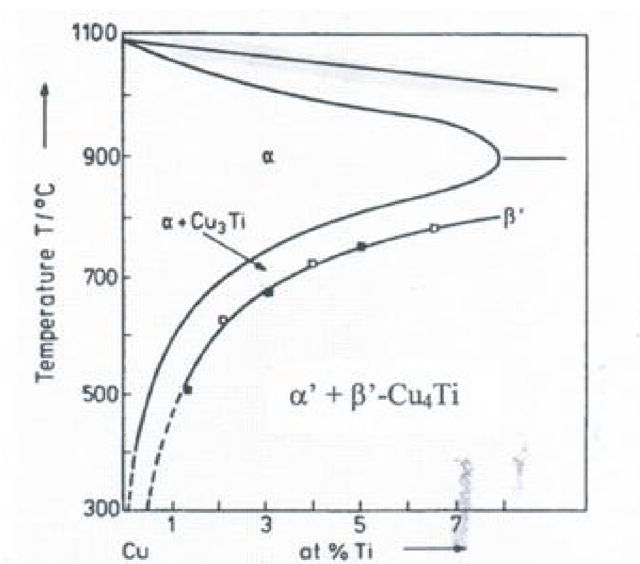


Figure 1. Copper titanium phase diagram

According to copper titanium phase diagram mentioned above, a low titanium concentration of 0.9 at% Ti and a low aging temperature of 300 °C are chosen, in order to assure the alloy to lie within the two phase region below the metastable coherent solvus line for Cu-0.9at% Ti and to make sure that the reaction kinetics are rather sluggish. Therefore, these slow-motion processes in phase separation kinetics during the early stages of the decomposition reaction can be followed experimentally.

The single crystal samples of Cu-0.9at% Ti necessary for this present study, were grown by the Bridgman technique, in which a mold containing the melt, is lowered from the hot zone of a vertical tubular furnace into the cold zone. In order to initiate a precipitation reaction, the alloy is first homogenized in the single phase region and then quenched into brine prior to isothermal aging at a temperature within the two phase region. The homogenization temperatures used are 750 °C and 850 °C, under a dried Argon atmosphere, and after this homogenization the single crystals are rapidly quenched into water. A salt bath and a vacuum furnace are used for a short and a long aging time respectively.

Many Cu-Ti samples had been homogenized at 750 °C; 850 °C, and then step by step aged at 300 °C for different aging times. Samples number 15 and 19 represent the two homogenization temperatures, namely sample 15 at 850 °C, and sample 19 at 750 °C. Aging times for these two Cu-Ti samples are shown in Table 1.

Table 1 : Aging treatments at 300 °C of samples 15 and 19

Homogenized	Sample 15 Aged [s]	Aged[min]	Sample 19 Homogenized	Aged [s]	Aged[min]
850 °C	20		750 °C	20	
	60	1		60	1
	120	2		300	5
	300	5		3600	60
	600	10			
	1200	20			
	3600	60			
	7200	120			
	18×10^3	300			
	36×10^3	600			
	486×10^3	8100			

2.2. Optimization of the Aging Temperature

As the objective of the present work is to study unmixing of the low alloyed Cu-0.9at% Ti during the early stages, the aging temperature must be optimized such that diffusion of Ti atoms in the Cu-matrix is still possible, i.e. the aging temperature TA must be sufficiently high. On the other hand, TA must be sufficiently low for the unmixing kinetics to be kept sufficiently slow.

For this purpose we chose T_A = 300°C (573 K) for following reason: The

diffusion length, $\bar{x}_{diff}$, covered by a diffusing Ti atom ought to be larger than the mean distance, $\bar{x}_{nuc}$, between two Cu4Ti nuclei. $\bar{x}_{diff}$ can be estimated from the chemical diffusion coefficient as

$$D_{Ti} = D_0 \cdot e^{-Q/kT} \qquad (1)$$

It was measured for a Cu -0,9at% Ti solid solution between 973 K and 1283 K [5]. It has been given as

$$D_{Ti}(T) = 1.4\times10^{-4}.\exp\left\{-\frac{204.10^3\,J/mol}{R_g T}\right\}\left[\frac{m^2}{s}\right] \qquad (2)$$

where Q is the activation enthalphy, R_g the molar gas constant. The diffusion coefficient D_{Ti} could not be measured at temperatures below 973 K. Thus, in order to estimate D_{Ti} at 573 K, one has to extrapolate the high temperature data which Eq. (2) is based on, to low temperatures. For 573 K one obtains

