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A review of the historical development of heat resisting stainless steels and high temperature alloys reveals that advances have occurred in three waves or generations over the past 50 years. These developments are the result of increased technical understanding of how alloying elements influence microstructure. Advances in steelmaking practice also have contributed greatly to these improvements.

While there are a number of important ferritic stainless steels used in high temperature service, the scope of this article encompasses the austenitic stainless and nickel-base alloy systems.

## First Generation Alloy Systems

During and immediately following the second world war, heat resisting stainless steels and alloys were primarily formulated with various combinations of chromium and nickel. The important operative systems are listed in Table I.

While silicon is present in these alloys, it was employed as a convenience of the melt practice rather than an intentional addition. Titanium addition in types 321, 600 and

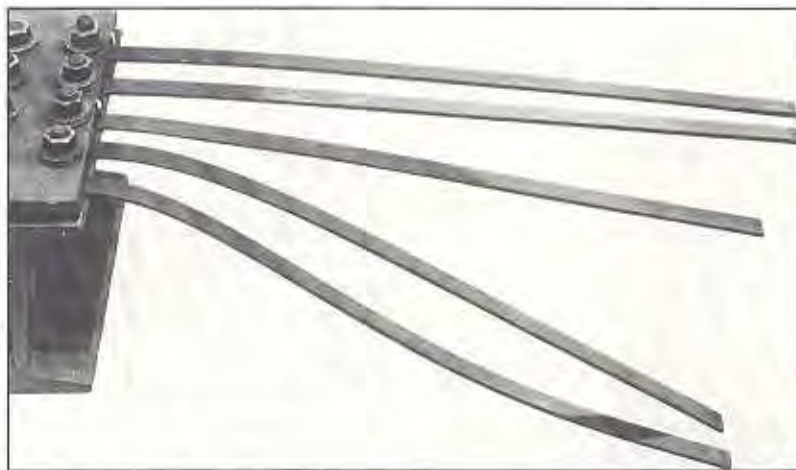


Fig. 1 Cantilever beam creep test of five heat resisting alloys. Exposure: 500 hours at 1600°F. Alloys front to rear are 309, 310, RA330, 601 and RA85H.

800 was for the purpose of improving welding and corrosion properties. It is a more active carbide former than chromium, reducing the free carbon available to form the less desirable chromium carbide. The net result was a way to produce a low carbon type alloy without sacrificing cost.

While Si, Ti and C are recognized as important contributors to creep strength, Fig. 1, this was not their major purpose in 1950. The primary method of improving creep and rupture strength was by adjustments in level and ratio of chromium and nickel. In all cases the alloys were designed to be fully austenitic in the annealed condition.

Alloy 600 was originally developed as a corrosion resistant alloy to compete with type 316L in the dairy industry. It was adopted by the heat treating industry because the high nickel content provided excellent resistance to carburization and adequate creep strength. Although it continues to be specified today, alternative economical alloys have been developed.

## Second Generation Alloy Systems

Industry demands for higher performance alloys led to a second wave of alloy development, beginning in the late 1950's and extending into

the early 70's. Some important alloy systems that became commercial during that period are listed in Table II.

Concerns for control of carbide embrittlement coupled with improvement in steel melting yielded a reduction in average carbon levels. To compensate for the loss in strength, silicon levels were intentionally increased above the residual levels that had been common. Silicon became a recognized alloy addition for heat resisting grades. Also, some producers increased grain size to enhance creep strength. This led to the modification of 800 alloy to 800H and subsequently to 800 HT. As discussed in more detail later, some properties are reduced (sacrificed) as grain size becomes more coarse.

RA330<sup>R</sup> was reformulated during this period with reduced carbon and increased silicon levels. This change improved creep strength, cyclic performance and resistance to carburization.

