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THE STRAIN INDUCED DECOMPOSITION OF THE QUASI BINARY Cu_3NiMn ALLOY DURING THERMAL AGEING

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Introduction

The Cu-Ni-Mn ternary system shows a strong thermal age hardening in the vicinity of the Cu-/NiMn/ quasi-binary composition /1/. Our previous investigations /2,3,4/ have shown that the processes taking place during the thermal ageing of the Cu_3NiMn alloy homogenised at 800°C previously depend on the temperature of the treatment but the fundamental tendency of the phase transition is the decomposition into separate Cu and ordered NiMn phases. Above 460°C the decomposition occurs by the normal nucleation-growth type precipitation, and between 410°C and 460°C by spinodal -decomposition. However, below 410°C a homogeneous ordered solid-solution is being formed which is similar to the NiMn lattice /Ll_0 type/ but diluted by random distributed copper atoms /5/. This is a metastable phase and its formation is connected with the extremely slow decomposition at lower temperatures due to the slower long-range diffusion. On the other hand all the processes are very slow; to reach the equilibrium state of the alloys one needs more than 10^3 hours for most temperatures. This is due to the strong tetragonal distortion of the new ordered phase causing a considerable deformation of the lattice and the deformation energy in first approximation is near to the energy of ordering /4/. This is in agreement with the observation that below 410°C the ordered phase nucleates at the grain boundaries where the deformation energy might be considerably smaller. On the contrary the samples having been deformed plastically before ageing show in the whole temperature range a much faster decomposition.

Experimental conditions

The composition of the alloy studied was Cu 59,2 at %, Ni 20,0 at %, Mn 21,0 at % and Fe 0,8 at %. In a few cases measurements were carried out on samples without any iron but that only proved that the iron content does not modify the processes considerably though it may slow them up slightly /6/.
Our investigation is based on X-ray diffraction experiments taken on filings and using a de Wolff type Guinier-camera. For the heat treatments the filings were sealed into evacuated glass capsules.

Experimental results

It is characteristic for the whole temperature range that the 200 reflexion of the alloy splits into three lines. Two of them correspond to the 200 and 002 lines of the ordered Ll_0 type lattice whereas the central one - belonging to the cubic disordered matrix - is shifted to higher angles showing a significant decrease of the lattice parameter a_c /FIGS. 1,2/. This indicates the decreasing NiMn concentration of the matrix.

This process differs from normal precipitation in that the new phase initially does not give sharp, well defined lines, and therefore is only observable in a progressed phase of the transition, though its lattice parameters change even after this considerably. It can be well observed on FIG.2. that with increasing the temperature a recovery of the lattice takes place which causes the deformation induced internal strains to relax above 450°C within a comparatively short time, and at the same time the decomposition process ceases, too. To indicate that this was not yet above the solubility limit we annealed a sample at 480°C which was previously heat treated at 445°C. Not only the tetragonal phase did not vanish, but even the line breadth, that means the lattice distortions remained considerably large /empty circles on FIG.2./.

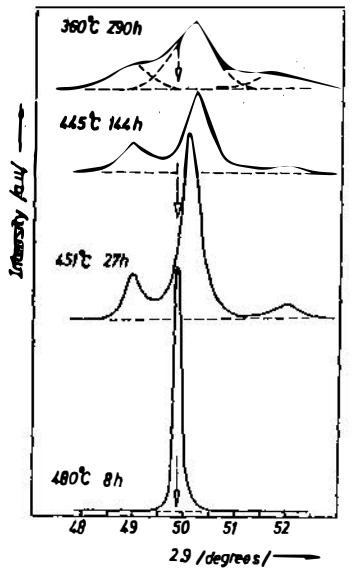

FIG.1.

The 200 reflexion of samples aged at different temperatures. All the samples were near to the equilibrium corresponding to the temperature of the treatment.

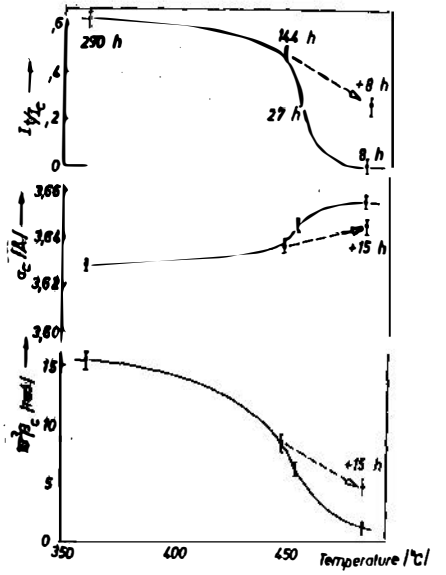

FIG.2.