$$D_{Ti}(573K) = 3.54\times10^{-23}\left[\frac{m^2}{s}\right] \qquad (3)$$

$\bar{x}_{\text{diff}}$ after aging time of t_A at 300^o C can be estimated from

$$\bar{x}_{diff} = \sqrt{D_{Ti}(573K).t_A} \qquad (4)$$

As we are interested in early stage decomposition reactions, $\bar{x}_{\text{diff}}$ after an aging time of t_A = 20 s at 300^o C can be accounted for by substitution of D_{Ti} from Eq. (4). One obtains

$$\bar{x}_{\text{diff}} = 2.6\text{x}10^{-7}\text{m} = 260\text{nm}$$

The average interparticle distance can be estimated from a relation $\bar{x}_{\text{nuc}} \cong \frac{1}{\sqrt[3]{N_v}}$, if one assumes that Cu4Ti particles to be arranged on cubic lattice with lattice constant $\bar{x}_{\text{nuc}}$.N_v can be estimated from :

$$N_v = \frac{f_e}{\frac{4\pi}{3}.R_{LSW}^{*\,3}} \qquad (5a)$$

and

$$f_e = \frac{c_o - c_e}{c_p - c_e} \qquad (5b)$$

Here f_e denotes the equilibrium precipitated volume fraction f_e $f(t_A$) which will be attained after long aging times once the nucleation process has terminated. R_{LSW}^* represent the size of the critical nuclei, and may be given as [6]

$$R_{LSW}^* = \frac{2\sigma_{\alpha\beta}V_m}{R_g T}.\frac{1-c_e}{c_p - c_e}.\frac{1}{\ln\frac{c_o}{c_e}} \qquad (6)$$

with : $\sigma_{\alpha\beta}$ = interfacial energy between Cu matrix and Cu_4Ti particle = 0.031 J/m^2 [7]

c_o = the nominal Ti concentration, which in this case 0.9 at%

c_p = the Ti content in the Cu_4Ti partcles, in this case 20 at%

c_e = concentration of Ti in solid solution with the fully precipitated Cu_4Ti microstructure

V_m = 7.8 cm/mol is the molar volume of Cu_4Ti particle

From Eq. [6] one obtains

$$R^*_{LSW}\left(t_A \rightarrow 0\right) = 0.79nm$$

which is in a good agreement with the experimental result.

If one now assume that at the earliest stage of unmixing, the precipitated volume fraction,

$$f(t\ \ 0)\ \frac{1}{10}\ f_e\,(t\ \ )$$

one finally obtains from Eqs. (5) and (6) :

$$\bar{x}\,\frac{1}{\sqrt[3]{N_v}}\,\frac{4\pi}{3}R^*_{LSW}\,\frac{10}{f_e}^{1/3}\;R^*_{LSW}\,\frac{4\pi}{3}\,\frac{10\left(c_p c_e\right)}{c_o c_o}^{1/3}\;nm$$

$$\bar{x}_{\text{nuc}} \cong 4\text{ nm}$$

This estimation clearly shows that

$$\bar{x}_{\text{diff}} \gg \bar{x}_{\text{nuc}}\ ,$$

and thus indicating that the mobility of Ti atoms in the Cu matrix is sufficient to migrate during 20 s at 300 °C over distances which correspond to more than the separation length between two nuclei.

One therefore may infer that one can follow the precipitation reaction in Cu-0.9at% Ti during isothermal aging at 300 °C within a time window ranging from a few seconds to some hours. Hence, an aging temperature of 300 °C seems to be appropriate for studying the early stage decomposition kinetics in a Cu0.9at% Ti alloy.

2.3. SANS Measurement of Cu-0.9at% Ti Samples

The Cu-0.9at% Ti sample is first measured in its homogenized condition in order to get a reference scattering curve before the phase separation has occurred. This data would be used as a standard for the analysis of scattering curves after the samples being aged and measured. The difference in SANS-curve taken from aged and homogenized samples contains actually the information on the aging process, or in other words, the information on the state of separation in the particular sample. These informations come from interparticle interference of the scattered wave.

