

Determination of Vacant Lattice Sites in Aluminium Alloys by X-ray Diffraction Technique

Rajendra Sharan
D. Swarup

THE study of the structure of metals and alloys is very important because this affords the possibility of developing new alloys with improved properties to be useful for meeting service requirements. Theories based on ideal crystals fail miserably when applied to real crystals of the metals and alloys, for example the calculated yield strength and breaking strength of ideal crystals are 100 to 10,000 times more than the observed strength of real crystals. The reason is that the crystals contain many flaws and irregularities, so it is felt that a detailed knowledge of vacant lattice sites in alloys will be useful, because of their effects on physical and mechanical properties. The object of this investigation is to find out the effect of copper on the lattice parameter and vacant lattice sites in aluminium.

Previous work

The lattice spacings and densities of solid solutions of zinc, magnesium, copper and silver in aluminium have been measured at room temperature and vacant lattice sites have been studied.

In the case of aluminium-zinc system¹ lattice spacings at room temperature as well as at high temperature were determined and effect of temperature on vacancies was found out.

The lattice spacing curve at 25°C is unusual. It decreases with increase of zinc content. It can be divided into four parts:

1. 0 to 4.0% Zn (non-linear relationship between lattice spacing and composition).
2. 4.0% Zn to 18.5% Zn (linear relationship between lattice spacing and composition).
3. 18.5% Zn to 25.0% Zn (non-linear relationship between lattice spacing and composition).
4. 25.0% Zn to 35.0% Zn (linear relationship between lattice spacing and composition).

If we compare the vacant lattice sites vs. composition curve with lattice spacing vs. composition curve, we find that in the regions where there is non-linear

relationship between lattice spacing and composition, the percentage of vacant lattice sites increases with the increase of zinc, while the linear portion of the lattice spacing vs. composition curve corresponds with the constant or decreasing number of vacant lattice sites.

In case of Al-Mg alloys¹, the effect of Mg is just reverse of that obtained in aluminium-zinc system. In this case the lattice expands with increasing Mg atomic percentage in aluminium. Percentage of vacant lattice sites increases up to 1% Mg. Between 1% Mg to 5% Mg percentage of vacant lattice sites decreases with increase of Mg content and there appears to be a peak at 1% Mg. Beyond 5% Mg, up to the solubility limit, there is gradual increase in the number of vacant lattice sites with the increase of Mg content in the alloy.

H. J. Axon and Hume Rothery worked on aluminium-copper² alloys and showed that the lattice spacing vs. composition is linear. There is a contraction of the lattice with alloying. The following density results show that there are probably no vacant lattice sites formed in the alloy containing less than 2 atomic % Cu.

Cu atomic %	Theoretical density	Measured density
0.41	2.715	2.712
0.84	2.736	2.732
1.28	2.753	2.754
1.73	2.777	2.774
2.17	2.798	2.798

There is a slight discrepancy in the alloy containing 2.17% Cu, but according to Axon and Hume Rothery, the difference may be due to the inclosed pores because this alloy was hard and was not reduced as much as other alloys by hammering. No work was done beyond 2% Cu.

From 1951 to 1952, E.C. Ellwood¹ studied the effect of silver on the lattice parameter of aluminium. Lattice spacing of aluminium is practically unchanged by addition up to 6% Ag. From 6% Ag to 14% Ag, there is a small but definite increase in lattice spacing. Silver addition between 14 and 27% probably causes no further increase in lattice spacing. No vacant lattice sites have been reported in this system.

Mr. Rajendra Sharan, M.S. (Met. Engg., U.S.A.), Lecturer and Dr. Daya Swarup, Ph.D. (Sheffield), F.I.M., Principal, College of Mining and Metallurgy, Banaras Hindu University, Varanasi.

Preparation of alloys

At first, a hardener alloy of about 50% Cu and 50% aluminium was made in a graphite crucible. Other alloys were then made from this hardener alloy by adding a weighed quantity of aluminium. Stirring was done to provide homogeneity in metal, and casting was done in cast iron metal mould.

Chemical analysis of alloys

The iodometric method was used. Copper was precipitated as copper sulphide and was ignited to the oxide. The oxide so formed was dissolved in nitric acid and fumed to evaporation with H_2SO_4 . The solution was then diluted, neutralised with Na_2CO_3 , and the iodometric titration was carried out in a weakly acidic medium (acetic acid). The standard solution used was sodium thio-sulphate and the results obtained from duplicate analysis were quite concordant.

Grain refining treatment

The samples prepared were given a grain refining treatment prior to X-ray diffraction study.