The ratio of the intensities scattered by the tetragonal and cubic phases, the lattice parameter of the cubic matrix and the width of the cubic 200 line as the function of the temperature /from FIG.1./ The open circles represent the result of a two-step ageing.

Very similar two-step heat treatments were carried out to analyse the re-solution of the precipitated phase and the data of FIG.4. show that for samples with 40% NiMn content the solubility limit is at about 500°C.

Discussion

From the experimental data it is quite obvious, that though the investigated process seems to be very similar to spinodal decomposition it is entirely different from it and it can only progress considerably if the lattice was strongly deformed beforehand. It is well known that the formation of

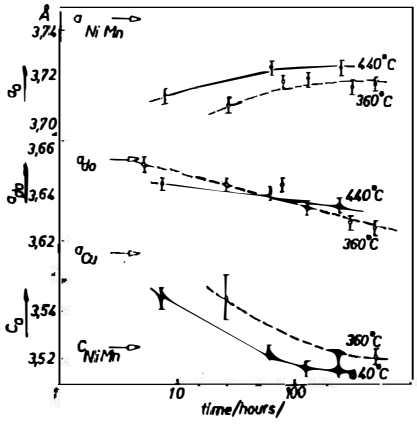

FIG.3.

Lattice parameters vs time for 360°C and 440°C. The subscripts do, c and o refer to the disordered initial lattice, to the cubic matrix and to the ordered lattice respectively.

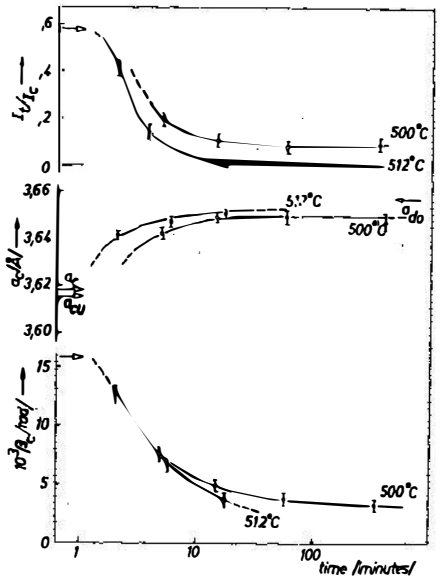

FIG.4.

The result of the two-step ageing. The samples were pre--aged at 360°C for 240 hours

an ordered NiMn phase causes considerable tetragonal distortions in the lattice /c/a 0,94/, along with a volume contraction of about 2%, and that is just the reason why this transition never takes place in a homogenized /or annealed/ sample. On the other hand, if the samples were deformed from the beginning, the ordered tetragonal structure that forms in the strongly contracted zones of the matrix, causes the internal strains to relax. This means that here the effective binding energy between the Ni-Mn pairs becomes larger, and that results the Ni and Mn atoms to diffuse against the deformation gradient. As a result certain domains of the matrix will have a higher NiMn concentration, where the new phase arises coherently with the parent matrix and the deformed state of the lattice remains stable.

On the basis of this model the temperature dependence of

the lattice parameter change is also clear /FIG.3./. For instance the two straight lines, indicating the lattice parameter change of the cubic phase, have an intersection, because at 360°C the whole process is very slow and the lattice strains do not relax considerably even during this long period of time; at 440°C however, the process, starting comperatively quickly, stops very soon, just because of the relaxation of the strains, which induce the whole decomposition process. /The continuous line on FIG.3. shows practically the end of the process./

Acknowledgment

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DISCUSSION :

E. Babić : Have any electrical measurements been made and what are the results obtained ?

T. Ungar : The system shows a strong age hardening effect which is accompanied by pronounced decrease of resistivity along with a volume contraction.

H.J. Seeman : Did you perform any magnetic measurements ?

T. Ungar : The ordered NiMn alloy is antiferromagnetic. There are some measurements on the magnetic susceptibility but the processes reported in our paper were not followed by this technique.