During this period, 600 alloy was modified and 601 was the result. Alloy 601 was developed to provide a high nickel alloy specifically designed for high temperature service. Aluminum was used for the first time to improve an alloys resistance to oxidation. While 601 alloy proved quite resistant to oxidation under steady

Table I Composition of First Generation of Heat Resisting Alloys

| Alloy | Cr   | Ni   | Si  | C   | Other |
|-------|------|------|-----|-----|-------|
| 309   | 23   | 13.5 | .6  | .1  |       |
| 310   | 25   | 21   | .75 | .1  |       |
| 321   | 18   | 10   | .6  | .08 | Ti .8 |
| RA330 | 15   | 35   | .75 | .08 |       |
| 800   | 20   | 32   | .4  | .06 | Ti .4 |
| 600   | 15.5 | 78   | .2  | .08 | Ti .2 |

**Table II Composition of Second Generation of Heat Resisting Alloys**

| Alloy | Cr   | Ni   | Si   | C   | Other                 |
|-------|------|------|------|-----|-----------------------|
| RA309 | 23   | 13   | .8   | .05 |                       |
| RA310 | 25   | 20   | .5   | .05 |                       |
| RA330 | 19   | 35   | 1.25 | .05 |                       |
| 800H  | 21   | 31   | .4   | .06 | Ti .4, Al .3          |
| 600   | 15.5 | 76   | .2   | .08 | Ti .2                 |
| 601   | 22.5 | 61.5 | .2   | .05 | Al 1.4                |
| RA333 | 25   | 45   | 1.5  | .05 | Co 3, Mo 3, W 3       |
| HASTX | 22   | 47   | .3   | .06 | Co 1.7, Mo 9          |
| 617   | 22   | 52   | .75  | .08 | Co 12.5, Mo 9, Al 1.2 |

**Table III Composition of Third Generation of Heat Resisting Alloys**

| Alloy   | Cr   | Ni   | Si   | C   | Other                                     |
|---------|------|------|------|-----|---|
| RA153Ma | 18.5 | 9.5  | 1.3  | .05 | N .15, Ce .04                             |
| RA253Ma | 21   | 11   | 1.7  | .07 | N .15, Ce .04                             |
| RA85H   | 18.5 | 14.5 | 3.5  | .2  | Al 1                                      |
| HR120   | 25   | 37   | .6   | .05 | Co 1, Mo 1.2, W .5, Cb .7                 |
| HR160   | 28   | 37   | 2.75 | .05 | Co 28                                     |
| 214     | 75   | 16   | .2   | .05 | Y   |
| 230     | 22   | 57   | .4   | .1  | La .02                                    |
| 556     | 22   | 20   | .3   | .1  | Co 18, Mo 3, W 2.5<br>N .2, Ta .6, La .02 |

state conditions, cyclic exposure tends to cause the protective oxide to crack, which leads to increased oxygen penetration. There also is a tendency for 601 to oxidize internally under some exposure conditions. However, the use of aluminum to enhance oxidation continues to be an effective addition in alloy systems today.

During the 70's, alloys containing refractory metal additions such as molybdenum, cobalt and tungsten became commercial. RA333<sup>R</sup>, HASTELLOY<sup>R</sup> X and 617 alloy are all part of this family. These highly alloyed systems retain creep strength to very high temperatures near the melting point and generally have very good atmosphere resistance. However, one shortcoming is that high additions of molybdenum will cause alloys to fail by catastrophic oxidation when exposed to stagnant air conditions. Therefore, a good knowledge of the service conditions is most important when choosing one of these grades. RA333<sup>R</sup> provides some advantage in that the molybdenum level is considerably less than that of the other two grades.

### Third Generation Alloy Systems

A new surge in alloy development began in the mid 70's. Some important new commercial alloys from this current period are listed in Table III.

The trends during this period have been the development of either very lean systems or complex highly alloyed, more expensive grades. There was much broader use of silicon and for the first time, rare earth additions were used to enhance oxidation resistance.

Developed in Sweden as modifications of types 304 and 309 stainless, RA153MA<sup>R</sup> and RA253MA<sup>R</sup> provide significant improvements in oxidation resistance and high temperature strength. These improvements are accomplished through additions of silicon and the rare earth element cerium. Nitrogen also is effectively used to stabilize the austenite which be-

comes unstable as silicon increases. Nitrogen is similarly used in the rich alloy 556.