The advantages expected are :

1. Clear rings in X-ray photograph resulting in accurate measurement of lattice parameters and easy interpretation thereof.
2. Breaking up of cast structure, shutting off all macropores which might otherwise give a wrong idea of the % vacancies.

The following treatment was given :

1. *Cold working* : The samples were heavily cold worked by rolling and hammering up to 50% reduction.
2. *Vacuum annealing* : The severely cold worked samples were nicely cut to small blocks and were put into the vacuum furnace for annealing.

The temperature of annealing was 150°C and the time at that temperature was 3 hours.

Metallographic study of the cast and treated samples

The cast samples were ground, polished, etched and studied under the microscope. They clearly show the characteristic cast structure with coring effects in some alloys. No cracks or macropores were detected under the microscope. The structure of the alloys after the treatment was also studied to see the recrystallisation. The structure showed that the appearance of coring and dendritic structure was completely eliminated.

Density determination

The displacement method was used. The liquid used was distilled water at 20°C. The water was boiled to remove all dissolved gases. The suspension wire used was a very thin copper wire.

X-ray diffraction technique

Back reflection camera was used for the determination. The above method was selected because of the following advantages :

1. Easy preparation of the sample.
2. Precision in lattice parameter at large angle values.
3. Ease of setting the camera, film and specimen.

Factors used in X-ray diffraction work

Tube current = 6.7 mA.

kVA = 38 for first 8 samples and for the rest kVA = 20.

Target material = Cobalt.

Filter at the window = Iron of '00007" thickness.

Distance of wrapper to specimen = 3 cm.

Thickness of aluminium foil and wrappers = 0.127 cm.

Total distance = 3.0127 cm.

In this case [331] and [420] lines both α_1 and α_2 have been used for the calculation of the lattice parameter ; curve has been plotted between $\cos^2\theta$ and lattice parameter a and actual lattice parameter has been calculated by extrapolating the value to $\theta = 90^\circ$.

Method for determining the percentage vacant sites

From the lattice parameter values, the theoretical density dt for each alloy was calculated by the given formula :

$$dt = \frac{m M.N}{a^3}$$

where m = mass of atom at unit atomic weight
= 1.66035×10^{-24} gm.

M = composite atomic weight.

N = number of atoms/unit cell.

a = lattice parameter measurement.

From the values of dt —theoretical densities and actual densities as determined by displacement method, percentage vacancies were found by the given formula :

$$\% \text{ V.L.S.} = \frac{100(dt-d)}{dt}$$

where dt = theoretical density as calculated from X-ray data.

Discussion of results

A careful study of the lattice parameter vs. composition curve and percentage vacant lattice sites vs. composition curve brings out the following facts :

1. No effect on lattice parameter is detected up to 0.5 atomic percentage Cu.
2. Lattice parameter decreases with increase of copper percentage between 1 to 2.5 atomic percentage copper and relation between lattice parameter and composition is nearly linear, as shown by Hume Rothery.

Alloy No.	Cu wt %	Cu atomic %	S.G. by displacement method	Lattice spacing	S.G. by X-ray	Percentage vacant lattice sites
1.	0	0	—	—	—	—
2.	1.1520	0.4921	2.728	4.047	2.728	0
3.	1.9077	0.8183	2.730	4.047	2.729	0
4.	2.7500	1.1860	2.749	4.046	2.745	—
5.	4.3500	1.8940	2.775	4.044	2.773	—
6.	5.4400	2.3840	2.779	4.042	2.807	0.9972
7.	7.4200	3.2910	2.815	4.040	2.845	1.054
8.	7.8000	3.4670	2.821	4.040	2.854	1.156
9.	9.9200	4.4670	2.872	4.040	2.897	0.8628
10.	12.1800	5.5590	2.920	4.040	2.941	0.7142
11.	13.7900	6.3560	2.950	4.0415	2.970	0.6733

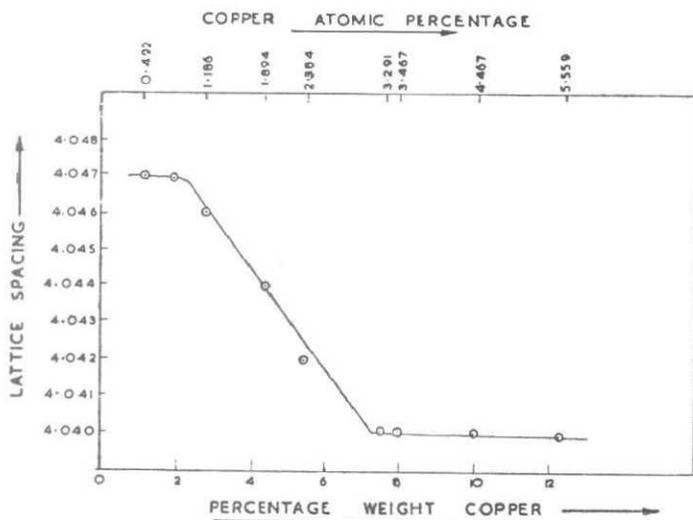


Fig. 1.

