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Review
Strengthening of nickel-base superalloys for nuclear heat exchanger applications

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Strengthening mechanisms of nickel-base superalloys have been discussed with the background of the Japanese research and development activities in this field. As candidates for materials of intermediate heat exchangers which will be used for a future programme of nuclear steelmaking systems, two kinds of alloys have successfully been developed in Japan. The designs of these alloys have been reviewed from metallurgical aspects including their composition and creep properties. In addition to the conventional methods to strengthen these alloys, such as solid solution hardening or particle precipitation hardening, a grain-boundary precipitation strengthening due to tungsten-rich α_2 phase in the Ni–Cr–W system, would be expected as a further advanced method.

1. Introduction

The development of heat resistant materials is closely related to the energy problem to which advanced countries are now faced. The countries all over the world are eager to promote energy saving and to develop those types of energy which can be used alternatively in place of petroleum or other fossil energies. With this move, the change from thermal to nuclear power generation will be further accelerated.

Under such circumstances, Japan had been proceeding with the Sunshine Project from 1974 to develop alternative energy and the Moonlight Project from 1978 to develop energy-saving technologies. The successful undertaking of the projects will strongly depend upon the research and development of heat resistant materials. The R and D activities are continuing with a view of utilizing them for many purposes including automobile exhaust valves and exhaust emission control devices, aircraft jet engines, various types of high temperature reaction vessels for the chemical industry, and nuclear reactors. Industries are expectantly looking for those materials which can be used under the severest conditions.

The present paper reviews the status of Japanese R and D in designs of heat resistant superalloy for heat exchanger tubes relating to the high temperature gas-cooled reactor (HTGR), the metallurgical basis for strengthening mechanisms of the developed alloys and further possibilities of strengthening of the alloys.

2. Status of Japanese R and D in superalloy design

2.1. Target of the alloy development

Research and development activities in superalloy technologies have been activated by the commencement of National Research Projects [1, 2] on nuclear steelmaking in 1973. In the steelmaking systems, the nuclear energy generated by HTGR is transferred to a reductive gas by an intermediate heat exchanger of He–He type. The superalloy to be used for the materials of this exchanger must have 1000° C(1273 K)–5×10^4 h(18×10^7 sec), (final target: 10^5 h(3.6×10^8 sec), rupture strength of higher than 9.8 MPa(1 kgf mm^{-2}) in addition to having sufficient formability into tubes. Several types of conventional iron- and nickel-base alloys which are formable into tubes were chosen as the candidate materials and tested. Among these alloys, the strongest Inconel 617 was estimated to have 1000° C–5×10^4 h rupture strength of about 9.0 MPa as shown in Fig. 1 [3], and apparently this level of strength is still insufficient. Thus, further efforts [4–9] extensively went on to develop a new alloy satisfactorily meeting the above mentioned requirements.

2.2. Developed candidate alloy

The primary policy for designing superalloy is to obtain an outstanding high temperature strength by further strengthening the solid solution strenthened

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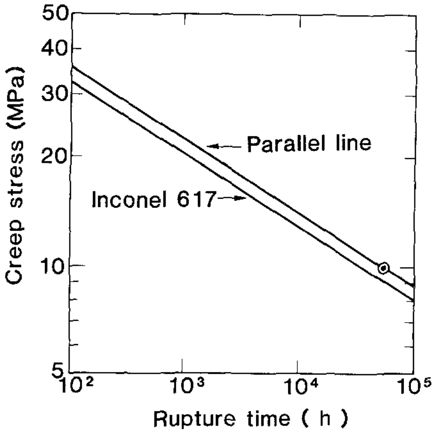

Figure 1 Estimated creep rupture strength of Inconel 617 and the parallel line drawn through the point (⊙) of 9.8 MPa at 5 × 10^4 h; 1273 K.

nickel-base alloy through the precipitation of γ' phase [10]. However, the γ' phase is usually dissolved at a service temperature of 1273 K (1000° C) or becomes rapidly coarse due to coalescence. Perhaps adding cobalt to the alloy so as to raise the solid solutioning temperature may be proposed as shown in Fig. 2 [11], but it has been pointed out [12] that the addition of cobalt is not adequate because of its induced radioactivity. In the alloys, on the other hand, which are strengthened by the precipitated carbides phase, the quite rapid coarsening of carbides occurs at high temperature. From this aspect, it should be noted that the amount of carbon is restricted to less than about 0.03 wt % [8, 9].

Thus, the basic type of alloys so far developed in Japan have turned out to be Ni–Cr alloys solid solution strengthened by tungsten. Table I shows the typical alloys developed as candidate materials for intermediate heat exchangers.

2.3. Theoretical promising composition range

In designing the Ni–Cr–W system alloys, Watanabe and Chiba [13] have determined the theoretical promising composition range for the system as shown in Fig. 3. The diagram is quite useful for alloy design, namely, alloy compositions in the lower and left-hand region under the $N_v = N_c$ border line with lattice parameter larger than $a_0 = 0.358$ nm are considered to have the highest solid solution strengthening effect without precipitating any intermetallic compounds, where N_v is the average electron vacancy number and the N_c is the critical electron vacancy number which is proposed by Barrows and Newkirk [14].

