### Discussion—High-Temperature Alloys Session

Microstructural Objectives for High-Temperature Alloys in Advanced Energy Systems by C. T. Sims

Question: J. M. Leitnaker<sup>1</sup>—I'd like to thank you for your boost for the breeder reactor. You mentioned the swelling problem in Type 316 stainless steel and showed a particularly bad example of that problem.

I'd like to report that at least partial solution to that problem is a triumph of microstructural analysis in that if you remove the impurities from Type 316 stainless steel, the swelling goes up dramatically. The secret in controlling the swelling in the Type 316 is to selectively increase those impurities and by modifying the composition slightly of Type 316, raising the nickel a little bit, lowering the chromium a little bit, and also lowering the molybdenum and increasing the silicon that you can reduce the swelling to a very negligible amount comparable to PE 16. It's just a very recent result that has come out following the picture that you've shown and fits right in with the message that you have.

Answer: C. T. Sims—That's good to hear. If Type 316 is capable of doing the job as a fuel cladding material, that's going to be a lot easier than trying to use a higher-cost superalloy.

Question: F. Sczenzenie<sup>2</sup>—In discussing LMFBR, you mention claddings as a potential component. I think I know what you mean, but could you expound a little bit more on what components and what material systems you're talking about?

Answer: C. T. Sims—Ok, I'll try to be very general. In a reactor, of course, the heat comes from the uranium or thorium as a fissioning material. The material may be an oxide, metal, or other component, depending on reactor design. It must be contained some way in order to release the heat and still not react with the heat exchanger fluid that cools it. So all reactors, at least those I know of, have the active ingredient—the

<sup>&</sup>lt;sup>1</sup> Oak Ridge Labs., Oak Ridge, Tenn.

<sup>&</sup>lt;sup>2</sup> Special Metals Corp., New Hartford, N. Y.

uranium-containing material—in a sheath or cladding of some sort. It could be a pin, it could be a ball, it could be a coated particle, but most commonly and for the near future, it's as a clad body like a fuel plate. The plate might be about 3 to 5 in. wide, many feet long, and  $\frac{1}{4}$  to  $\frac{1}{2}$  in. thick. It will contain a layer of the uranium-containing material. The fluid heat-exchange medium moves by the protecting alloy cladding, removing the heat. Thus, those fuel plates grow rather hot.

The pebble bed helium gas reactor is most interesting. The fuel elements are a 6-cm graphite ball, admixed with a coated  $UO_2$  or other fissile particles containing carbon-coated  $UO_2$  or other fissile particles distributed within it. That whole ball acts as the container. A metal sheathing is not needed.

Question: S. Banerji<sup>3</sup>—Would you care to comment a little bit about the single crystal materials that are being developed for turbine blades?

Answer: C. T. Sims—Single crystal blades are generated by directional solidification. First, there's an intermediate product—directionally solidified alloys—that are composed of alloys with grains that run directionally in the strength-needed direction. In a turbine bucket for instance, they are parallel to the major stress direction, and thus the lack of transverse grain boundaries sharply reduces the possibility of transgranular fractures. I understand some are now in service,

If then, as Pratt & Whitney has done, one develops a process for producing a single crystal part, not only will there be no horizontal or transverse grains to initiate and promulgate fracture, but no vertical ones will be present also. However, I keep hearing that this process is pretty expensive, and one wonders whether it can come through economically. Someone from Pratt & Whitney may want to comment on this.

Comment: R.  $King^4$ —We have made a couple of engine sets of monocrystal blades in the new foundry in Middletown with that automated process, but I will agree at this point in time it's more expensive than the directionally solidified process.

*Reply: C. T. Sims*—Would you think that because it's expensive, that perhaps we'll see a day when single crystals will be in use as a part of the high-temperature part, bonded to it, where the single crystal is used to resist low-cycle fatigue, perhaps as a turbine blade leading or trailing edge?

Comment: R. King—I really don't have any comment on that. I don't think the technology is that far along. I think the monocrystal today is in

<sup>&</sup>lt;sup>3</sup> Foote Mineral Co., Exton, Pa.

<sup>&</sup>lt;sup>4</sup> Pratt & Whitney Aircraft, East Hartford, Conn.

the same category as the directionally solidified blade was, let's say, five or six years ago when it was in its infancy.

