

X-ray Study of the Decomposition of Metastable Al-Rich Al-Fe Solid Solutions

A. TONEJC

The extension of the solid-solubility limit obtained in Al-Fe alloys up to 4.4 at. pct Fe by rapid quenching from the melt and the appearance of metastable Al_6Fe phase for 4 to 20 wt pct Fe have been reported in the past. Present experiments with isochronal and isothermal annealing of Al-Fe solid solutions containing 3.6 at. pct Fe have shown that the solutions are very stable at room temperature, and less stable at 200°C, while at 300°C they decompose very rapidly and a metastable Al_6Fe phase appears. This phase is replaced by Al_3Fe after annealing for 10 min at 550°C or for 16 hr at 400°C. The Al_6Fe phase remains stable for 76 hr at 300°C, while taking more than 670 hr to be replaced by Al_3Fe . The author discusses the operation of the "two-piston" quenching apparatus and concludes that the sample thickness cannot serve as a sufficient criterion for quenching effectiveness.

THE technique of rapid quenching of metals from the liquid state developed by Duwez, Willens and Klement¹ has led to the formation of new amorphous and crystalline metastable phases and an extension of solid-solubility limits in many alloy systems.

Using rapid quenching technique, Matyja, Giessen and Grant,² Tonejc and Bonefačić,³ and Jones⁴ have investigated binary alloys of aluminum with iron, Fig. 1. Matyja *et al.* were concerned with the relationship between dendrite size and cooling rate in Al-1 at. pct Fe alloys, while Tonejc and Bonefačić published the lattice parameters of metastable supersaturated Al-Fe solid solutions up to 4.4 at. pct Fe. Jones found that Al-Fe alloys, containing 4 to 20 wt pct Fe, rapidly solidified by the splat cooling technique, contain two different zones, zone A and zone B. Zone A corresponds to an Al-Fe supersaturated solid solution, while zone B revealed the metastable Al_6Fe phase. This phase was observed previously only in continuously cast Al-2 wt pct Fe⁶ and in Al-1 wt pct Fe⁷ solidified with a cooling rate more than 3°C per sec⁻¹. Al_6Fe has an orthorhombic (Cmmm) structure and is isomorphous with other Al_6M type phases (Al_6Mn ,^{8,9} $\text{Al}_6(\text{Mn}, \text{Fe})$,⁸ $\text{Al}_6(\text{Mn}, \text{Fe}, \text{Cu})$,⁸ Al_6Tc and Al_6Re ^{10,11}). The lattice parameters of all these compounds are within ± 1.5 pct of 6.51, 7.55 and 8.90Å.

Jones also confirmed the results of Tonejc and Bonefačić about lattice parameters of Al-Fe solid solutions. In examining the behavior of an Al-Fe solid solution containing about 4 at. pct Fe, and after annealing for an hour at temperatures of up to 600°C, Jones found that the solid solution decomposed at between 300° and 400°C. The Al_6Fe pattern became detectable at 400°C and in both zones was replaced by Al_3Fe at 500° and 600°C.

The present paper gives detailed information on decomposition of supersaturated Al-3.6 at. pct Fe solid solution during isochronal and isothermal annealing. The stability of metastable Al_6Fe phase and some aspects of the "two-piston" rapid cooling technique are also discussed.

A. TONEJC is Assistant in Physical Metallurgy, Institute of Physics of the University of Zagreb, Zagreb, Yugoslavia.
Manuscript submitted July 7, 1970.

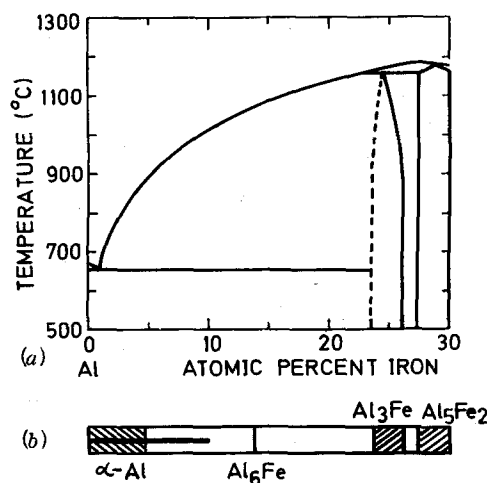


Fig. 1—(a) Aluminum-rich end of the equilibrium phase diagram Al-Fe;⁵ (b) Schematic representation of stable (marked above the diagram) and stable (marked below the diagram) alloy phases obtained by splat-quenching to 20°C. The thicker line (in the left part of the diagram) represents the concentration ranges of Al-Fe alloys examined by the author.