Introduced in the mid 80's, RA85H<sup>R</sup> alloy is unique in a number of ways. The 3-1/2% silicon is very effective in improving carburization resistance even though the nickel content is only 14.5%. The addition of aluminum assists silicon in providing good oxidation resistance. The alloy was designed with 0.2% C to provide both strength and grain size control in service. This alloy is also unique as being the first iron base austenitic stainless steel that will resist reducing sulfur conditions in service and is being used in a number of hot corrosion applications.

The series of highly alloyed heat resisting grades, developed by Haynes, tend to be much more use specific and are designed for optimization of a single performance characteristic. They make extensive use of refractory elements introduced in the second generation alloy systems. Three of the five grades also utilize rare earth additions to enhance oxidation and high temperature strength. The alloy HR120 also utilizes coarse grain size to improve creep strength in the same way as 800H was modified in the 60's.

### Creep and Rupture Properties

Alloys designed for high temperature service must have sufficient strength to maintain structural integrity at the maximum service temperature. A number of methods have been developed to measure strength. The more common are hot tensile strength, stress rupture and creep. Each of these properties provide different information. Hot tensile strength measures short time effects of increasing load conditions. Stress rupture provides information concerning the stress required to produce failure of sample under constant load and temperature. Creep measures sample distortion with time at con-

stant load and temperature. Each property provides the materials engineer with useful data to predict performance in service. However, an alloy with high rupture strength may not be appropriate where failure by distortion is the concern. This is particularly true in most heat treating applications. Distortion from excessive creep is one of the more common modes of failure in furnace parts and fixture service.

While rupture data is uniformly and consistently presented, the same is not true of creep data. Generally, creep data is presented as either minimum creep rate or total creep. Accuracy of minimum creep rate data is dependent on interpretation of the slope of the curve in the secondary creep region. In heat resisting stainless steels the secondary region may be very short or perhaps non-existent. The other method, though less widely reported in the literature, is to present the data as the time to reach a specific level of distortion. This condition is usually expressed as time to 1% total creep. While these results are more variable to measure, they do provide a truer picture of the effect of creep on field performance.

Regardless of which type of data is used it is important to recognize that more than one type of data exists and direct cross comparisons between reporting methods do not provide valid results.

To further illustrate the point that distortion is a prime cause of failure, Fig. 1 is a demonstration of how various alloys react under identical thermal and stress conditions. These test coupons were pre-machined to identical width and thickness and clamped to the I-Beam to provide each with a uniform overhang. The test rig was then installed in a furnace at 1600°F and held for 500 hours. The alloys are from front to back; types 309, 310, RA330, 601 and RA85H. Type 309 sample distorted under its own weight in 8 hours, contacted the fur-

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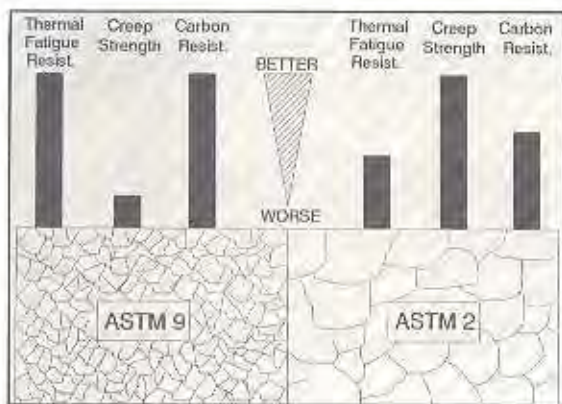


Fig. 2 Influence of grain size on properties of heat resisting alloys.

nance base and continued to creep as illustrated by the reverse bend. Type 310 contacted the furnace base in 48 hours showing no further tendency to creep. RA330 distorted about 2" in 500 hours and alloy 601 and 85H showed less than 1/2" distortion from creep in 500 hours. Distortion from creep as illustrated, rather than rupture failure, should be a major concern of high temperature application engineers. With rare exceptions creep distortion will render a component unsuitable for continued service long before rupture occurs. Therefore, the use of stress to rupture data in design should be done with caution.