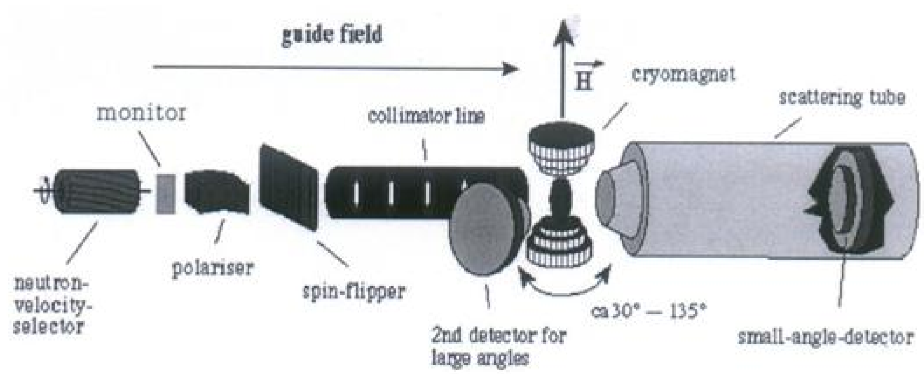


Figure 2. Schematic view of SANS-2 at GeNF-GKSS-Geesthacht

SANS-2 facility at Geesthacht Neutron Facility (GeNF) in GKSS Research Centre (Geesthacht-Germany) was used for this work. SANS-2 is one of the two SANS beam lines at GeNF. The neutrons produced in the nuclear reactor FRG-1 and cooled down in the cold source are guided through neutron guide No. 8 to this instrument. A sketch of the SANS-2 set-up is shown in Fig. 2.

Velocity selector with $\Delta\chi/\chi$ of 10 % (standard) and 20 % resolution are used as monochromators. Wavelengths of 0.4 and 0.57 nm were used during the measurements. Two Cu-0.9at% Ti single crystal samples were chosen to show the phase separation kinetics process in these alloys, and in addition for wide angle measurement (WANS) with the 2nd detector, a pure copper sample was used as a reference. This copper sample was measured together with the Cu-Ti samples in each step during measurements, in order to assure the acceptable conditions of the neutron flux during experiments. Measured intensity was corrected for sample transmissions, background, and detector efficiency. The absolute cross-sections were calculated by comparison with the incoherent scattering from vanadium.

Data Reduction and Data Analyses

Since a great deal of the theory of neutron scattering involves the calculation of the differential cross-sections, the data reduction and data analyses must also be related to the differential cross-sections.

The terms of data reduction and data analyses, technically refer to different procedures. Data reduction refers to procedures such as background subtraction, whereas data analyses refers to procedures of data interpretation, fitting theoretical models to the experimental scattering curves, etc.

A set of software programs for viewing, reducing, and analysing SANS data which have been written by colleagues from GKSS Research Centre Geesthacht were used for this work.

One of the program mentioned above is SANDRA (as an abbreviation of **SAN**s **D**ata **R**eduction and **A**nalyses), which is used to view SANS spectra and calculating scattering curves by radial or sector integration of the spectra.

SANDRA calculates the macroscopic differential cross-sections from the recorded experimental data as follows

$$\frac{d\Sigma}{d\Omega}(k) = \frac{I(\Omega)}{M.\left(\frac{I_0}{M}\right)\Delta\Omega\eta T_R L} \qquad (2)$$

where M = monitor for the neutron count rate after monochromator
η = detector efficiency
T_R = sample transmission

Table 2. Time-dependent parameters of the Cu_4Ti precipitate microstructure

Sample 19				
t_A/300 °C	$\bar{C}$ x 10^3	$f(t_A)$ x 10^{-2}	$\bar{R}$ [nm]	N_V (t) x 10^{19} [cm^{-3}]
00s	8. 76	not determ.	Not determ.	Not determ.
20s	8. 27	0.29	0.483	0.63
60s	8. 03	0.38	0.495	0.78
300s	7. 55	0.63	0.529	0.98
3600s	6. 49	1.03	0.572	1.16
Sample 15				
t_A/300 °C	$\bar{C}$ x 10^3	$f(t_A)$ x 10^{-2}	$\bar{R}$ [nm]	N_V (t) x 10^{19} [cm^{-3}]
00s	8.75	not determ.	not determ.	not determ.
20s	8.36	0.26	0.363	2.75
60s	8.32	0.28	0.380	2.31
120s	8.29	0.29	0.391	2.11
300s	7.92	0.44	0.404	2.60
600s	7.81	0.49	0.409	2.61
1200s	7.64	0.56	0.435	2.07
3600s	6.95	0.84	0.464	2.29
7200s	6.12	1.17	0.484	2.58
18.10^3 s	4.08	1.69	0.528	2.41
36.10^3 s	2.79	2.51	0.634	1.77
$486.\ 10^3$	2.01	2.82	1.470	0.14

Since the incident neutron count rate in front of the sample (I o) could not be measured right at that posotion where the incident neutron beam enters the sample, it was necessary to use a relation with the neutron count rate (M), from a detector which was positioned behind the monochromator (c.f. Fig. 2.). After reducing the measured data from its background and other corrections needed, one receives a corrected curve which then is ready for further interpretation.