EXPERIMENTAL PROCEDURE

The Al-Fe alloys were prepared from carefully weighed quantities of the elements, inserted into an alumina tube 2 mm in diam, and melted by means of a resistance-heating element coiled around the alumina tube. Rapid cooling from the liquid state was achieved in an apparatus described previously by Dixmier and Guinier¹² and Tonejc and Bonefačić.³ In this "two-piston" technique ejected drops of molten alloy are caught between two fast moving steel-pistons.

The resulting flakes were approximately circular (about 1 to 5 mm in diam) and from a few to 70 μm thick. They were examined in a Siemens 114.6 mm diam Debye-Scherrer camera. Straumanis asymmetric film position and nickel-filtered $\text{CuK}\alpha$ or iron-filtered $\text{CoK}\alpha$ radiation were used. The lattice parameters were computed taking $\lambda(\text{CuK}\alpha) = 1.54178\text{\AA}$ or $\lambda(\text{CoK}\alpha) = 1.79020\text{\AA}$ for unresolved, and $\lambda(\text{CuK}\alpha_1) = 1.54050\text{\AA}$ or $\lambda(\text{CoK}\alpha_1) = 1.78890\text{\AA}$ for resolved doublets. The pres-

ence of the Al_6Fe or Al_3Fe phase was examined by means of a Nonius Guinier-de Wolf quadruple focusing camera, with crystal monochromated radiation.

The isothermal or isochronal heat treatment was carried out by placing the samples in a furnace with a nitrogen atmosphere. After each annealing the samples were air quenched.

The concentration of iron in the quenched flakes was established by means of electron probe microanalysis using the JEOL-JXA5 electron microprobe analyzer. Some results are given in Table I. No great differences were found between nominal and measured iron concentrations.

RESULTS AND DISCUSSION

Quenching Effectiveness

Quenched samples of Al-Fe alloys with iron concentrations from 3.6 to 10.0 at. pct were investigated. The estimated distribution of phases in 27 samples is presented in Table II. In the samples where both Al_6Fe and Al_3Fe phases were present, the estimated relative intensities of X-ray reflections from Al_6Fe and Al_3Fe phases are given. Crosses indicate the samples where only one phase was present.

For most quenched alloys up to 4.4 at. pct Fe solid solutions were obtained in samples not thicker than 15 μm . In thicker flakes the Al_6Fe pattern could be detected but no trace of Al_3Fe was found. Referring to Jones⁴ results about zones A and B, we may state that the presence of zone A depended exclusively on the effectiveness of quenching. When the cooling rate was high enough, only the solid solution, *i.e.* zone A, was present. In cases where the quenching was less effective, *i.e.* in thicker flakes, the metastable Al_6Fe phase was found, which is a characteristic of zone B. Where the cooling rate was different in different regions of the flakes, zone A and B were simultaneously present in the flakes.

When alloys with higher concentrations than 4.4 at. pct Fe were quenched, both Al_3Fe and Al_6Fe phases were detected in most cases.

The data in Table II confirm the findings of Ruhl¹³ and Dixmier and Guinier¹² that the average cooling rate varies with the thickness of the sample: as a rule, thinner flakes are better quenched. However, this need not occur in all cases. Thus samples Nos. 4 and 5, both 9 μm thick, were of different structure (Table II). How can this be explained?

Fig. 2 represents the operation of the "two-piston" apparatus. A are fast moving metal pistons and B is the alumina tube with the resistance-heating element. When the liquid globule is placed exactly at the mid-

Table II. Estimated Distribution of Phases at Room Temperature in Al-Fe Alloys Rapidly Quenched from the Melt

Act. Pct Fe	No.	Sample Thickness, μm	Al_6Fe	Al_3Fe	Al-Fe Solid Solution
3.6	1	15	+	-	-
	2	20	+	-	-
	3	37	+	-	-
	4	9	-	-	o
	5	9	+	-	o
	6	12	-	-	o
	7	7	-	-	o
	8	11	-	-	o
4.0	9	10	-	-	o
	10	25	+	-	-
	11	20	+	-	-
4.3	12	35	+	-	-
	13	30	+	-	-
	14	40	+	-	-
	15	8	-	-	o
5.4	16	20	w	m	-
	17	15	-	+	o
7.8	18	20	-	+	-
	19	20	m	m	-
	20	10	w	m	-
	21	10	-	+	o
	8.0	22	18	m	m
23		35	s	m	-
24		25	m	s	-
10.0		25	65	w	s
	26	40	m	s	-
	27	25	s	w	-

+ Al_6Fe or Al_3Fe phase present.

o Al-Fe solid solution.

o Partial Al-Fe solid solution.

