The application and interpretation of the "time law" to the growth of β grain size and martensite plate thickness in copper-based martensites

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Isothermal growth of β grain size in Cu–AI and Cu–AI–Zn martensitic alloys can be described approximately by the well-known "time law", $D = K \cdot t^n$. The martensite plate size (thickness) d_m , formed in quenched β grain is a function of the β grain size, d_β . The mutual relationship can, to a good approximation, be described by the expression $d_m = C \sqrt[3]{d_\beta}$, where $C \cong 1$, which means that the exponent *n* for β grain size is three times that for the martensite plate size. This important empirical relationship emphasizes the fact that while the β grains can grow in three dimensions, the martensite plate can grow only in one dimension, i.e. in a direction perpendicular to the austenite/martensite interface. A Hall-Petch relationship exists between the yield stress and the β grain size and the martensite plate thickness.

1. Introduction

In a number of previous communications [1-7] it was shown that the martensite plate size (thickness) in copper-based alloys is a function of the β grain size in which it subsequently forms and also that a Hall-Petch relationship exists between the yield stress and the β grain size/ martensite plate thickness. The most important basic contributing factor to the strength of martensite is the martensite plate size. The β grain size is a function of the annealing time and so also is the martensite plate size subsequently formed in it. The β grain size, d_{β} , and the martensite plate thickness, d_{m} , are closely interrelated.

It is now universally accepted that martensitic transformations are diffusionless transformations which utilize the co-operative movement of many atoms over very short distances and thus retain their immediate neighbours but in somewhat differently arranged positions. The short co-ordinated displacement of atoms and the macroscopic shear or shape change are the two basic criteria to define a martensitic transformation [8]. The martensitic transformations take place by the movement of dislocation 1290 interfaces which become glissile under the influence of either chemical or mechanical driving force.

Even though the kinetics of isothermal growth of martensite is well-understood and is also well-documented and the mechanism of nucleation and growth of martensite plates has lately been dealt with extensively [8-13], there are still very few measurements of the rate of growth of martensite plates. A number of models incorporating arrangements of lattice defects for which no experimental proof is available have been suggested to describe the growth. Contrary to this, there are many more measurements of the growth of bainite plates but they lack agreement between the theoretical models and the experimental data [8].

Thermodynamically, martensite forms in metals or alloys when the free energy of the transformed martensitic phase is lower than that of the parent phase. The nucleation of martensite requires extra energy to overcome the barriers such as interfacial and strain energies. At below the M_s , (temperature at which martensite begins to form) the free energy of the martensitic phase is lower than that of the parent phase and marten-

site begins to form and proceeds as the temperature falls. Most of the martensitic transformations are temperature dependent and proceed with the fall of the temperature. The growth of martensite plates in these transformations is very fast and approaches the speed of an elastic shear wave in solid. Because of such fast growth rates, the overall kinetics of athermal martensites depends on the nucleation frequency [8-13].

The isothermal growth of austenite grain size and its effect on the martensite burst size (i.e. first formed plates) in Fe-Ni-C was studied by Entwisle and Feeney [10] who observed that the magnitude of the burst size is a function of the austenite grain size and of the temperature at which burst occurs. Marder and Krauss [14] have shown that both the austenite grain size and the martensite packet size (consisting of parallel laths) in Fe-0.2% are functions of the austenitizing temperature and that the ratio of grain size to packet size remains more or less constant. A Hall-Petch relationship holds for both grain size and the packet size. Similar results have been obtained by others in many ferrous martensites [15-18].

Coincidentally, the twin thickness [19, 20] and the sub-grain size [21] have also been found to be functions of the grain size in which they form and a Hall-Petch relationship can be used to describe the yield or flow stress as a function of twin thickness/sub-grain size.

This paper describes the isothermal growth of

 β grain size in Cu-Al and Cu-Al-Zn martensitic alloys and its effect on the martensite plate size formed in it on quench. It has been shown that the well-known "time-law" applies to the growth of both the β grain size and the martensite plate size and that the exponent *n* for β grain size is 3 times the *n* for martensite plate size.

2. Experimental procedure

The materials (for composition see Fig. 1) with a constant electron concentration were supplied by Ampco Metal Inc, Milwaukee, USA, in the form of forged bars of about 60 cm length and 2.5 cm diameter. They were further hot swaged to 1 cm diameter. Cylindrical specimens, 10 mm long and 8 mm diameter, were prepared from the swaged bars turned to about 8 mm.

