Effects of cooling rate on the formation of kappa phase in the Cu-Al-Ni-Fe-Mn system

E. S. BHAGIRADHA RAO and A. T. PAL

SYNOPSIS

Nickel-aluminium bronzes of Cu-Al-Ni-Fe-Mn system are one of the more promising of the several alloy types considered for propeller castings. Castings of this alloy type in the composition range of 79% Cu-10 Al-5 Ni-5 Fe-1 Mn, combine high strength and ductility with excellent corrosion resistance. Since these optimum properties are very closely associated with the introduction of an additional phase, designated k (kappa), in the microstructures of this alloy system, an attempt has been made to study the types, size, composition and hardness of this phase and the factors responsible for it.

The paper first discusses the basic principles involved in melting the nickel-aluminium bronzes and producing sound test pieces in sand casting so as to reproduce the standard mechanical properties. The k phase formed therein has been studied, analysed and its hardness measured. Subsequently, various melts have been taken to observe the effects of different cooling rates on the types, amounts and sizes of k phase formed.

Studies suggest that slower cooling rates favour predominant formation of massive and large k phase, whereas rapid cooling results in predominant formation of fine k phase. Further, it has been observed that these two types (large and finely divided) of k phase, in general, have different degrees of etching characteristics, indicating that the phases have variable compositions. The phase compositions have been determined by electron microprobe analysis.

FOR the past twenty five years, aluminium bronzes of the 'complex' type have been produced by the additions of iron, nickel and manganese in amounts of the order of 5%, 5% and 1% respectively, with aluminium close to 10%. Since the alloy combines excellent strength, ductility and corrosion resistance of both static and fatigue type, with a high degree of castability, it finds widespread use as naval propeller material and in other marine applications. Other useful properties of complex aluminium bronzes include high wear resistance, oxidation resistance, good croop strength and also elevated temperature tensile strength.

The excellence of the mechanical properties of the alloy is ultimately attributed to the transformation of the high temperature beta phase to an additional phase termed kappa (k) in an alpha-matrix, in the temperature range of 780°-800°C.[1] As the mode of formation of the k phase is reported to be influenced by the cooling rate which, in turn, affects the mechanical properties and corrosion resistance of the alloy[2], an attempt has been made in the present work to study the effects of cooling rates on the types, sizes, shapes, hardness and composition of the k phases, using metallographic techniques and electron micro-analysis.

Brief review

The typical values of some of the properties in different conditions of the alloy are given[3] in Table I. The foundry of this alloy presents some major practical difficulties due to its special characteristics, and as such, necessitates considerable modification in melting and casting techniques which deviate from normal copper-base foundry practice. The special characteristics are :[4,5]

1. Heavy shrinkage of the alloy (Approx. 4%).
2. Short freezing range : about 10°C.
3. Consistency of melt composition is hindered by the reactions between aluminium and copper oxide, and aluminium and oxygen, in the absence of an appropriate cover, resulting in variation of final aluminium content.
4. Gas troubles are likely to occur due to hydrogen because of the reduced solid solubility of hydrogen in aluminium bronzes.
5. The irreducible aluminium oxide layer does not coagulate with other oxides or deoxidants, and is likely to be entrapped in the casting proper during pouring, due to turbulence.
6. Melt preparation consistent with uniformity in composition is rendered difficult by alloying additions of Fe, Ni and Al.

Messrs E. S. Bhagiradha Rao and A. T. Pal, Defence Metallurgical Laboratory, Hyderabad.

TABLE I Typical properties of complex aluminium bronze

Type as per BS 1400 condition	Al %	Composition				0·1% proof stress tons/in²	Tensile strength tons/in²	Elongation percentage on 2″ G.L.	IZOD value ft/lbs	Hardness VPN	Air fatigue tons/in²	Salt water fatigue tons/in²	Tensile strength at 400 °C tons/in²
		Ni%	Fe%	Mn%	Cu%								
AB1 Die cast	8·5 to 10·5	1·0 max.	1·5 to 3·5	1·0 max.	Rest	14	38	30	40	180	Not available	—	—
AB1 Sand cast	do	do	do	do	do	12	35	25	30	140	—	—	—
AB2 Die cast	do	3·5 to 5·5	4·5 to 6·5	1·5 max.	do	19	45	25	12	210	—	—	—
AB2 Sand cast	do	do	do	do	do	18	42	17	18	180	15	11	—
AB2 Sand cast & heat treated	do	do	do	do	do	28	49	13	—	210	—	—	—
AB2 Hot rolled	10·0	5·0	5·0	—	do	30	50	18	15	225	21	11	24

The techniques generally adopted to overcome these difficulties include :[6,7]

1. Provision of generous feeders suitably located to effect gross shrinkage.
2. Rapid pouring with least turbulence and conformity to directional solidification to counter the short freezing range.
3. Provision of charcoal cover over the melt to minimise variations in aluminium content.
4. Final flushing of the melt by nitrogen and use of dry sand molding to minimise gas porosity.
5. Modification of the gating system, provision of dross traps and adoption of 'semi-Durville' method of pouring to minimise turbulence.
6. Adoption of either of the following practices of melt preparation for ensuring better alloying effect :
   (a) Direct melting by master alloy additions
   (b) Melting virgin stock for pre-ingoting with subsequent remelting.

