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PRECIPITATION HARDENING

and Discussion.

By Professor D. Hanson, D.Sc.

Report of a Meeting of the Midland Metallurgical Societies held at the James Watt Institute, Birmingham, on Thursday, 25th March, 1943.

Present :—Mr. A. Pinkerton (in the Chair), Professor D. Hanson, and some 45 Members.

Several apologies for absence were received through the Secretary (Mr. Plant).

The Chairman, in opening the proceedings, said there was no need for him to introduce Professor Hanson, who was well known in Birmingham as Professor of Metallurgy at the University.

“Precipitation Hardening” was an interesting subject, and he felt sure that members would enjoy Professor Hanson’s lecture.

LECTURE.

Professor Hanson.

The subject upon which I have been asked to speak to-night is very important, and is one of the noteworthy trends of modern metallurgy. It is still very much in the development stage, both as regards theory and practice. I propose to review our present theoretical knowledge of this subject, from which you may get a better view of the practical possibilities of the process of precipitation hardening, and I may also be able to indicate in what direction further work needs to be done.

Precipitation hardening covers heat-treatment which is twofold inasmuch as quenching is followed by tempering. In order to get the quenching effect, we must have an alloy which at high temperature exists in a state different from that in which it exists at a low temperature. The object of the quenching is to preserve that or some other intermediate state, and the object of tempering is to modify the condition induced by the quenching.

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When we quench an alloy, one of three things may happen :—

(1) Either we preserve the state which exists at high temperature; or

(2) The state which exists at low temperature; or

(3) We may obtain some state which exists normally neither at a high nor a low temperature : that is, we get a metastable state.

I am going to assume that the act of quenching preserves in the alloy, the moment it gets cold, the state which exists at high temperature; that is, a supersaturated solution.

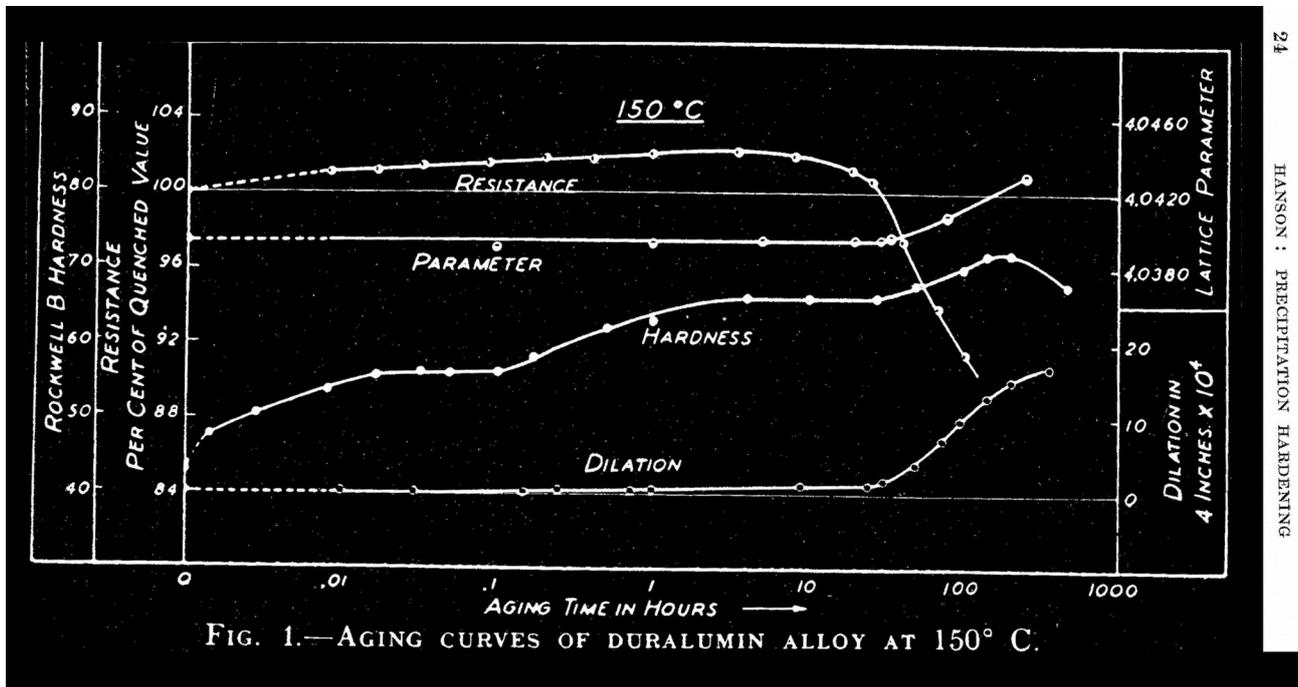
The act of tempering allows the alloy to proceed towards the state which is stable at the tempering temperature. The supersaturated solid solution tends to precipitate that substance which