Comment: W. Jones<sup>5</sup>—I would like to add that the candidate alloys you've discussed are going to appear on energy conversion lists other than the ones you have discussed. Currently, in solar thermal boiler design and in geothermal hot rock drilling schemes, these kinds of alloys are again going to be considered. No matter which innovative energy scheme you consider, one will encounter less than desirable environments and high temperatures. The list of potential uses for these alloys then includes solar thermal, geothermal, fusion, coal, and fission energy conversion.

Answer: C. T. Sims—Thank you very much. That is a most appropriate comment, and I appreciate that you have made it. For this talk, I have just picked a few energy systems of a major type. Further, if I may, I would like to mention water-cooled turbines and ceramics.

The thought may have gone through your mind that in those kinds of systems we will be using no superalloys. Nothing could be further from the truth. All we will be doing is to move the then intermediate temperature problems further down in the gas turbine. For instance, if one were to conceive that one could develop a gas turbine with first-stage bucketing of a ceramic material, superalloys would then be used at their limits in the latter stages, because design would minimize the stages using ceramics.

Water cooling is the same circumstance. Superalloys will be needed in latter stages, and also to protect water-cooled interiors from corrosion. So superalloys are going to be here for a long time.

#### Melting of Superalloys by L. W. Lherbier

Question: F. Sczenzenie—You showed that arsenic, antimony, and tin remain stable under VIM melting. The levels didn't decrease. Could you comment on the ability of the various remelt processes to reduce those elements?

Answer: L. W. Lherbier—I think, basically, the remelting processes do not do much to reduce those elements either. There is a possibility they can be minimized in a remelting via electroslag. I just don't think there's been enough work done yet to define how much or even if they can be reduced to acceptable levels. We generally look at elements of that type as having to be controlled in the charge of raw materials.

Question: W. Mankins<sup>6</sup>—I would just like to reemphasize a comment

<sup>6</sup> Huntington Alloys, Inc., Huntington, W. Va.

<sup>&</sup>lt;sup>5</sup> Sandia Labs., Albuquerque, N. M.

that you made concerning the tandem use of the electric arc furnace and the AOD furnace. I think that one of the benefits of this process is that both pieces of equipment are utilized for the purpose that they do best. The electric furnace is very efficient for melting, but it is not the most functional equipment for refining. Using the electric furnace—I don't know other's experiences—but having worked in our melt shop, I've always felt that there was a lot of *witchcraft* (melter's art) associated with electric furnace refining, watching melters read carbon tests, and perform other steps that seem to be shrouded in an aura of mysticism that challenged metallurgical explanation.

By contrast, transferring a heat to the AOD vessel for refining, the process adheres to metallurgical theory. Refining is being done in a device that is thermodynamically sound. The operator knows exactly how much oxygen is needed to blow the carbon to the level desired, and when it's completed, the metallurgist says lo and behold, it works just like the textbook says it would.

Answer: L. W. Lherbier—Not having worked as a melter, I can sympathize with your witchcraft, and I think it may apply to all melting techniques, not just the electric furnace. However, a computer calculation is not going to make a heat every time. In fact, when a heat does not final as forecast, the experience of the melting person is necessary to correct the failure.

Question: Dr. M. K.  $Koul^7$ —I'd like to comment on this thing that everybody looks at, the AOD process as the solution for all problems. But one thing you have to see is that when you were making very high purity alloys, in the past, melters placed very very severe specifications on the raw materials they used. That is, raw materials like chromium, manganese, nickel, and other alloying elements.

Now, when you go to the AOD process, one of the incentives there is to go to low-cost material—high carbon chrome and things like that.

And for 15 cents a pound or 20 cents a pound, you are not going to get very high purity material as compared to electrolytic chrome or electrolytic manganese. So when you look at a process bringing in AOD, you should think about this, if you are going to get very high purity alloying elements with the AOD process combination with the electric furnace.

Answer: L. W. Lherbier—That's true. However, I think you have to recognize what the end application is, and what the customer requires. Customers are generally open to suggestions that potentially will reduce the cost of the metal that they're buying. And although for critical rotating parts you're locked in in many cases, if you present enough evidence,

<sup>&</sup>lt;sup>7</sup> Foote Mineral Co., Exton, Pa.

they will give you a lot of deviation so that you can make some changes and perhaps go a lower cost route.