Experiments in sand casting

The following experiments were undertaken to make sand cast test bars, with a view to reproducing standard mechanical properties and to obtain the related structural characteristics :

Molding

Molding sand of the following composition and properties was used :

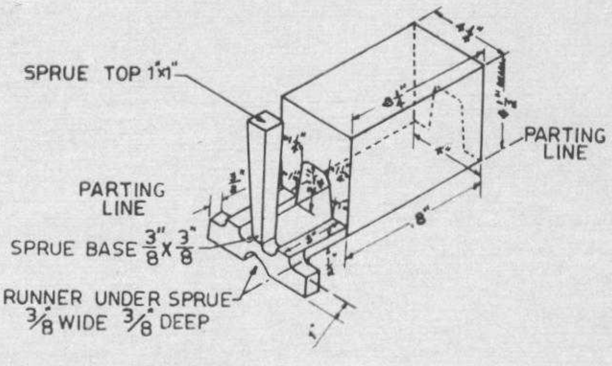
50 : 50 mixture of foundry sand and pure silica sand

Bentonite	...	3 to 4%
Green strength	...	6·5 lb per sq. in.
Permeability	...	190 AFS
Moisture	..	4%

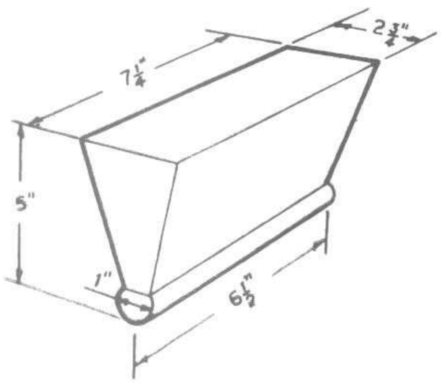
Two test bar molds, one conforming to ASTM : B208 : 63 and the other to BS 1400 : AB2, were made. The casting designs together with gating system are given in Figs. 1 and 2. The prepared molds were thoroughly dried before pouring.

Melting

The charge consisting of the materials as shown in



1 *ASTM testbar casting*



2 *BSS testbar casting*

TABLE II Charge for pre-ingoting

Metal	Grade	Percentage
Copper	Electrolytic	79
Aluminium	Commercial	10
Nickel	Shot	5
Iron	Armco	5
Manganese	Electrolytic	1

Table II was melted in crucible furnace, for pre-ingoting.

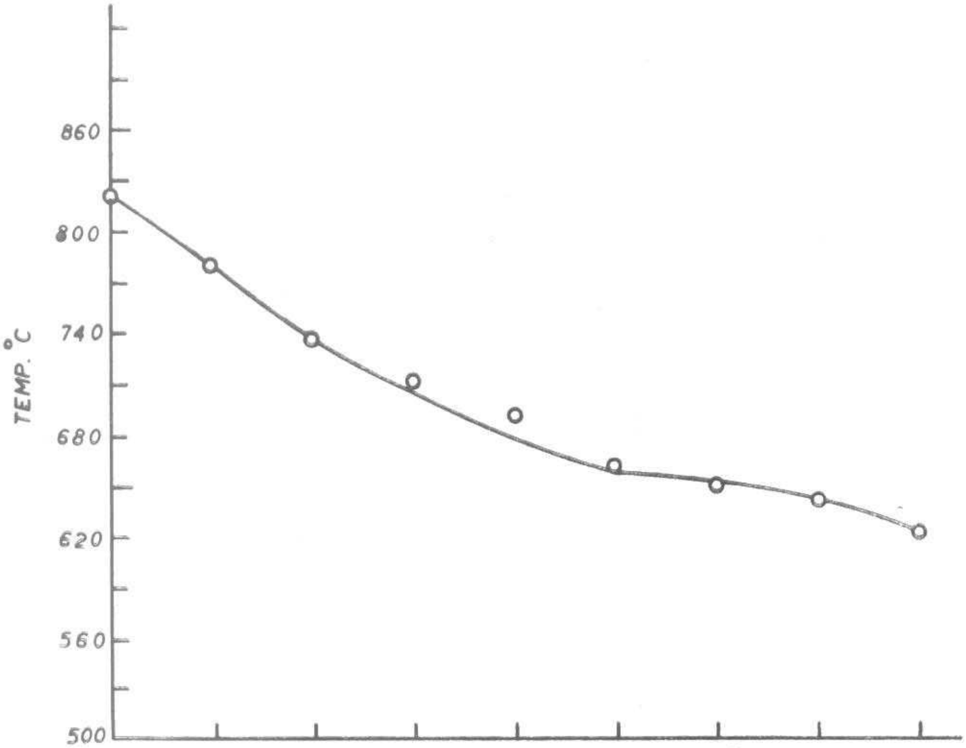
The pre-ingoted metal was remelted with a charcoal cover followed by final flushing with nitrogen for about 2–3 minutes. The metal was poured at 1250°C.