has been held in solid solution by the quenching, and the resultant effects are therefore known as “precipitation hardening.”

Let us consider the effect of this precipitation. Certain things can be definitely deduced. The act of dissolving something in the alloy has certain definite effects, e.g., it increases the electrical resistance. It also causes certain volume changes to take place., The magnitude of these effects is entirely dependent on the amount which is dissolved. When precipitation occurs the final state of the alloy depends partly on the amount and distribution of the precipitate and partly on the amount left in solid solution.

Properties like electrical conductivity, density, and lattice parameter do not depend mainly on the state of division of the particles but rather on the amount remaining in solution. But there are other properties (e.g., strength) which do depend not only on the amount which is precipitated but on the state in which it exists in the treated alloy. We all know that a very fine structure has a degree of hardness substantially greater than a mixture of the same constituents in massive form ; so that the strength, hardness, and elongation are affected not only by the constitution but also by the structure of the alloy. These are represented by a different type of curve, shown in Fig. 1, and illustrating the tempering effect.

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To summarise, we are really dealing with two effects; first there is precipitation, followed by coalescence of those particles onto bigger masses, when the effect on properties begins to diminish again, so that for practical purposes we have a combination of these two effects, since they occur simultaneously although they vary in magnitude.

If we consider the effect of tempering on one of these supersaturated solutions, we get a varying behaviour according to the extent to which these different actions occur, and Fig. 2 shows a succession of curves to illustrate this. At the highest temperatures the coalescence effects only are to be observed.

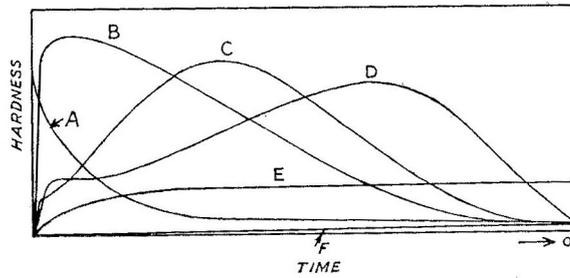


FIG. 2.—Curves Representing Time-Hardness Changes at Different Ageing Temperatures.

Curve A—Upper Temperature Limit of Ageing: Both Stages of Ageing Take Place Excessively Quickly. Curve B.—Second Stage of Ageing, Perhaps Slight Indication of First Stage. Curves C and D.—First and Second Stage of Ageing Both Apparent. Curve E.—First Stage of Ageing and Perhaps Entry of Second Stage at an Excessively Slow Rate. Curve F.—Lower Temperature Limit of Ageing: Both Stages of Ageing May Take Place Excessively Slowly.

Thus “*structure sensitive*” and “*structure insensitive*” properties can best be represented by different kinds of curve. Structure insensitive properties, like resistivity or lattice parameter, are represented by a type of curve shown in Fig. 8, which shows diminution during precipitation and no further alteration as particles aggregate.