*Comment: Dr. Koul*—You see, in titanium alloys, for example, half of the load is taken away from the melters and producers by the raw material producers, so that the raw material producers supply a very pure material at high price. What I'm saying is that you cannot put similar specifications on the producers of low-cost ferro alloys. You are going to have to do everything in your shop. This should be kept in mind when you talk about very high purity materials.

## Forging and Processing of High-Temperature Alloys by A. J. DeRidder and R. Koch

Question: Dr. R. Cremisio<sup>8</sup>—I think that we rarely get a chance to see such an excellent review, particularly on a new technology such as powder forging. I may have missed it, but I didn't see anything about argon entrapment. Does that mean this problem is pretty well licked?

Answer: R. Koch—I don't really have a lot on argon entrapment. I presume it would occur; I haven't recognized it as argon entrapment. We do see small voids. Much of the powder we see has a lot of very small voids in it, and apparently during a mechanical property test is they're at a limit of being small enough, they don't have a great impact on mechanical properties.

#### Review of Superalloy Powder Metallurgy Processing for Aircraft Gas Turbine Applications by J. L. Bartos

Question: F. Sczenzenie—In talking about your success on forging the as-HIP parts, you mentioned that you raised the gamma prime solvus. Would you explain that please?

Answer: Dr. Bartos—The gamma prime solvus of powder metallurgy René 95 is higher than in the conventional cast plus wrought version. The slight change in chemistry—reducing the carbon and chromium contents—raises the solvus in powder metallurgy René 95 to 2120 to 2150°F. This 25 to 50°F increase in solvus temperature relative to cast plus wrought René 95 permits a higher solution temperature in as-HIP that is largely responsible for the competitive property levels. However, the higher solvus has very little effect on the forged powder parts, since the solution temperature is much lower than that used on as-HIP parts.

Question: F. Sczenzenie—A second question. You mentioned that in order to control gas porosity, you were going to finer powder particle

<sup>&</sup>lt;sup>8</sup> Materials Technology Associates, Clinton, N. Y.

sizes. I normally associate finer powder with higher specific surface and more potential for gas problems. Could you explain your rationale and what powder size ranges you're working in?

Answer: Dr. Bartos-Finer powders generally mean more surface area, which raises concerns about the oxygen and nitrogen contents. However, these interstitial levels are still at acceptably low levels in the finer mesh powder we've evaluated. On the other hand argon, the gas that causes porosity problems, doesn't react with powder surfaces, so the increased surface area of finer powders is not a concern. The major benefit relative to porosity levels derived from finer powders is the fact that most of the powder particles containing entrapped argon are eliminated. The nature of the argon atomization process results in a substantial number of hollow particles, primarily concentrated in the larger size range, which contain entrapped argon. This entrapped argon cannot be removed by evacuation and causes porosity in the HIP compact. By screening down to a finer particle size, many of these larger hollow particles are eliminated, thus reducing the overall quantity of argon contained in the compact. Both the number and size of argon pores are reduced substantially by utilizing a finer mesh powder. General Electric is currently evaluating the feasibility of using powders in the -100 to -150mesh size range.

Question: M. Woulds<sup>9</sup>—I'm glad at last someone is recognizing powder metallurgy as its own production technique, and not something you can convert castings and forgings into. On that line, with your development of AF 115, is any work being done by you or anyone else in the field in going one step beyond, that is, taking an elemental phase dispersion type powder and blending? That is to say, taking gamma prime with a high hardener content and a matrix powder alloy and combining them; this way, one could have an alloy with high tungsten, that because of segregation in a VIM system could not be easily cast.

Answer: Dr. Bartos—We've never attempted to process René 95 in the manner you suggest. The technique you describe sounds like mechanical alloying, something we've never considered for superalloy rotating components like turbine disks. We've always felt the best way to achieve the desired high level of homogeneity is to use prealloyed powder production techniques. Homogeneity is going to be a problem when you try to mix a dozen or more different elements together to make a typical superalloy. On the other hand, prealloyed powders, in which every powder particle has essentially the same composition, are a much more efficient method of achieving homogeneity rather than relying on some exotic blending

<sup>&</sup>lt;sup>9</sup> Certified Alloy Products, Long Beach, Calif.

technique to distribute all elements uniformly. We don't feel that blending techniques are really practical at this time.