- Absent

w Weak

m Medial

s Strong

point between the moving pistons, the quenching is ideal because a rapid removal of heat is now achieved from two sides of the thin liquid layer when the pistons collide. But when the liquid globule [globule (b) in Fig. 1] touches one of the moving pistons before it does the other, local cooling occurs and the beginning of the nucleation of the solid phase in this part of the globule cannot be prevented. As indicated by Duwez,¹⁴ in this case the quenching rate is probably decreased by several orders of magnitude. This is a most essential result for the "two-piston" technique because mere

Table I. Nominal and Measured Fe Concentrations in Aluminum-Rich Al-Fe Alloys

Nominal Concentrations At. Pct Fe	Measured Concentrations, At. Pct Fe
0.675	0.705
0.70	0.69
0.70	0.64
1.88	1.82
4.40	4.55
5.90	5.80

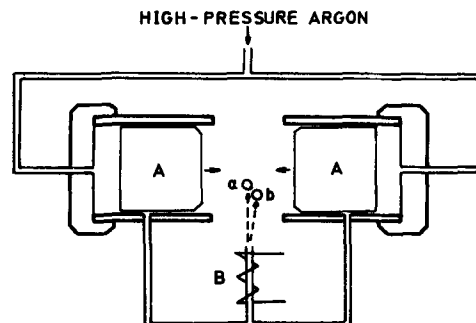


Fig. 2—"Two-piston" quenching device.

knowledge of the sample thickness cannot be a sufficient criterion for quenching effectiveness. Quenched samples must therefore be examined by X-ray diffraction techniques before they are used for other investigations (e.g. electrical-resistance measurements, mechanical properties).

The X-ray diffraction pattern of sample No. 17, taken immediately after quenching, showed a partial solid solution and presence of Al_3Fe phase. This sample probably contained regions which were quenched with very different cooling rates. After annealing this sample for 20 min at $400^\circ C$, lines of the Al_6Fe phase appeared on the X-ray diffraction pattern besides the already existing Al_3Fe , Table III.

Isochronal Annealing

The plot of the lattice parameter change of the solid solution of the rapidly quenched Al-3.6 at. pct Fe alloy after annealing for 10 min at temperatures up to $550^\circ C$ is shown in Fig. 3. Uncertainties in spacings are approximately indicated by the attached error bars. The solid solution decomposed at between 200° and $350^\circ C$ with a maximum increase in the lattice parameter between 250° and $300^\circ C$. The Al_6Fe pattern became detectable at $300^\circ C$. At $400^\circ C$ the (333) doublets (taken with $CuK\alpha$ radiation) became resolved, and at $450^\circ C$ this happened to the (422) doublets as well. At this temperature the Al_3Fe pattern became evident, while at $500^\circ C$ the lines of the Al_6Fe phase were disappearing. At $550^\circ C$ only the equilibrium terminal phases of aluminum and Al_3Fe were present.

Table III. Annealing of the Sample Containing Partial Al-Fe Solid Solution and Al_3Fe Phase

At. Pct Fe	Annealing Temp	Phase	Annealing Time, Min	
			0	30
7.8	$400^\circ C$	Solid Solution	+	-
		Al_6Fe	-	m
		Al_3Fe	m	m

*Present
m Medial
-Absent

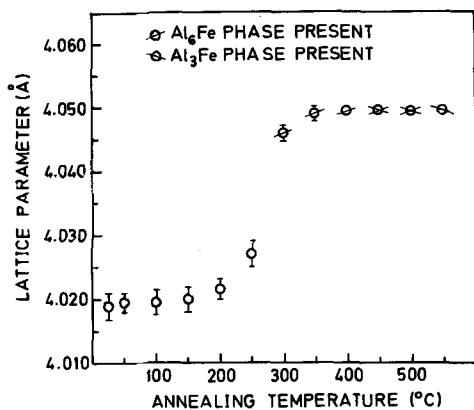


Fig. 3—The variation of lattice parameter of Al-Fe solid solution with annealing temperature for Al-3.6 at. pct Fe after annealing for 10 min at each temperature.

Comparison of our X-ray measurements on the decomposition of the Al-3.6 at. pct Fe solid solution with the metallographic investigation of isochronal annealed Al-0.68 at. pct Fe solid solution made by Kunstelj and Bonefacić,¹⁵ suggests that in the first stage of annealing (up to $150^\circ C$) a coarse cellular structure with globular precipitates develops along the cell walls, followed by the appearance of particles of Al_6Fe phase at the α -Al subgrain boundaries (up to $300^\circ C$). With further annealing and due to subgrain and grain boundary migration these particles coagulate into plate-like particles of the Al_3Fe phase (up to $450^\circ C$), and finally a coarsening of these particles is observed at the grain boundaries (above $450^\circ C$).

Isothermal Annealing

From Fig. 3 three points were chosen for isothermal annealing: at 200° , 250° , and $300^\circ C$. The results for Al-3.6 at. pct Fe solid solution are presented in Fig. 4.