The specimens, three at a time, were sealed in evacuated quartz tubes and heat-treated at 950°C for 1, 4, 16 and 64 h to obtain different β grain and martensite plate sizes. The high temperature stable bcc phase, β , in these alloys transforms to an ordered orthorhombic 3R-type martensitic structure on quenching into water [5, 7].

The average β grain size, d_{β} , was determined by the standard lineal analysis and the average martensite plate thickness, $d_{\rm m}$, was measured from a large number of blocks or packets of parallel plates, as is shown in Fig. 2.

The compression tests were carried out on a TT-DM-L Instron testing machine at an initial



Figure 1 Cu-Al-Zn ternary diagram showing the composition of the alloys investigated.



Figure 2 (a) Schematic representation of martensitic structure and (b) martensite plate blocks in Cu-Al-Zn β -type martensite (\times 200).

deformation rate of $5 \times 10^{-2} \text{ min}^{-1}$. The faces of the specimens were lubricated with molybdenum disulphide to reduce friction.

3. Results

The observations made on various alloys have 1292

been summarized in Table I. The values of the constants K and n from d_{β} or $d_{m} = K \cdot t^{n}$, from the time law which describes the normal isothermal grain growth in metals and alloys [22-26], have also been included in the table. It can be seen that the exponent n for d_{β} is 3 times the

Alloy	Time (h)	<i>d</i> _β (μm)	$\sqrt[3]{d_{eta}}(\mu\mathrm{m}^{1/3})$	<i>d</i> _m (µm)	d _m ³ (μm ³)
1	1	250	6.30	5.49	165
	4	340	6.98	6.17	235
	16	1050	10.17	8.58	630
	64	4940	17.20	12.13	1795
			$d_{\rm m}=4.40$. $t^{0.245}, d_{eta}=180$). $t^{0.735}$	
			i.e. $d_{\rm m} = 0.79 \sqrt[3]{d_{eta}}$		
2	1	280	6.50	6.42	265
	4	530	8.10	7.90	490
	16	860	9.51	10.40	1126
	64	3000	14.42	13.74	2590
			$d_{\rm m}=6.16$. $t^{0.185}, d_{eta}=2$	200 . t ^{0.556}	
			i.e. $d_{\rm m} = 1.05 \ \sqrt[3]{d_{\beta}}$	r	
3	1	270	6.46	6.29	248
	4	520	8.04	7.97	505
	16	1250	10.77	11.76	1624
	64	3330	14.93	14.87	3270
			$d_{\rm m} = 6.29$. $t^{0.207}, d_{\beta} =$	240 , $t^{0.622}$	
			i.e. $d_{\rm m} = 1.01 \sqrt[3]{d_{\rm f}}$	3	
	$ \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{$	(d _m) (d _β)	e e	(1). (1). (1) (1) (1) (1) (1) (1) (1) (1)	$ \begin{array}{c} $
	1	1 2 3	4 5 10 2	20 50	100 200

TABLE I Data on the growth of β grain size and martensite plate thickness as function of annealing time. The validity of time law is obvious

Figure 3 The growth of β grain size (d_{β}) and martensite plate thickness (d_m) as a function of holding time at 950°C.

TIME t (HOURS) -

exponent n for d_m and K for d_m is approximately equal to $K^{1/3}$ for d_{β} .

Fig. 3 shows the same data in graphic form. In Fig. 4 the inter-relationship between the β grain size and the martensite plate thickness has been

given; $d_{\rm m}$ has been plotted against the cube root of the β grain size, i.e. against $\sqrt[3]{d_{\beta}}$, and shows a linear relationship between the two parameters. As a matter of fact, a single line can be drawn, instead of the separate lines for each of the



Figure 4 Relationship between the cube root of B $(\sqrt[3]{d_{\beta}})$ and martensite plate thickness (d_m) for alloys 1, 2 and 3.

alloys, to pass through the origin to represent the linear relationship between the martensite plate thickness and the cube root of the β grain size. Such a line has also been drawn in Fig. 4.

The existence of the Hall-Petch relationship is obvious from Fig. 5 in which the yield stress (0.2%) has been plotted against d_m^{-1} and against $(\sqrt[3]{d_\beta})^{-1}$. The same relationship is also valid for the reciprocal of the square root of the β grain size, i.e. d_{β}^{-1} . It should be noted that if in Fig. 5 a different vertical scale (i.e. 1 cm = 2 kg mm⁻² instead of 1 cm = 1 kg mm⁻² which has been used) is chosen single lines can be drawn to represent the relationship between the yield stress and the martensite plate thickness and the β grain size. The six lines in Fig. 5 would then be reduced to three to represent the same relationship.