Chemical analysis and mechanical properties of the testbar castings were determined. Micro-examination was carried out by using metallographic techniques and phase compositions analysed in electron microprobe.

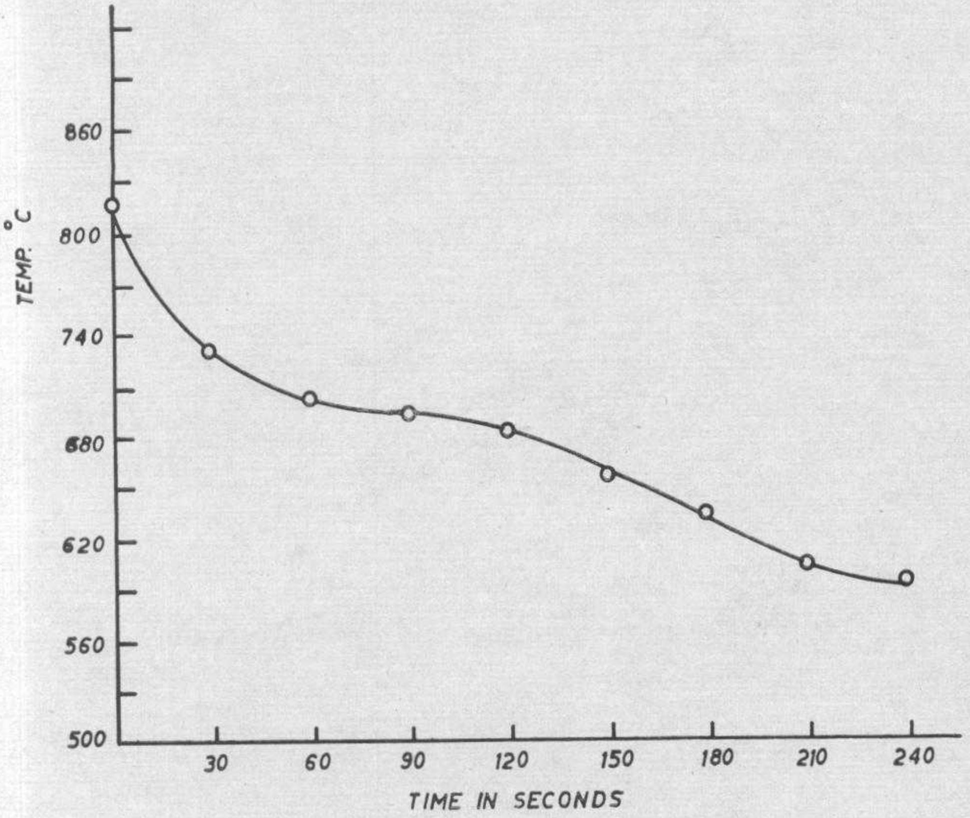
Experiments for cooling rate studies

The same composition as used for sand casting (79/10/5/5/1) was selected for cooling rate studies. In brief, melting was done in a 12 KW induction heating coil, capable of holding crucible of 1 kg capacity in terms of copper. Graphite crucibles were machined out from used electrodes. Pre-heated charcoal was used as cover during melting, followed by stirring a small quantity of a fluoride flux for scavenging the metal, and final degassing with nitrogen. The whole melting operation was carried out as rapidly as possible.

In order to facilitate the study of the effects of cooling rates, a metal mold of 0·75 inch dia. 6 inches length, was selected. The metal mold was pre-heated to different pre-determined temperatures viz. 1000°C, 900°C, 800°C, 700°C and 600°C and maintained at the respective temperature for half hour prior to pouring. The



3a *Cooling curve for mold temperature 1000°C*



3b *Cooling curve for mold temperature 900°C*

molds were coated with a refractory slurry, before preheating. The time lag between taking out the mold from the pre-heating furnace and start of the pouring was around 12 seconds. This was kept approximately constant in all cases. Cooling curves, showing the temperature of the mold as the melt froze, versus time were determined and plotted as in Figs. 3a, 3b, 3c and 3d, in order to indicate the general trend in cooling rates obtained with the different mold temperatures. The temperature was determined with the help of a Pt/Pt-Rh thermocouple inserted in the mold wall.