One naturally asks, what is the reason for this hardening? These changes can all be explained by the true precipitation theory, which assumes first of all that precipitation from the supersaturated solid solution consists of the separation of the second phase at many nuclei and that these, first increase in number as

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precipitation proceeds but that the crystals so formed subsequently coalesce and diminish in number. The structure insensitive properties are controlled at any moment by the amount of the dissolved substance in solid solution and are therefore not affected by the precipitate; whereas structure sensitive properties are controlled by the amount precipitated and the form in which it occurs. That is a completely satisfying picture of what happens in a large number of systems to which this form of treatment applies. The maximum hardness occurs at a critical dispersal of the particles in conformity with the theory first suggested by Jeffries and Archer¹.

That would be all very well if all the alloys to which this treatment can be applied all conformed exactly to the type illustrated, but on examination we find that is not so.

An alloy of silicon in aluminium or of magnesium silicide in aluminium behaves exactly in this way, and so do alloys in the silver-copper system. Duralumin alloys, however, do not always behave in a manner which can be explained by the theory of Jeffries & Archer¹. When quenched Duralumin is allowed to age at room temperature, it hardens spontaneously; but the changes which occur in its properties cannot be explained by simple precipitation. The resistance which ought to fall does nothing of the kind. Actually, it goes up. The lattice parameter remains constant. The dilatation is also very nearly constant. There is no evidence here of precipitation, yet we get the hardening. If we examine the same alloy aged at 191°C, we find that the resistance falls away; the lattice parameter remains constant for a little time, then definitely changes. The dilatation or density also shows a big change. The changes in this instance are quite consistent with the pure precipitation theory. Here is an alloy which behaves differently at different times.

Clearly there are phenomena involved in the process of separation of a constituent from solid solution, that can set up hardening but do not involve complete precipitation. These are called “pre-precipitation phenomena.”

Immediately after quenching, the solute atoms are believed to be uniformly distributed throughout the solid solution. The mechanism of precipitation is not yet fully understood. _ Merica² suggests that the reason for the “abnormal?” pre-precipitation hardening of duralumin is that the copper atoms diffuse together

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to form “knots” in the lattice before precipitation occurs and these knots cause distortion of the lattice and thus produce hardness. It is only at a later stage that a complete rearrangement occurs and we get a sufficiently big concentration of copper atoms to form a nucleus for true precipitation of CuAl_2 .

Various other people have contributed ideas of a like nature, including Dr. Gayler of the N.P.L. I do not think they are satisfactory. My chief objection is that this process of knot formation involves “uphill” diffusion, from a region of low concentration to one of high concentration, and I do not understand where the motive force originates, Neither is it clear why the distortion produced by a large number of atoms should not be at least as big as the distortion produced by a “knot” or segregation of atoms at lattice positions of the parent lattice. There is no profound interruption of the slipping planes.

The subject has been taken further in studies made by Preston³, whose work is extremely pertinent to any theory of precipitation or pre-precipitation hardening.

One thing which began to emerge as the question of precipitation was studied was that it did occur preferentially on crystallographic planes. Thus Fink and Smith⁴ have detected the beginnings of precipitation in a copper-aluminium alloy at a magnification of x500 or so. There is a tendency to separate on crystallographic planes, and this has also been noted by other people.

Preston³ studied the copper-aluminium alloys by means of X-rays. He prepared a single crystal of this alloy and quenched it from about 500°C ., and studied its ageing properties at room temperature and elevated temperatures. Age-hardening developed at room temperature over a period of a few days, and he found that when the alloy was heated further it softened considerably, and then hardened again. By means of X-rays he was able to follow certain changes in structure during these processes. During ageing at room temperature there was definite evidence that atoms of copper collected on crystallographic planes of the aluminium, forming little flat plates not more than five atoms thick and not more than one hundred atoms wide.

On heating to a higher temperature, the effect produced

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by the copper atoms was diminished and another effect became apparent ; in place of the copper plates other flat crystallites appeared, but in this case they had a different structure in which both copper and aluminium atoms were involved. That effect gradually developed and the plates gradually increased in size (though still very thin) and developed a crystal structure different from normal CuAl_2 , although it contained the same ratio of copper and aluminium atoms (i.e., a polymorphic form of CuAl_2).