The calculated time-dependent values of $f(t_A)$ for both samples 15 and 19 are shown in a Table 2.

Results and discussions

Figure 3 and 4 show the two dimension spectra of sample 15. These four of 2d-SANS pattern of <100> oriented single crystal clearly show an anisotropic scattering intensity maxima along the <001> and <010> directions. The anisotropy pointing towards strong alignment of the longer c-axis of the tetragonally distorted Cu4Ti particles into <100> directions, increases during longer aging times of sample 15, starting from its homogeneous condition (Fig. 3) to the longest aging times of 135 h (8100 min) at 300° C (Fig. 4).

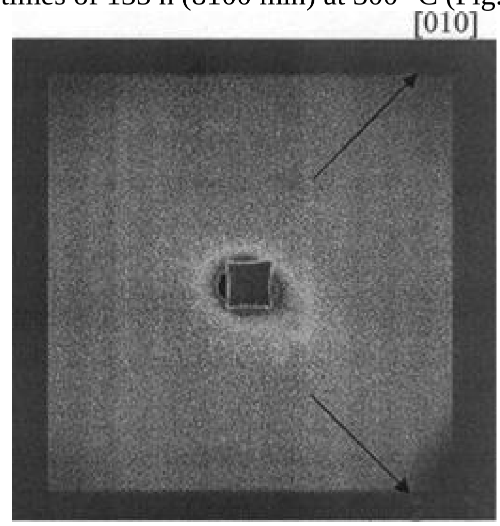


Figure 3. Sample 19; Homogenized at 750 °C and quenched

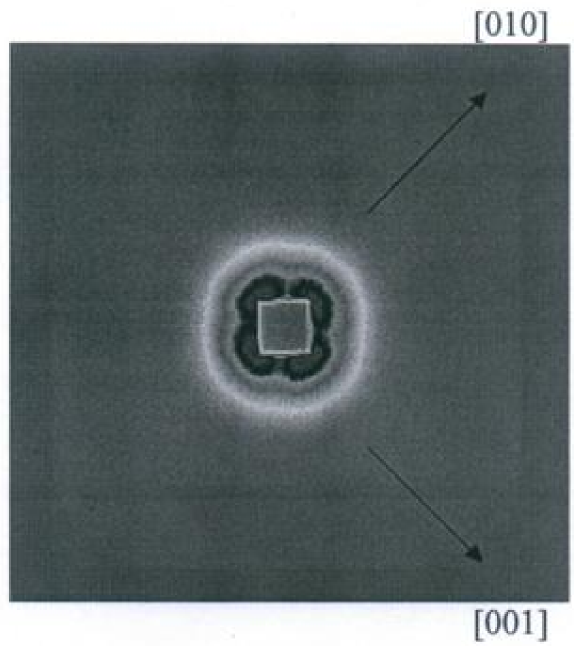
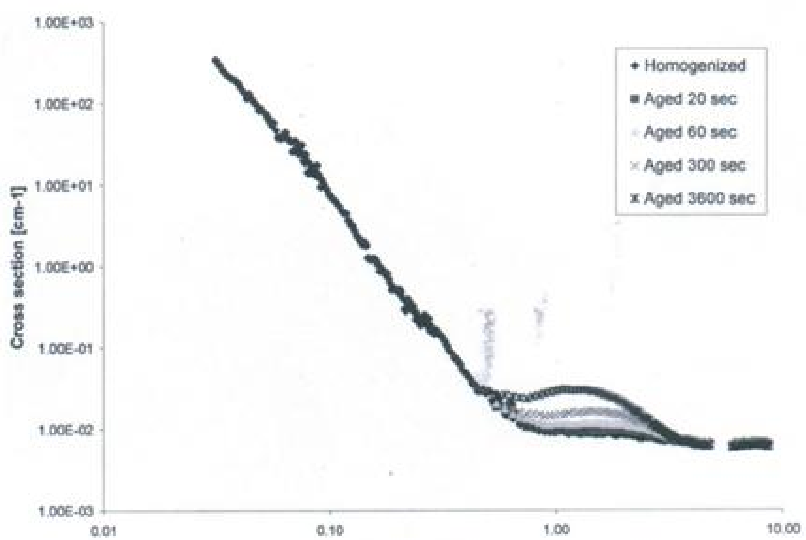