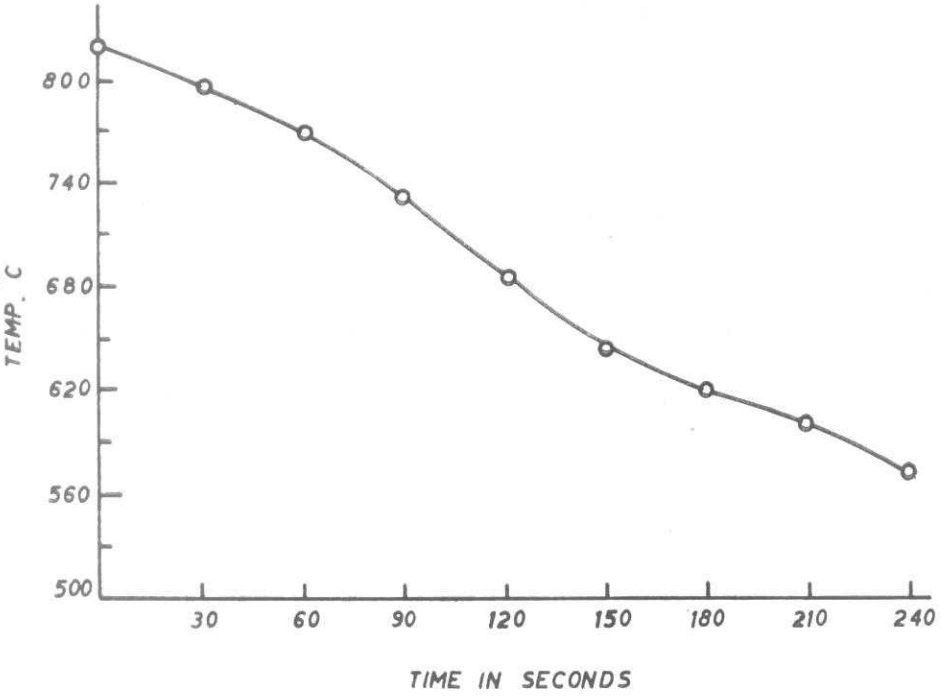
Melt composition was determined in each case. Metallographic studies and microprobe analysis were conducted on samples for each cooling rate.

Sand-cast test pieces

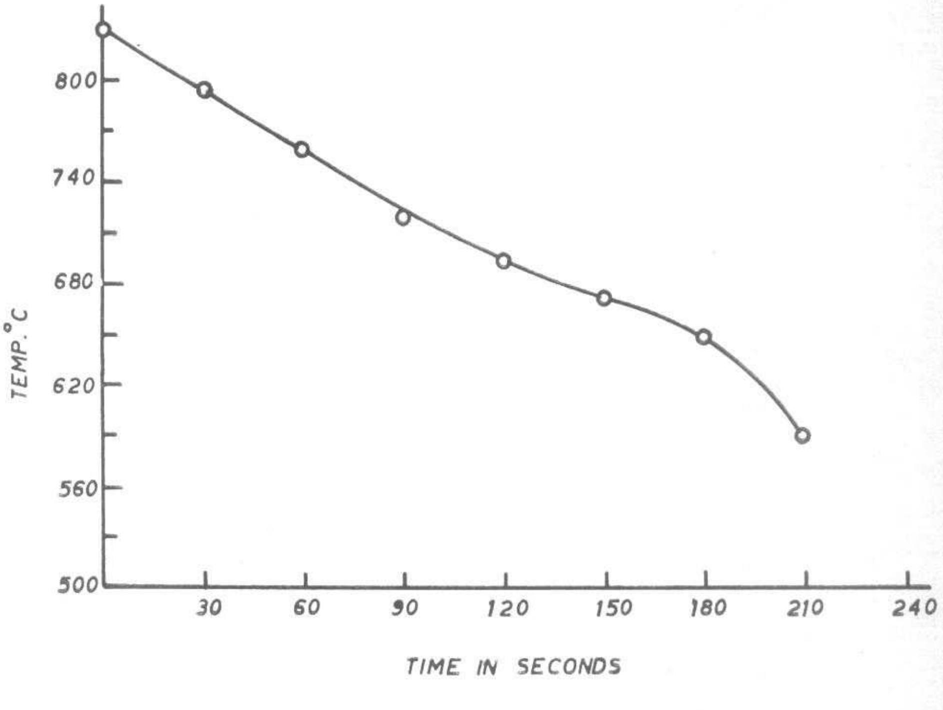
The chemical composition and mechanical properties viz. ultimate tensile strength, elongation and hardness of the test pieces cast from the same melt are recorded in Table III.