The next important stage is probably due to Cohen⁵ in America and, almost simultaneously, to Gayler⁶ in this country. Very broadly, they suggested that pre-precipitation hardening and precipitation hardening were both normal features of the ageing phenomena of supersaturated solid solutions ; that duralumin was not an exceptional alloy but rather a typical alloy.

Let us examine other systems and see if we can make them behave according to the alternative processes. The copper-silver alloys had been regarded as the ideal of the true precipitation type. They were known to age-harden at about 300°C. ; and they conformed to the precipitation theory in the manner shown in one of my earlier illustrations to-night. Cohen tried ageing them at a lower temperature (between 100 and 200°C.), He found that if the ageing temperature were reduced, the copper-silver alloys now behaved exactly like Duralumin at ordinary temperature; that is, they set up a type of hardening without precipitation. He was able to separate the ranges: the hardening became more and more pre-precipitation hardening as the temperature fell. There was definite evidence in Cohen's experiment that this pre-precipitation hardening occurred prior to true precipitation hardening, and the theory is that precipitation hardening always involves these two processes, If the temperature is a high range, true precipitation is the dominant character, if low range, the pre-precipitation hardening is pre dominant.

Examination of beryllium-copper and beryllium-nickel tends to confirm the generality of this theory, but it is not finally accepted yet. I am not going to deal with the alternatives at the moment, but I do want to deal with work which has recently been published and which aims at explaining nucleus formation and the maximum of this pre-precipitation hardening. It is entirely theoretical and a little speculative, but it is the first

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glimmering of light as to how these dissolved atoms get together and produce these hardening effects without precipitation occurring.

Up to now we have assumed that in a solid solution the dissolved atoms are distributed regularly throughout ; this is no doubt statistically correct, but at quenching temperatures diffusion is rapid and solute atoms are moving through the lattice of the solvent. In such circumstances we ought to be able to apply the law of probability to determine the occurrence of certain groupings. For example, let us take a grouping of 48 atoms, which we may suppose to be just big enough to form a nucleus of Cu Al_2 . If you apply the theory of probability to this problem and consider the probability in the solution at a high temperature of groups of 48 atoms containing 16 copper atoms and 32 aluminium atoms, you find out how: many, on pure chance, there would be of such groupings which were just ready for the formation of a nucleus. In each cubice millimetre of a 4% copper solution in aluminium there would be 22,500 groupings of such atoms which had all the requirements for making a nucleus. Therefore these solutions can contain within themselves, in a purely random distribution of atoms, numerous groupings capable of forming crystal nuclei. At high temperatures they do not do so since they are unstable, and are continually being formed and dissipated by diffusion, When the alloy is quenched, atomic movement becomes difficult or impossible, and these groupings now have an entirely different order of stability. It is not difficult to imagine that they might in the quenched alloy, because of their instability, rearrange themselves in a way which would make them a closer approach to the normally ordered arrangement. Preston's work does suggest that something of the kind occurs. He finds quite definite evidence of these layers of copper atoms. An interesting paper published recently by Samans⁷ in America suggests

a possible mechanism for this rearrangement, without involving diffusion in the ordinary sense, and without the necessity for assuming “uphill diffusion” at any stage. The final state may be reached through more than one definite stage, and may thus account for the observed changes in properties.

In this way we find views which enable us to explain nucleus formation.

The first movements of atoms are in direction of re-orientation

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to a more stable form, and this reorientation is of a type which would offer a resistance to interference from slip. It accounts for the observed diffraction defects and the final change to CuAl_2 , but it is the first idea I have seen that offers a rational explanation of this behaviour.

I am afraid I shall have to leave my analysis of the subject at this stage, but before doing so there are one or two points which I should like to mention which I think have a very great practical importance. These discoveries have now extended our range of knowledge of precipitation hardening effects and have brought different mechanisms into the one broad theory. It is going to be necessary to re-examine many of the alloy systems to which this process can be applied, in order to separate out these effects.