Question: M. Woulds—What about two or three master alloys with different phases, rather than all the elements?

Answer: Dr. Bartos—We feel the same type of problem, inhomogeneity, would still be present, especially when different input master alloy particle sizes are involved. Mr. Koch showed you how powders segregate by particle size even though they're the same composition. The distribution of all elements by this mechanical mixing technique may lead back to the segregation present in cast plus wrought products locally high concentrations of certain elements. Since homogeneity is one of the principal desirable features of powder metallurgy processing, pre-alloyed powder appears to us to be the best production technique at this time.

Question: M. Hart<sup>10</sup>—How do the cyclic rupture properties compare for the as-HIP microstructure versus the cast and wrought necklace microstructure.

Answer: Dr. Bartos—The cyclic rupture properties of as-HIP René 95 are essentially equivalent to those of the cast plus wrought product containing a duplex necklace microstructure. Mr. Koch showed that a fine-grained, fully recrystallized wrought structure yields lower cyclic rupture properties than the duplex necklace structure. The as-HIP structure is essentially fine grained, but it's not recrystallized in the same manner as the cast plus wrought product, and it also is given a different heat treatment. Apparently, the microstructure produced during HIP combined with the heat treatment results in improved cyclic rupture relative to that of the conventional forged fine grain product. Cyclic rupture is a property prone to fairly significant scatter, so slight differences may be hidden. We're still gathering data to evaluate this question but from what we've seen so far, there doesn't seem to be a great difference in the cyclic rupture properties of the three forms of René 95-as-HIP, HIP plus forge, or conventional necklace microstructure cast plus wrought.

# Super Waspaloy Microstructure and Properties by D. J. Deye and W. H. Couts

Question: G. N. Maniar<sup>11</sup>—Is it mandatory that you keep the carbon low? Because it seems you refine the grain size by keeping gamma prime out to inhibit the grain size.

<sup>&</sup>lt;sup>10</sup> Cameron Iron Works, Houston, Tex.

<sup>&</sup>lt;sup>11</sup> Carpenter Technology Corp., Reading, Pa.

Answer: D. J. Deye—In order to develop the best tensile and low cycle fatigue properties, we feel that it is necessary to keep the carbon content low. We forged conventional chemistry Waspaloy using the same forging parameters that we used for Super Waspaloy and showed an improvement in the tensile and low cycle fatigue properties. However, it was not to the extent that we saw with Super Waspaloy.

Question: G. N. Maniar—Did you have to balance any elements such as titanium or boron when you lowered the carbon or did you keep them the same?

Answer: D. J. Deye-The titanium content was increased and the boron content range was tightened up.

Question: Kuang-Ho Chien<sup>12</sup>—What is the difference in stress rupture ductility between conventional Waspaloy and Super Waspaloy?

Answer: D. J. Deye—At the higher temperatures, the rupture ductility for Super Waspaloy was slightly higher than that for conventional Waspaloy. At the lower temperatures, that is 1350°F, the rupture ductilities were equivalent.

Microstructure and Mechanical Properties of INCOLOY Alloy 800 After 14 Years of Service as a Catalyst Tube in a Steam-Methane Reformer by W. L. Mankins and D. E. Wenschhof

Question: L. Thompson<sup>13</sup>—We've been working on the age-hardening in commercial heats of Alloy 800H ourselves. The investigation has been directed at five heats supplied by Huntington Alloys, and in the asreceived condition, we find titanium carbides, titanium carbonitrides, and  $M_{23}C_6$  type carbides all present in small amounts. We have aged these alloys at 538, 593, 649, 760, and 816°C (1000, 1100, 1200, 1400, and 1500°F) for times approaching 20 000 h. The maximum aging response was observed at 593 and 649°C (1100 and 1200°F) with the aging response at the other temperatures much lower.