TABLE III **Sand-cast test pieces—chemical analysis and mechanical properties**

	Chemical composition					ASTM test pieces (2)			BS test piece (1)		
Serial No.	Al%	Ni%	Fe%	Mn	Cu%	UTS T/in²	Eln%	Hardness (average)	UTS T/in²	Eln%	Hardness (average)
1	10·2	4·1	6·4	1·1	Rest	43	18	150 BHN	41	12	150 BHN
2	10·2	4·1	6·4	1·1	Rest	43	18	150 BHN	—	—	—



3c *Cooling curve for mold temperature 700°C*



3d *Cooling curve for mold temperature 600°C*

4 *Sand cast sample, unetched ; showing coarse kappa* ×500

Metallography

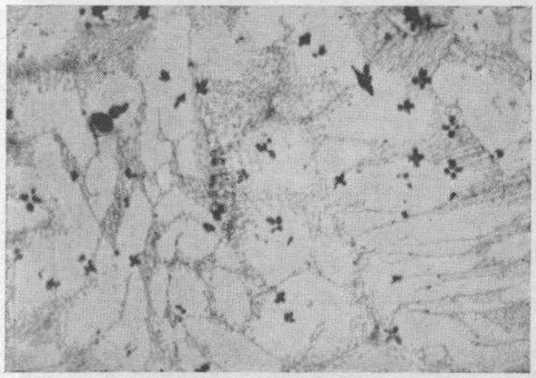
Examination at 500 × revealed, in the unetched condition, plenty of gray-coloured, coarse kappa phase of varying shapes and sizes, (photomicrograph at Fig. 4), as well as fine kappa and also several rosettes (star-like) of the same in an alpha matrix. On etching with ferric chloride etchant, the star-like phase and a few fine globular particles turned dark (Fig. 5) while the large areas of kappa both coarse and fine showed no change in colour. Besides, lamellar eutectoid areas were also present, which correspond to alpha plus kappa. The gray kappa areas, however, were found to turn dark on prolonged etching.

Microhardness

Microhardness values of phase, viz. alpha, coarse and fine kappa, and dark-etching rosettes (star-like phase), determined at various points are recorded in Table IV.

Microprobe analysis

Mounted samples of the sand cast alloy, finally polished on diamond paste, were studied in the electron micro-

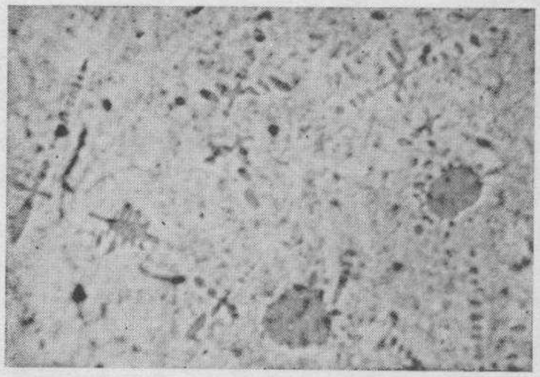


5 *Sand cast sample, etched ; showing dark rosettes* ×500

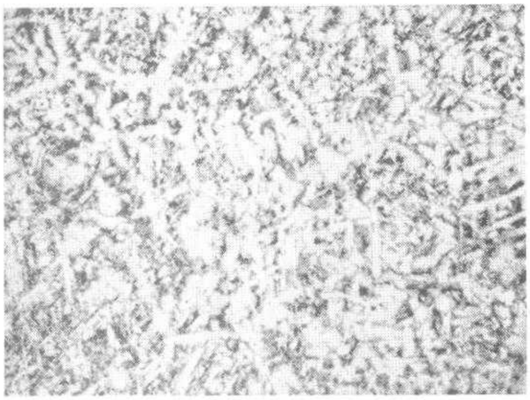
6 *Sample from 1000°C mold temperature, unetched ; showing coarse and fine kappa* ×200

TABLE IV Microhardness of phases in sand-cast sample in VPN (15 gm load)

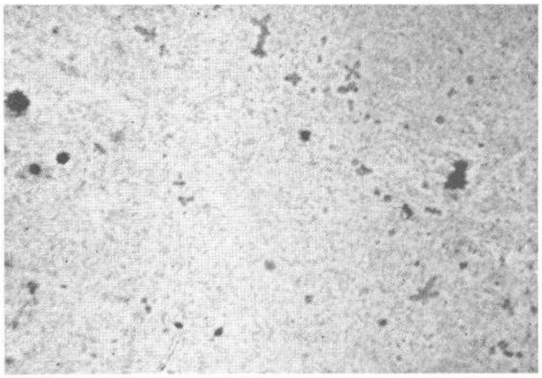
Serial No.	Phase alpha	Coarse gray kappa	Fine kappa	Dark etching rosettes
1	165	308	250	193
2	168	296	260	187
3	170	308	254	190
4	164	315	265	195
5	165	326	252	200
Average	166	306	256	193