Annealing at $300^\circ C$ gave a very rapid increase in lattice parameter approaching the equilibrium value within the first 12 min when the lines of Al_6Fe could be detected. After annealing for 5 hr at $300^\circ C$ the lattice parameter reached equilibrium value. No X-ray evidence of the Al_3Fe phase was present at this stage of annealing.

At $250^\circ C$ the lattice parameter increased almost linearly with the annealing time. Al_6Fe phase was detected after 5.5 hr, while after 34.5 hr the lattice parameter reached equilibrium value.

At $200^\circ C$ the lattice parameter was recovering very slowly. A certain increase could be observed within the first hour of annealing. This is probably due to the annealing-out of quenched-in vacancies.¹⁶ The Al_6Fe phase was detected after annealing for 260 hr (not indicated in Fig. 3) and the lattice parameter reached equilibrium value after further annealing for 1000 hr.

The annealing of solid solutions containing 3.0 and 3.9 at. pct Fe, at room temperature, for 2 years produced no change in the lattice parameters.

Stability of the Al_6Fe Phase

Samples of Al-3.6 at. pct Fe which contained mixtures of aluminum and Al_6Fe were isothermally annealed at 300° , 400° , and $550^\circ C$ respectively. The results are presented in Table IV. The Al_6Fe phase remained stable for 76 hr at 300° when it began to pass into the equilibrium Al_3Fe phase. However, after 670 hr the Al_6Fe phase was still present in the sample.

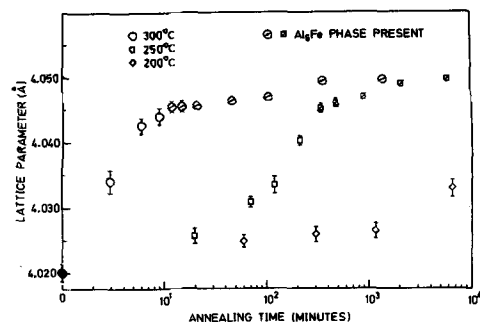


Fig. 4—The variation of lattice parameters of Al-3.6 at. pct Fe solid solutions with annealing time (annealing temperatures: 200° , 250° , and $300^\circ C$).

Table IV. Isothermal Annealing of Al-3.6 At. Pct Fe Alloys Containing Al₆Fe Phase (Annealing Temperatures: 300°, 400°, and 550°C)

Annealing Temperature	Phase	Annealing Time, hr												
		0	0.16	0.25	0.50	1.1	2.6	7.7	16	21	76	117	300	670
300°C	Al ₆ Fe	m	s	—	s	s	s	—	—	s	s	ms	ms	m
	Al ₃ Fe	o	o	—	o	o	o	—	—	o	o	vw	vw	w
400°C	Al ₆ Fe	m	s	—	s	ms	m	w	o					
	Al ₃ Fe	o	o	—	vw	w	m	ms	s					
550°C	Al ₆ Fe	m	—	o										
	Al ₃ Fe	o	—	s										

— Not measured.
o Absent
vw Very weak
w Weak
m Medial
ms Medial strong
s Strong

After annealing for 30 min at 400°C the Al₃Fe phase could be detected on the X-ray diffraction pattern, while after 16 hr the Al₆Fe phase disappeared and only the aluminum and Al₃Fe equilibrium phases remained present.

At 550°C the same process took only 15 min.

CONCLUSIONS

The results of the investigation can be summarized as follows:

1) Al-Fe solid solutions were produced for alloys up to 4.4 at. pct Fe for samples thinner than 15 μm. In thicker samples the metastable Al₆Fe phase appeared. These results agree with those published by Jones.⁴

2) In quenched samples containing 4.4 to 10.0 at. pct Fe metastable Al₆Fe and stable Al₃Fe phase appeared more often than metastable Al₆Fe alone. Partial solid solutions were also present.

3) Sample thickness cannot be a sufficient criterion for the quenching effectiveness of the "two-piston" method.

4) Al-Fe solid solutions passed always into the equilibrium aluminum and Al₃Fe phase over the metastable Al₆Fe.

5) The Al-3.6 at. pct Fe solid solution was very stable at room temperature, but less at 200°C, while at 300°C it decomposed rapidly to aluminum and Al₆Fe phase (in our experiment after 350 min).

6) The Al₆Fe phase remained stable for 76 hr at 300°C, but at 400°C for only 30 min. It gradually changed to the equilibrium phase Al₃Fe within the next

15 hr at 400°C, and within about 10 min at 550°C. However, at 300°C the process was not yet completed after 670 hr.

ACKNOWLEDGMENTS

The author wishes to thank Prof. A. Bonefačić for his valuable suggestions and interest in the experiment, and Prof. M. Paić for his helpful discussion of the manuscript.

This work was a part of a program sponsored by the Federal Fund for Scientific Work, Belgrade.

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