Effect of copper on the lattice parameter of aluminium.

- Lattice parameter remains constant between 3.2 to 5.5 atomic percentage copper.
- No vacant lattice sites are formed up to 1.9 atomic percentage copper.
- The rate of increase of percentage vacant lattice sites is enormous within the range 1.9 atomic % Cu to 2.4% Cu.
- Beyond 2.4% copper the rate of increase is flattened until at 3.46% a peak is formed beyond which the percentage vacant lattice sites fall gradually with alloying.

Previous workers seem to have attributed the formation of vacant lattice sites to the filling up of Brillouin zones. In the present work since no vacant lattice sites are found to form in the solid solubility range it is reasonable to assume that in Al-Cu system the Brillouin zone effect is practically absent. This has already been shown by H. G. Axon and Hume Rothery from their work on Al-Cu alloys.

It is worthwhile here to consider the equilibrium diagram of the Al-Cu system and to see how the increasing amount of copper in the solid solution effects the percentage vacant lattice sites. With increased alloying, the electron/atom ratio varies linearly and this variation may be assumed to cause internal strains in the structure and thus make it relatively unstable. Vacant lattice sites may bring a measure of relief just the same way as the changes from f.c.c. to b.c.c. structure.

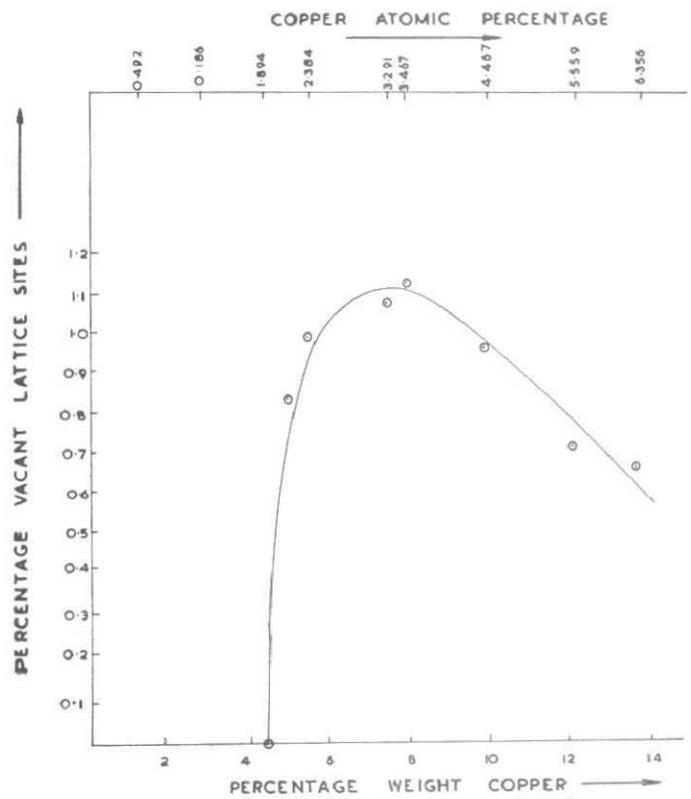


Fig. 2.

Effect of copper on percentage vacant lattice sites.

It is interesting to note that the rate of increase of percentage vacant lattice sites is high at 1.9 atomic % Cu up to the solubility limit. The rate then suddenly flattens and a maximum value is reached at just beyond the solubility limit and vacant lattice sites decrease gradually. The following explanation can be given:

The electron concentration, i.e. electron/atom ratio reaches a critical value at 1.9 atomic percentage copper at which point the vacant lattice sites first appear and their number increases rapidly till the solid solubility limit is reached beyond which the electron/atom ratio reaches a value proper enough for the 2nd phase (in this case Cu-Al= θ phase) to form.

With more and more alloying the amount of θ phase goes on increasing, bringing more and more relief, in the internal strains thus decreasing percentage vacant lattice sites after 3.46 atomic percentage copper.