With regard to the effect of precipitation hardening on properties ; pre-precipitation hardening in general has no effect on the electrical properties and little on the chemical properties, but can have a big effect on the mechanical properties: so that if an alloy is required with improved mechanical properties without change in electrical properties, it may be obtained by low temperature treatments. Similarly, minimum resistivity or optimum dimensional stability can be attained, in conjunction with high strength, by full precipitation hardening in a higher temperature range. By a suitable manipulation of the tempering temperatures we can, by the two processes, have the same mechanical properties relating to widely different electrical, chemical and other properties. This explanation of the theory indicates the possibility of developing new materials through the differences in properties due to structure sensitive and structure insensitive effects.

(Professor Hanson here brought his lecture to a close by saying that he would be unable to remain at the Meeting to take part in the discussion, but he hoped that Members would carry on without him).

Mr. Pinkerton called upon Dr. Johnson to propose a vote of thanks, to be seconded by Mr, Stewart.

Dr. Johnson. We have listened to-night to a most delightful exposition by Professor Hanson. He has enlarged upon a

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theory and phenomenon which takes its place in that vast romance of metallurgy about which I hope somebody will some day write an entertaining volume, because a good deal of metallurgy is pure romance, I think Professor Hanson has presented it to us to-night in an admirably clear way, and the quality of his description has been supported admirably by the quality of the diagrams shown on the screen, all of which were extremely instructive.

I ask the Meeting to accord to Professor Hanson a very cordial vote of thanks for this extremely interesting lecture, which was well worth the time spent in coming to hear it.

Mr. Stewart. Listening to Professor Hanson has been a very great pleasure to me, because it has taken me back to years before the War when I used to listen to the same able, quiet voice explaining much more elementary points of metallurgy. I think it does us all good to get away from the hurly-burly of works practice and to come and listen to a purely academic lecture on fundamental principles. In view of Professor Hanson's desire to get away early, I can only express on behalf of the Meeting, and in support of Dr. Johnson, our very great pleasure in listening to such an able discourse.

(The vote of thanks was carried unanimously ; the Chairman then threw the Meeting open to discussion).

(At this stage Professor Hanson unfortunately had to leave the Meeting and could not reply to the discussion).

DISCUSSION.

Dr. Johnson. With regard to the lecture, I am sure there are many other aspects of the subject on which Professor Hanson would have touched, had he had time. For example, the effect of beryllium in copper is, I think, a most extraordinary instance of this phenomenon of precipitation hardening. Who would have dared to predict that the addition of 2% of beryllium to copper would enable a tensile strength of nearly 80 tons to be reached, as against a tensile strength of rather less than 30 tons ? I think the lecturer also rather queried the point as to whether there is any possibility of an inter-metallic compound retaining its identity even when deposited in solid solution in the space lattice. My own view is that this does not occur, When an

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inter-metallic compound goes into solution, it actually splits up and its atoms find their place wherever they can in the lattice.

Another point to which the lecturer made no reference at all was the ferrous alloys, and martensite which is a very fascinating subject and in regard to which I would have liked to have seen some correlation between the modern theories and the phenomenon in the hardening of steel.

Professor Hanson mentioned the application of the laws of probability. I do not know whether any members remember a lecture given by Mr. Jude about twenty years ago. At that time I don't think anyone thought that it would be of very much use to metallurgists, but now the subject looks like coming into its own. (This was only probability as applied to chemical analysis.—[Ed.]