7 *Sample from 900°C mold temperature, unetched; showing coarse and fine kappa* ×200



8 *Sample from 700°C mold temperature ; showing coarse and fine kappa* ×200



9 *Sample from 600°C mold temperature, unetched ; showing coarse and fine kappa* ×200

probe using 20 kV electron beam (1 micron dia.), for estimating composition of the alpha matrix and the different precipitates as given in Table V.

TABLE V Phase compositions—microprobe analysis sand-cast sample

Element	Percentage in matrix	Percentage in coarse, gray kappa (of size 20 microns and above)	Percentage in fine kappa (of approx. 10 microns and below)	Percentage in dark-etching rosettes (of size approx. 5 microns)
Cu	81·0	11·5	10·6	40·0
Al	9·4	8·5	7·5	14·5
Ni	3·8	6·0	4·9	7·9
Fe	3·2	71·5	72·5	35·1
Mn	1·8	1·8	2·4	2·2
Si	Trace	1·0	2·3	1·0

A general observation made in the probe analysis is that, whereas the matrix composition is quite homogeneous, the iron contents of coarse and fine kappa varied from precipitate to precipitate within a range of approximately 69–74%. Similarly, the iron and copper contents of rosettes varied considerably, but the sum of iron and copper percentages significantly remained uniform around 75% approximately.

Samples from cooling rate experiments

The cooling curves shown in Figs. 3a, 3b, 3c and 3d indicate the general increase in the average cooling rate with the decrease in the mold pre-heating temperature viz. from 1000°C to 600°C. The average cooling rates calculated from the solpes are shown in Table VI, which indicates the general trend.

TABLE VI Cooling rates

Mold pre-heating temperature	Fig. No.	Average cooling rate in °C/min.
1000°C	3a	47
900°C	3b	55
700°C	3c	63
600°C	3d	74

The chemical analysis of the five melts subjected to the different cooling rates are given in Table VII.

TABLE VII Chemical analysis of the different melts

Melt No.	Mold temperature	Chemical composition Al%	Ni%	Fe%	Mn%	Cu%
1	1000°C	8·65	5·07	7·90	0·66	Rest
2	900°C	8·80	5·80	6·26	0·60	Rest
3	800°C	Off melt				
4	700°C	10·36	6·40	7·50	0·55	Rest
5	600°C	10·56	5·16	7·10	0·72	Rest

Metallography

All the four samples revealed, in the unetched condition, distribution of coarse, massive and fine gray kappa phases in varying degrees of size, shape and content, besides, gray rosettes or star-like precipitates and areas of alpha plus kappa eutectoid (Figs. 6, 7, 8, and 9). On etching with ferric chloride etchant, most of the rosettes

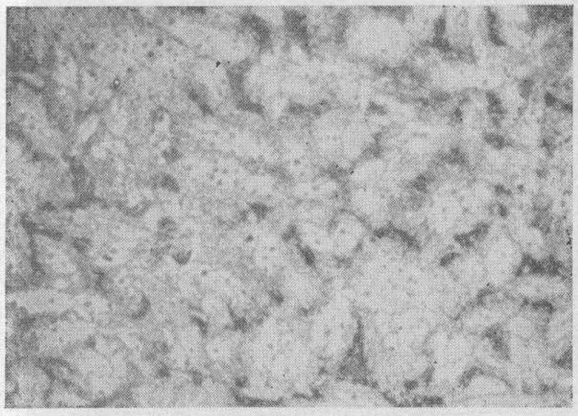
10 *Coarse kappa turned dark on prolonged etching* ×*500*

turned dark, (Figs. 11, 12, 13, 14) while most of the coarse and fine globular kappa remained unaffected, which, however, were found to turn dark with prolonged etching (Fig. 10). The relative quantitative distribution of the different forms of kappa phase are given in Table VIII.