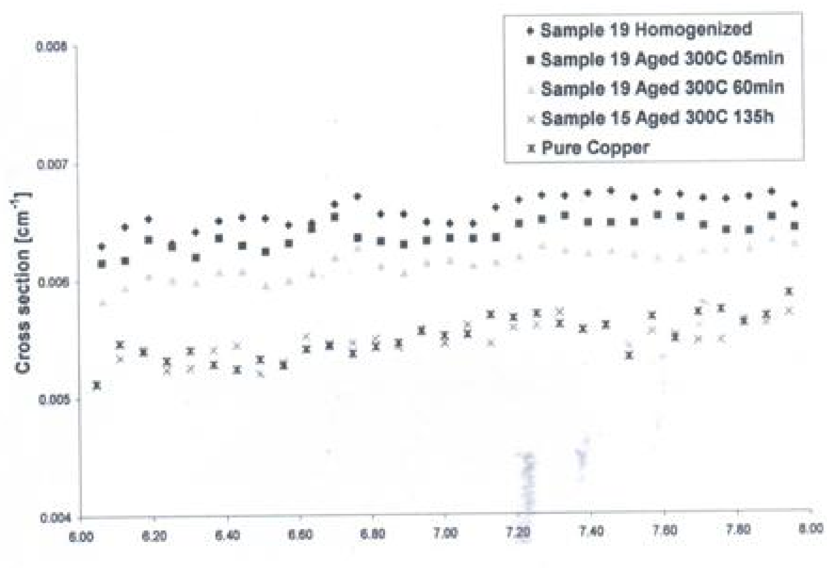
Figure 4. Sample 15; Aging for 8100 min at 300 °C



Scatt vector [nm^{-1}]

Figure 5. Scattering curves for sample 19 in different aging states ; both SANS data and WANS data were used for obtaining the shown scattering curves.

Fig. 5 shows the scattering curves of sample 19 for five different states of heat-treatment. Even in its homogenized condition, it can be clearly recognized that very small precipitates had been formed already during quenching, i.e. the state of a homogeneous solid solution could not be sustained upon quenching; the finely dispersed precipitation become discernible by a weak broad maximum in the cross-section of the dark-blue (homogenized) curve. Using SANS allows one to distinguish between different states of precipitate microstructures even if the sample has been aged for only 20 s at 300 °C following quenching. This clearly indicates that diffusion and associated unmixing is rather fast. Those differences in the scattering behaviour of a sample aged for 20 s are only disclosed by SANS but not WANS. However, the potential and benefit of employing also WANS shows up in samples which had been aged at, 300 °C at considerably longer aging times (e.g. $t_A \geq 5$ min; Fig. 6). Fig. 6 shows the differences of Laue scattering (K ≥ 6 nm $^{-1}$) as determined by WANS of sample 19, in comparison to the longest aging times, 8100 min (135 h), of sample 15, and a pure copper sample. From the rather similar Laue scattering of the long aged aged (135 h / 300 °C) sample 15 and the pure copper sample, one may infer most of the titanium atoms in the Cu-0.9 at% Ti alloy had already been consumed for the nucleation process and for further growth of the Cu4Ti particles; only a few Ti atoms are left in solid solution.



Scatt vector [nm^{-1}]

Figure 6 The Laue scattering intensity of sample 19 as determined by WANS, in comparison with the longest aging times (135h) of sample 15, and a pure copper sample

Conclusions and recommendation

The present study shows that a supersaturated Cu-0.9at% Ti had already undergone some unmixing during quenching, thus a homogeneous solid solution could not be established at the beginning of isothermal aging at 300 °C. However, nevertheless during short term aging at 300 °C the supersaturation was still sufficiently high to drive further unmixing. As the kinetics at 300 °C are rather sluggish, it became possible to follow the phase separation process experimentally in the early stages where nucleation still has occurred, by using small angle neutron scattering techniques (SANS). SANS provided the kinetic parameters to determine the time evolution of the precipitate volume fraction, the cluster size distribution and, hence, the cluster number density, and the mean cluster size, in fact, during the early stages of decomposition prior to significant coarsening. The scattering pattern clearly proved the precipitates to be of the metastable coherent type Cu_4Ti. The large coherency strains associated with the high number density of Cu_4Ti particles will give rise to an efficient and strong strengthening of the two phase Cu-Ti alloy.

As the present work has yielded quantitative insight into time evolution of the precipitate microstructure and, on particular, the time evolution of the mean size and the number density of the Cu_4Ti particles, all relevant parameters for following the strengthening potential of the precipitate microstructure at different aging stages have been obtained. It is thus recommended to correlate the evolution of the precipitate microstructure with its influence on age hardening. For this purpose, single crystals with the same composition and aging treatments should be subjected to a study of their yield strength or hardness.

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