#### Microstructure Effects

The microstructure of heat resisting alloys consists of several interactive elements. While most of these systems are designed to be "fully austenitic", thermal processing, stress, service temperature and atmosphere exposure tend to bring about changes. These changes are usually related to structural instability that may be inherent to the alloy system or result from environmental interaction during service. Some of these changes are undesirable and need to be controlled or avoided.

Grain size of alloy systems in ser-



Fig. 3 Typical thermal fatigue damage after repeated quenching.

vice has multiple impacts on various properties. Some of these are illustrated in Fig. 2. Creep strength increases dramatically as grain size becomes coarser. Alloy systems like 800HT and HR120 advantageously use this factor to enhance creep properties. It is important to recognize that some properties deteriorate as grain size coarsens. These include resistance to the environment such as oxidation, carburization, etc. Also, thermal fatigue resistance decreases with coarser grain size, resulting in a loss of structural integrity as illustrated in Fig. 3. This bar from a heat treat basket was subjected to repeated quenching, with the resultant crack pattern being a typical failure mode for alloys.

To further illustrate the impact of grain size on this mode of failure, a basket was prepared by the laboratory from a number of alloys with varying grain size. A bar sample of each alloy having a particular grain size was tested before and after thermal cycling and the ratio of original to final ductility provided a measure of thermal fatigue damage. The overriding factor determining thermal fatigue performance was grain size as shown in Table IV.

Another important consideration in heat treating service is how well an alloy resists the combined impact of oxidation and carburization. Concerning this resistance, a significant body of data exists in the literature as based upon parts exposure to furnace atmosphere formed by adding methane (to create carbon potential) to a hydrogen carrier gas. Since nearly all heat resisting alloys depend on a surface oxide film to inhibit carburization, scientific data using sharply reducing atmospheres is not a realistic measure of how an alloy will perform in service. Thus, for many alloys the comparison data obtained under these test conditions is deceiving.

Silicon has become recognized as a high impact addition for improving carburization resistance and thus the

major commercial alloys include this element. RA85H was developed with 3-1/2% silicon in a lean alloy base. While virtually all commercial heat treating alloys absorb carbon during service, there are important differences as to how the individual alloy microstructure accommodates this added carbon. Most alloys tend to form a continuous carbide along grain boundaries and twin bands. This

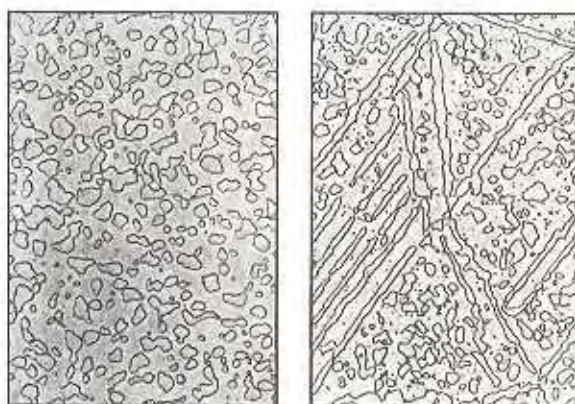


Fig. 4 Influence of alloy content on carbide morphology.

Table IV Influence of Grain Size on Thermal Fatigue Resistance as Indicated by Ratio of Final to Original Ductility

| Original Grain Size, ASTM Number | Ratio Final Ductility / Original Ductility |
|----------------------------------|--|
| 10.8                             | 106  |
| 4.0                              | 62   |
| 7.2                              | 63   |
| 3.6                              | 61   |

stringer-like morphology is responsible for providing a convenient crack path and high loss of ductility in service. The high silicon RA85H on the other hand forms discrete globular carbides and retains higher ductility for equivalent carbon absorption than RA330. This difference is illustrated in Fig. 4. Understanding the role that microstructure plays in creating properties is an important consideration in the alloy selection process; its influence on various properties in addition to strength must be considered.

#### Summary

The properties of metals and alloys are strongly determined by the composition of the alloy and the microstructure that is present or develops as a result of service conditions. Over the past 50 years, much has been learned about how these two factors interact. This knowledge has significantly increased the ability to design and use alloys to their fullest advantage.