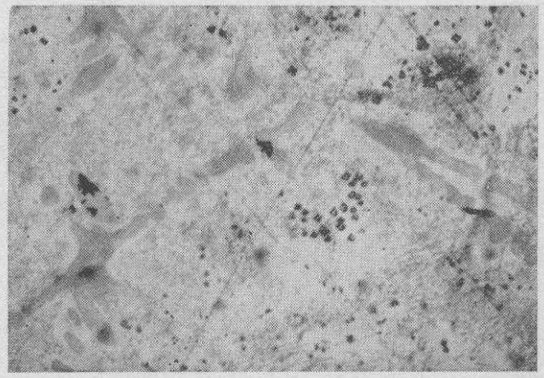
TABLE VIII Relative distribution of different forms of kappa phase with respect to amounts present

Melt No.	Mold temperature	Photomicrograph at Fig.	Coarse, massive kappa	Fine kappa	Dark etching rosettes	Remarks
1	1000°C	11	a*	d	a	It appears that the tendency to coarsening increases with slower cooling rates in all the precipitates.
2	900°C	12	b*	c	b	
3	700°C	13	c*	b	c	
4	600°C	14	d*	a	d	

*Estimated quantities of different phases—a>b>c>d.



11 *Sample from 1000°C mold temperature etched; showing dark rosettes* ×*500*



12 *Sample from 900°C mold temperature partly etched; showing dark rosettes* ×*500*

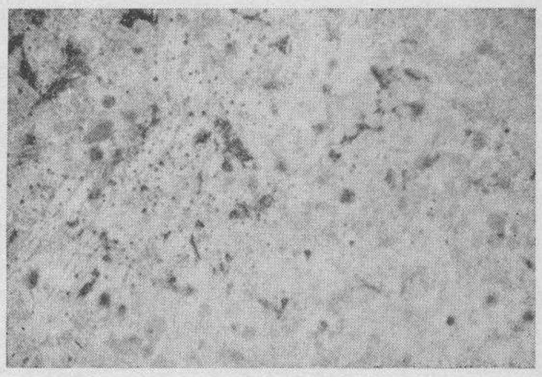
Microhardness

Microhardness of the different phases for the cooling rates are given in Table IX. It may be mentioned that the values given are more or less average, with divergences from precipitate to precipitate of the order

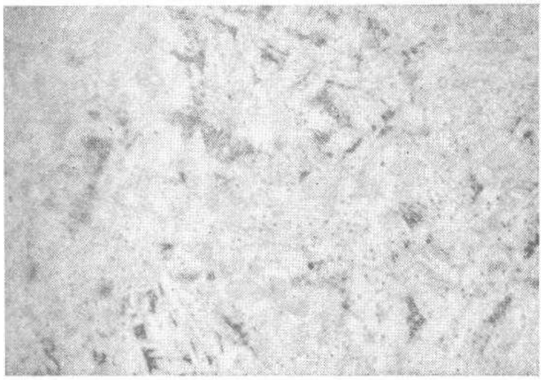
TABLE IX Microhardness values* of the phases in VPN (load 15 gm)

Melt No.	Mold temperature	Matrix	Coarse massive K	Fine K	Dark etching rosettes
1	1000°C	160	295	262	200
2	900°C	156	316	265	201
3	700°C	160	300	260	205
4	600°C	165	300	240	195

*Average of ten measurements



13 *Sample from 700°C mold temperature partly etched; showing dark rosettes* ×*500*

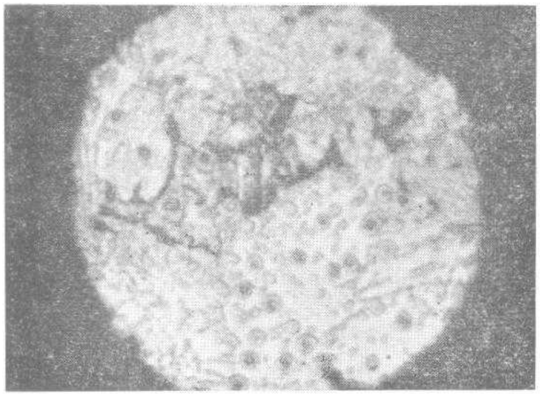


14 *Sample from 600°C mold temperature, partly etched ; showing dark rosettes* ×*500*

of 20 VPN. Further, since both fine kappa and rosettes are very small, the smallest indentation that could be taken with the tester (15 gm load) covered either of the precipitates and surrounding portion of the matrix. Hence the hardness figures for these two types are only indicative. The absolute values could be higher than these since the matrix is soft.

Microprobe analysis

Mounted samples, finally polished on diamond paste, were studied in the probe for estimation of phase compositions. In all the four samples, the very small size of fine kappa and rosettes—usually of the order of 3 microns—rendered the precise determination of their compositions difficult, owing to the limitations of the probe-area and the beam-centering, thus causing interference from adjacent matrix composition. An attempt was, however, made to determine the rosette composition with respect to Al and Ni only as these elements registered sharp increases on the probe counter as compared to the matrix. The fine kappa, in general, did not yield to satisfactory analysis, except to give an indication that it is an essentially iron-base precipitate. The iron and copper contents have, however, not been recorded in view of their very wide fluctuations.