Internal strains are relieved partially by the precipitation of the second phase and partially by the generation of more vacant lattice sites and not like 1.9 to 2.4 atomic percentage copper where the relief is only by

generation of vacant lattice sites, and thus the slope between percentage vacant lattice sites vs. composition goes on decreasing between 2.4 atomic % Cu to 3.46% atomic percentage copper.

With more and more alloying the amount of θ phase goes on increasing, bringing more and more relief, in the internal strains thus decreasing percentage vacant lattice site after 3.46 atomic percentage copper.

Acknowledgement

The authors are thankful to Messrs A. S. Sastri and Yudhvir Singh for their help in carrying out this investigation.

References

- ¹ E. C. Ellwood, J.I.M., 1951-1952, p. 217, 605 and 608.
- ² H. G. Axon and Hume Rothery, Proc. Roy. Soc., 1948(A), 193, 1.

Mr. R. K. Dubey, NML: May I know from the author as to how the theoretical density of the alloys be calculated from the lattice parameter of aluminium as also how the porosity in the alloy is avoided to eliminate errors in specific gravity measurements?

Mr. Rajendra Sharan (Author): I have followed the method adopted by Axon and Hume Rothery. In the formula for finding out the density, viz., $\frac{M}{a^3}$, a is the lattice parameter of aluminium, N is the atomic weight and M is the composite atomic weight. The composite weight has been calculated by taking the different amounts of copper in aluminium and not of copper in solution only. This method has been adopted by other workers as well and the composite atomic weight will give the average density of the alloy quite accurately. As mentioned in the paper, the sample was rolled to 50% reduction and this rolling will close all macropores so that the sample will be quite compact to find out the density reading. The sample has been well polished and etched out to remove all oxide layer from the surface. The other precaution that has been taken is to take distilled water.

Dr. V. G. Paranjpe, Research and Control Labs., TISCO Ltd., Jamshedpur: It is known that there is a solid solution ending around 4-5% by weight which would correspond roughly to a content of 2 atomic per cent. The abnormal increase in the calculated lattice vacant parameter just occurs around that point.

I was just wondering how the specific gravity calculated from the lattice parameter of the alpha phase only could be compared with the specific gravity of the bulk which would be alpha plus the other phase.

Dr. E. G. Ramachandran, NML: May I supplement Dr. Paranjpe's question with another small question? Although the solid solubility limit is 4% as Dr. Paranjpe mentioned, at a temperature of about 500°C, this measurement, I presume, has been made at room temperature after annealing at 150°C and the solid solubility at room temperature is considerably smaller than 4 wt. % or 2 atomic %. It may be of the order of 0.01-0.05% at the most. So in all these alloys the matrix whose lattice parameter has been measured is unchanged and that is perhaps the reason why there is no change in the lattice parameter as reported, whereas the alloy itself is a two-phase alloy, the proportion of the second phase increasing to anything, up to 30%. In the alloy containing 14% copper, there may be about 30% CuAl₂, i.e. of the θ phase. The specific gravity of the solid solution cannot be much different from 2.7, viz. that of aluminium, whereas that of the θ phase is something of the order of 4.5. So the observed increase in the specific gravity is due to the increase in proportion of the second phase and I am not able to understand how that can be compared with the calculated theoretical density of a matrix phase whose composition does not alter at

DISCUSSIONS

all in all these alloys. I would be grateful if some light is thrown upon this point by the authors.

Mr. Rajendra Sharan (Author): So far as I see, the same type of work has been done in the case of aluminium-magnesium system, too, where the same problem of solubility is there and work has been carried out up to about 5% Mg and even higher than that. So far as I have come across the literature, I have not found out any other method for this determination. I will be glad if Dr. Ramachandran can supplement this and suggest some other method for determination of theoretical density, as I am very much interested not in this work at room temperature only but also at high temperatures. So, I have done similar work as has been done in the case of alloy systems like Al-Mg, Al-Ag, Al-Zn, etc. Maybe, I am going to a higher per cent where θ phase predominates wherein much error may be introduced but in this particular work θ phase is quite small. The composite atomic weight what we take will give the average density and not the density of one phase only. This gives the consideration for the total percentage of copper.

Regarding Dr. Paranjpe's question it is not actually beyond the solubility limit. In the beginning it is just near the solubility limit where we find that vacant lattice sites are generating at a very fast rate in a particular range. Beyond this, when one increases the copper content, the electron atom concentration will go on increasing or with the same increase in copper content, the relief of stresses may be needed and at that time vacant lattice sites are being generated and also the second phase is precipitating. I think that may be the particular reason for the decrease. I will be glad to receive suggestions for improving the techniques for finding out the density.