Mr. Hall. I would like to ask if the so-called laws that Professor Hanson has expounded with regard to precipitation hardening can be applied to the ferrous metals. Is it true that the electrical conductivity is lowered with the precipitation of martensite ? I would have liked to ask whether Professor Hanson could correlate the ordinary quenching temperature of the ferrous alloys with this new theory of precipitation hardening,

Mr. Milverton. That was a point which occurred to me - whether the hardening in steels did bear any relation to the precipitation hardening which you get with other alloys,

Mr. Primrose. Not only does high carbon in quenched steels give it a distinct hardening, but at low carbon contents, of the order of 0.08% and under, water-quenching, either directly from rolling the rod or by subsequent water-hardening, e.g.,

barrelling, produces a complete solution of the low carbon, so that microscopically it is quite invisible. With ordinary atmospheric temperatures there is a very distinct rise in tensile strength ; as much as from 26 to 36 tons per square inch, over a period of 10 to 12 days, and that is usually associated with what is commonly called “precipitation” of minute particles of free cementite from the supersaturated solution produced by quenching. That is certainly a type of so-called precipitation hardening because, as Professor Hanson has made out, you can get hardening both with and without this precipitation.

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As far as I gather from the work done in the research laboratories of the British Aluminium Company, and particularly under Dr, Gwyer at Warrington, there appeared to be what the lecturer called a sub-microscopic precipitation from complete solution. Some of the temperatures now advocated for aluminium alloys do not, in my opinion, obtain complete solution, so that you get a state of partial precipitation hardening or incomplete solution, and therefore get a very different set of properties from those obtained by the higher temperature quench.

Reverting to the steel analogy, I think that the study of very low-carbon steels is a fruitful source of further investigation, because it certainly brings about remarkable conditions in the steel, enabling the deep drawing very low carbon steels, a fact which has been pointed out in various researches both in this country and in Germany.

Dealing with the question of electrical conductivity, I had to deal in Warrington with an alloy which had a maximum of 1% combined silicon, manganese and iron, and whilst on heat treatment the tensile strength of that alloy rose to above 40 tons with a drop of fully 30% in the electrical conductivity. By ageing at comparatively low temperatures (below 200°C.) the tensile strength decreased, but there was a large increase in electrical conductivity, so that it raised the value of the original pure aluminium by 82 to 85%. This gives a very complete answer to the present-day difficulty of having steel-cored aluminium cables for our grid scheme ; the idea being to cut out the steel core and to use an aluminium alloy suitably heat-treated and precipitation hardened, which obviates the necessity for a duplex cable.

Dr. Johnson. As I understand it, the real difference between the low carbon steel and the martensite to which Mr. Hall made a reference, is that the solubility of carbon in alpha iron increases with temperature in precisely the same way as the solubility of “alpha” increases in the very first slide shown on (the screen by Professor Hanson. But that is alpha iron, whereas the martensite to which I have been making reference to-night is the solid solution resulting from an attempt to quench and retain a solid solution of carbon in gamma iron.

Mr. Daniels. I think I can perhaps clear up Dr. Johnson's difficulty about martensite. Professor Hanson showed us

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a slide illustrating precipitation along planes. In the original paper from which that was taken, that picture was intended to illustrate that there are actually identifiable particles occurring along those lines. That was preceded by a picture at much lower magnification, showing a number of grains and showing precipitation effects along bands rather than - specific crystallographic planes, and was referred to by the authors as a martensitic structure.

Mr. Hall. One naturally relates papers of this type to one's own material, and there is a phenomenon in malleable cast iron which is at the moment unexplained. Briefly, the facts are that

normal blackheart composition white cast iron, when annealed, gives a graphite distribution of 14 or 15 graphite nodules per unit area. If the same white cast iron is given a pre-quench treatment at about 800°C. and then given the normal annealing treatment, the graphite nodules are increased to something like 200 per unit area as against 14 to 16 under normal treatment.

Mr. Pinkerton. Dr. Johnson has made reference to the copper-beryllium alloys, which show a remarkably great increase in hardness with the appropriate treatment. I don't suppose that many people have had an opportunity of annealing these alloys. I have never done so myself, and should like to ask Dr. Johnson if the hardening there is entirely precipitation hardening, which I take to be sub-microscopic.

Dr. Johnson. Yes; I understand that it is precisely on the same lines as the precipitation hardening to which Professor Hanson has referred to-night: obtained first by quenching and then tempering, but there is no possible evidence of that precipitation so far as the microscope can produce it.

END OF MEETING.

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