4. Discussion of results

The nucleation and growth of martensite plates is so well-documented [8-11] and well-understood that it hardly needs any detailed discussion. We would, however, like to point out that the long period annealing at 950°C results in disappearance of lattice imperfections, such as dislocations, stacking faults, sub-grain boundaries etc, which serve as nucleus sites for martensitic transformation. The longer the annealing time, the lower is the number of the sites available for plates to nucleate. As the number of the sites available is reduced, each plate has more space to grow and broaden before being obstructed by another plate. Furthermore, the semi-coherent interface between the parent phase and the martensitic phase is subject to being hung up by the lattice imperfections thereby restricting the interface movement and plate thickening. High-temperature holding anneals out the lattice defects and thus minimize the pinning effects. Such an effect would level off when the defect density in the parent phase drops to a minimum, i.e. when the material is in a fully annealed state. Further annealing would not result in reduction of either defect density or additional plate thickening. Our observations on the variation in plate thickness (due to change in holding time) which directly depends upon the number of plates lead to the logical conclusion that the number of nucleated plates depends upon the holding time. If then our assumption about the annealing out



Figure 5 $\sigma_{0.2}$ as a function of $d_{\rm m}^{-\frac{1}{4}}$ and $(\sqrt[3]{d_{\beta}})^{-\frac{1}{4}}$ for alloys 1, 2 and 3.

of defects as a result of holding the material at high temperature is correct, we believe that the number of the plates nucleated in quenched material is directly proportional to the concentration of lattice defects in the β phase at the time of quench.

From these observations, therefore, we feel justified in concluding that the "time law" which was originally used to describe the normal grain growth, but has since been found to be valid for the growth of martensite plate size, is also applicable to the annealing out of the lattice defects in the β -phase.

It is worth mentioning that the thickening of martensite plates can continue with the same speed even if the length-wise growth is stopped by the impingement with another plate, sub-grain or β boundary, as has also been observed by Speich [27] and Goodenow and Heheman [28].

Of great scientific interest is the relationship $d_{\rm m} = C\sqrt[3]{d_{\beta}}$ where $C \cong 1$, which means that the exponent *n* for β grain size is three times that for the martensite plate size. Similarly, *K* for d_{β} is equal to $K^{1/3}$ for $d_{\rm m}$. This empirical relationship can be explained by the fact that whereas β grains grow three-dimensionally, the martensite plates can grow only in one dimension, i.e. in a direction perpendicular to the parent/martensite interface.

5. Conclusions

It has been established that long period annealing of Cu-Al and Cu-Al-Zn β -type alloys at high temperature results in β grain growth and martensite plate thickening which can be described by the well-known "time law", $D = K \cdot t^n$. The size of the martensite plates formed on quenching these alloys is a function of the β grain size and their subsequent growth can, to a good approximation, be described by the same law. The martensite plate growth can be expressed by the relation $d_m = C\sqrt[3]{d_\beta}$, where $C \cong 1$. This means that the exponent *n* for the β grain size, d_β , is three times the exponent *n* for the martensite plate thickness, d_m .

This can be explained by the fact that a β grain grows in three dimensions but a martensite plate can grow only in one dimension, i.e. in a direction perpendicular to the parent/martensite interface. Furthermore, if the number of martensite plates nucleated is directly proportional to the number of lattice defects in the parent β phase, then it can be concluded that the "time law" is also applicable to the annealing out of the defects in the β phase.

Acknowledgements

This investigation was carried out at the Department of Metallurgy, Katholieke Universiteit Leuven, Heverlee, Belgium, and the author wishes to express his gratitude to Professors L. Delaey and M. J. Brabers for their keen interest and valuable guidance. He is thankful to Professor A. Deruyttere for the provision of the research facilities, to the Belgian Ministry of Education (Directorate International Cultural Relations) for the grant of a Research Fellowship and to Ampco Metal Inc, in general, and Mr R. J. Cox, Vice-President-Engineering, in particular, for the donation of the alloys used in this investigation. The author also wishes to thank Ir. A. Langstraat, Head of Materials Engineering Department, FDO, for the encouragement and facilities which enabled the preparation of this paper.

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Received 14 January and accepted 15 February 1974.