Dr. E. G. Ramachandran, NML: I would just like to answer this point in this way. While this investigation has, of course, a very interesting objective, I think it has not been done in the way it should be done. Axon and Hume Rothery have quenched alloys from the solid solution phase and have measured the lattice parameters of the quenched alloys and have taken or tried to take all possible precautions to see that the θ phase does not precipitate. Now, in this case, we see a treatment which very deliberately forces out the θ phase. After cold work, there is an annealing at 150°C for 3 hrs. After the θ phase is brought out, the specific gravity is measured and naturally, this will be higher as the Cu content increases and that is what the authors report rightly. But if they calculate the theoretical density from the lattice parameter with these proportions of θ phase by the back-reflection technique, they can detect only the lines due to the terminal solid solution phase. This phase is virtually identical, in all these alloys and that is the point which apparently has been missed by the authors. I can give an example. In all annealed steels, the ferrite is virtually identical only the proportion of cementite in the steels increasing as the carbon content increases. If you measure the properties of the ferrite only, you will find that all the steels do not show appreciable differences. In this paper,

though the authors record certain changes in the lattice parameter in the third or fourth place of decimal, I don't think that they are real changes and in my view, appear to be within the limits of experimental error. I feel that no change in the parameter should occur, because the phase they are investigating by X-rays has not changed. It would be wrong to think of or calculate the proportion of vacant lattice sites by comparing the density of one phase measured by a certain method with the density of a composite alloy measured by a totally different method. This is the point I wish to make out. Axon and Hume Rothery have not gone beyond 2% in their investigations, because above 2% Cu, you cannot get a single phase alloy. They also show that there is no appreciable vacant lattice site generation. My colleague, Mr. Ved Prakash, has examined the age-hardening characteristics of Al-Cu alloys* and he finds that his results are consistent with the idea that vacant lattice sites are removed, even at high cooling rates. Naturally, when these alloys are subjected to prolonged annealing, we can expect that the proportion of residual vacant lattice sites, if any, will be very negligible. This paper tries to compare things which cannot be compared and I think that justifiable conclusions cannot be drawn.

Mr. Rajendra Sharan (Author): I am thankful to Dr. Ramachandran for his valuable suggestions and contribution to the above paper. I do not agree with his views completely. Dr. Ramachandran has mentioned that the authors have used quenched alloy. I do not know how they have used. When we use the quenched alloy at a time, we do not study the vacant lattice at room temperature but we actually study the vacant lattice sites at that temperature at which we quench. If at all we use that particular method, then stresses may also develop during quenching and may alter the lattice parameter. Of course, this method has been adopted in the case of Al-Zn system for finding out the vacancies at different temperatures. They have heated the alloy to a particular temperature and they have quenched the alloy from that temperature. Here, after rolling we have made the alloy compact. Mr. Hume Rothery has also cooled the alloy for density measurements. If at all he says that he has quenched the sample, he had done it to get the value at that particular temperature. We are also interested in this work to get the lattice vacancies at that particular temperature and for that we are not using the quenching technique but high temperature camera for the study. I am still conducting experiments in the matter to study with the high temperature camera. I don't say that this type of result obtained is the confirmed result and we are going to check these particular results. The technique you suggest, Sir, will never be a correct technique because quenching will vary the lattice parameter because of stresses and second thing is that we will study the lattice parameter at that particular temperature. Of course, we are planning to study the problem

* Ved Prakash and Entwistle, K. M.—"J. Inst. Metals", 87 (1958-59), p. 262.

at high temperature by using high-temperature camera and we will take all the precautions and will probably be in a position to study at that particular range. In the formula of course the lattice parameter of the first phase has been taken but the composite atomic weight substitution gives the average density and not of one phase only.

Prof. P. R. Dhar, I. I. T., Kharagpur: The authors' experiment depends on the precision determination of lattice parameter. Since the back reflection pattern used in the experiment always gives broadened lines due to various causes (like internal stresses, etc.), it is very important that exact position of the peak heights of the

lines should be found out by scanning the pattern with a Microphotometer.

Mr. Rajendra Sharan (Author): We are having a Microphotometer but that is not of recording type. If it had been of a recording type, we would have known the peak of broadening. We appreciate your suggestion and will check up the results by finding out the actual peak with the help of recording photometer which we have in our Science College. Previous work has shown that the method using recording photometer is not more accurate than the method adopted in this work. For a broad line, reading has been taken at both sides of the line and average has been taken.