The majority of the age-hardening was observed to occur within 500 to 1000 h of exposure. We have performed extensive transmission electron microscopy to look for the gamma-prime phase and other precipitating phases, as well as, extraction analyses similar to those that you've performed. We did not observe any gamma-prime precipitation within 1000 h of exposure. However, we have observed gamma-prime after aging 4000 to 8000 h. What we observe are small, spherical precipitates coherent with the matrix, with strain fields around the precipitates of the order of 100 Å in diameter. The precipitates themselves are not resolv-

<sup>&</sup>lt;sup>12</sup> Cameron Iron Works, Houston, Tex.

<sup>&</sup>lt;sup>13</sup> General Atomic Co., San Diego, Calif.

able, but, by the size of the strain fields, they are certainly much smaller and are probably of the order of 30 Å or so in diameter.

The only consistent observation we've made within the 500 to 1000 h exposure time period has been the precipitation of  $M_{23}C_6$  carbides at the grain boundaries. At 649°C, (1200°F) they form a continuous network along the grain boundaries that could possibly inhibit slip transferral from one grain to the adjacent grains. No cross-slip has been observed for this alloy. At higher temperatures 760 and 816°C (1400 and 1500°F), we see the carbide present much as you did, as very large, discrete carbides, and at these temperatures no strong aging response was found. No gamma-prime precipitation has ever been observed to form at these higher temperatures in our lab.

At lower temperatures, the kinetics for the precipitation of  $M_{23}C_6$  are retarded and the aging response is delayed. There is still, however, much work to be done in this alloy system, and the results that you present are very interesting.

I should also mention that I'm having four experimental heats melted at the Lawrence Berkeley Laboratory, through the University of California, with controlled variations in carbon, aluminum, and titanium, and hopefully some of the confusion will be cleared up within the next year.

Question: R. Anderson<sup>14</sup>—Do you think that this problem of the gamma-prime precipitates dissolving in your extraction electrolyte might be a similar reason for not finding gamma-prime in 718, where it's often been postulated and some people have said it's there, but it's difficult to show in extraction?

Answer: W. L. Mankins—I really believe it is. It's a good question and my own personal feeling is that you do extract it. Let's assume it's there. You extract it. It falls down to the bottom of your beaker and is simply chemically digested, particularly if it's real fine. So you go to look for it, and it isn't present.

Question: Dr. W. Jones—For the component that you discussed, was there any thermal fatigue superimposed on the low static loading during its life? In other words, was there any creep—fatigue history?

Answer: W. L. Mankins—I couldn't be specific about that, but creep damage was one of the things we did examine the tube for. In cutting it all apart, many more micros were made than were shown in this presentation—we did examine it for creep damage. It was very minimal or if there was creep damage, it was not sufficient that I was willing to say that it was observed.

<sup>&</sup>lt;sup>14</sup> Universal Cyclops Specialty Steel, Bridgeville, Pa.

Question: Dr. W. Jones—In ferritic and austenitic stainless steels that we've been looking at, which were mechanically tested at 1100°F, we find that in creep-fatigue conditions very long hold times and therefore relatively few cycles at modest strain ranges, that we find there are enough vacancies generated during the fatigue cycles to greatly influence the kinetics of, in these cases, carbide precipitation. And it may be here, in this case, that if you have marginal phase stability, that if you happen to have the right high-temperature history and extra vacancies, that in some cases people will find the marginally stable gamma-prime primarily as a result of enhanced kinetics, while others may never see it.

Answer: W. L. Mankins—One comment on that. One of the ideas that gets batted around a little bit on this subject is that the observed strengthening may result from a pre-precipitation phenomena, such as GP zones or some other pre-precipitation occurrence.

Comment: L. Thompson—I'd like to emphasize one point that I glossed over earlier. That is that we saw two strengthening responses one after a short aging time, up to about 1000 h, and then one after a longer period of time that seemed to be consistent with when we have observed gamma-prime precipitation. By far, the stronger of the two happened to coincide with the precipitation of  $M_{23}C_6$  carbides at the grain boundaries. Some of this work is documented in a paper by R. E. Villagrana and his associates that will appear in *Metallurgical Transactions* in July 1978, while considerable other documentation has been made in General Atomic Company's Department of Energy quarterly progress reports for the Generic Technology Program.

Comment: D. J. Deye—You showed a pretty significant improvement after 120 000 h, but do you have any 200 000-h pipe data?