15 *Dark etching rosettes in sample from 600°C mold temperature* ×*800*

The phase compositions, as determined in one typical sample, are shown in Table X. The values therein are only representative.

TABLE X **Phase compositions—microprobe analysis as determined in one sample (mold temperature 900°C)**

Element	Percentage in matrix	Percentage in coarse kappa	Percentage in fine kappa	Percentage in dark rosettes
Cu	80·0	15·8	Found to be	—
Al	9·9	8·0	essentially	15·0
Ni	3·6	5·2	iron-rich	10·1
Fe	5·4	70·1		—
Mn	1·1	1·1		—
Si	Trace	Trace		—

Discussions

It is well-kown that 'complex' nickel aluminium bronze is difficult to cast, in view of its certain inherent characteristics and compositional fluctuation. Various techniques and modifications have therefore been suggested in the melting and casting techniques in order to obtain sound casting under controlled composition with optimum mechanical properties. The melting and casting techniques adopted here, in producing the sand cast test pieces, have yielded satisfactory results, particularly in respect of composition and strength values, as can be seen from Table III in comparison to Table I.

Table VIII indicates the relatively high sensitivity of the kappa phase occurring in this system to fluctuations in cooling rate. The phase diagram predicts a uniform distribution of kappa in an alpha matrix with areas of eutectoid. Maximum conformity to this distribution has been obtained in the sample cast in metal mold of 1000°C preheating temperature, (Fig. 11), which in these experiments, may be termed as having the slowest degree of cooling rate approaching equilibrium conditions. It has been observed that the slowest cooling rate contributed to the precipitation of most of kappa phase in massive and coarse areas (Fig. 11), whereas the precipitation of finely distributed kappa has been favoured by fast cooling rate, i. e. mold temperature 600°C (Fig. 14), the precipitation of intermediate sizes of kappa precipitates being influenced by the intermediary cooling rates. Even though the differences between successive cooling rates are not significant, as for example, with mold temperature 1000°C to 900°C or 700°C to 600°C, the observations on relative distribution of precipitates resulting from the two extreme cooling rates confirm the general trends (Table VIII).

The general features that have been observed in the study of this alloy under various conditions are the occurrence of the kappa precipitates in essentially three different forms, viz. coarse, fine and rosette-like, distributed in a matrix of alpha. Fine and rosette-like precipitates are usually difficult to be distinguished in the unetched condition even at 500 ×. On etching, however, most of the rosette-like precipitates turned dark as observed at 500 × while the fine kappa remained unaffected. This differential etching can be attributed to the basic difference in the phase composition, as given in Tables V and X with consequent difference in microhardness (Tables IV and IX). It can be seen from the above tables, that both coarse, gray kappa precipitates and fine gray kappa are iron-base, with more or less similar composition having comparable microhardness. This suggests that coarse and fine kappa (gray) are essentially the same phase, but their morphology is controlled by cooling rate, other factors such as composition etc. remaining the same. Incidentally, it may be mentioned that the alpha phase (matrix) was copper-base with microhardness around 160 VPN (Tables IV, V, IX and X), and was not found to be sensitive to cooling rate effects.

Although the rosette-like dark-etching precipitates in the sand cast specimens are easily discernible in their shape at 500 ×, the same constituent in the samples of cooling rate experiments offered difficulty to be identified as star-like at 500 ×. This behaviour may be due to the wide difference in the cooling rates between the two sets of experiments. However, these dark etching precipitates were found to be essentially rosette-like in shape, when examined at 1800 ×, in Vickers 55 microscope (Fig. 15).

In this connection it may be recalled that earlier workers[8] have identified a so-called delta-phase in 9–10% Al composition which is globular or rosette-like, but not readily identified metallographically. Some difficulty in identification of their shapes has also been experienced in the present work. The dark etching rosette-like precipitate as discussed in this paper has a distinctly different composition and hardness from fine and coarse kappa. This suggests that this rosette-like precipitate may perhaps be identifiable with the delta-phase referred to earlier.

Conclusions

1. The formation of kappa phase in nickel aluminium bronzes of 10/5/5/1 type, is influenced by the cooling rate.
2. Slower cooling rates favour formation of massive gray kappa, and faster cooling rates, fine, gray kappa.
3. A dark-etching, rosette-shaped precipitate has been found to occur under the conditions studied, having a distinctly different composition and hardness from that of fine gray kappa, and coarse gray kappa.
4. Both the coarse and fine kappa prectpitates are found to be essentially iron-rich having comparaable hardness.

It is suggested that the effects of size, shape and quantity of coarse and fine kappa, and the dark etching rosettes on the mechanical properties need further study.

Acknowledgments

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