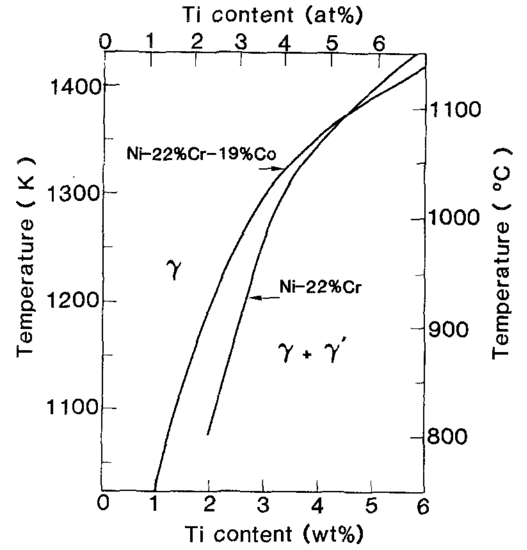

Figure 2 Effect of cobalt addition on the γ' solvus in Ni–22% Cr alloy, where Ti–Al ratio = 1 : 1.

Using this diagram, Watanabe and Chiba [9] designed an Ni–23% Cr–18% W alloy with small amounts of carbon, titanium and zirconium having an extrapolated 1000° C–10^5 h(1273 K–3.6 × 10^8 sec) creep rupture strength of 14.7 MPa.

2.4. Phase diagram of Ni–Cr–W system

It is important to grasp the maximum soluble amounts of chromium, molybdenum and tungsten in nickel for designing the nickel-base solid solution strengthening type superalloys. Based on the thermodynamic equilibrium theory, the isothermal section of an Ni–Cr–W ternary phase diagram at 1273 K has experimentally been determined by Kagihara *et al.* [15] as shown in Fig. 4. Plotting the alloy compositions shown in Table I into this diagram, most of them, with an exception of some alloys, are bound to settle in γ–(γ + α_2) boundary region, although all these alloys also contain either titanium, zirconium or boron with levels of 0.3, 0.03 and 0.004 wt %, respectively. Indeed, it is found from Table I that these alloys except for B and D in Table I comprise tungsten-rich, b c c α_2 phase and $M_{23}C_6$/M_6C carbides, rather than γ single phase.

2.5. Stress–rupture time data

Fig. 5 shows the stress–rupture time curves of the various nickel-base alloys so far developed [5, 16–18]. The remarkable improvement of the rupture strength is attained by the additions of chromium and tungsten into nickel. However, we have clarified that tungsten

TABLE I Chemical composition and precipitate phases of the developed superalloys for use in intermediate heat exchanger materials in HTGR

Alloy	Element (wt %)													Precipitate Phase
	C	Cr	W	Si	Mn	P	Mo	Ti	Ni	B	Y	Zr	Other	
A	0.05	23	18	–	–	–	–	0.5	Bal.	–	–	0.035	–	$M_{23}C_6$, α_2
B	0.06	18	15	–	–	–	0.5	0.2	Bal.	–	0.02	0.02	–	carbide
C	0.03	16	26	0.03	< 0.002	0.01	–	–	Bal.	–	–	0.05	Nb	α_2
D	0.03	27.5	5	–	–	–	5	–	Bal.	0.004	–	0.03	–	$M_{23}C_6$
E	0.08	20	20	–	–	–	–	–	Bal.	–	–	0.01	Al	α_2, M_6C, $M_{23}C_6$?

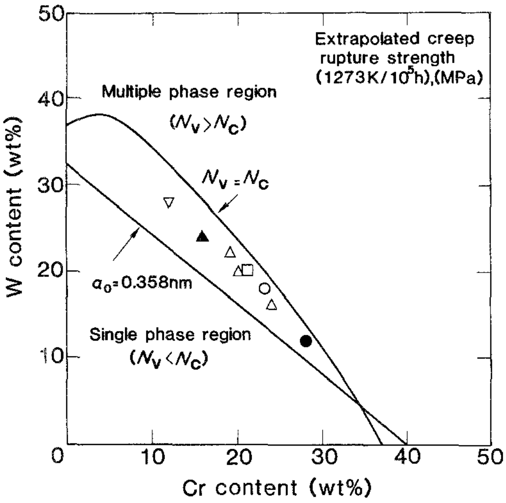

Figure 3 Relation between the balance of chromium and tungsten in the theoretically promising composition range of Ni–Cr–W system and extrapolated 1273 K/10^5 h creep rupture strength (MPa): (○) 14.7 (Alloy A), (□) 11.8, (△) 10.8, (▲) 9.8, (●) 7.8, (▽) 5.9.

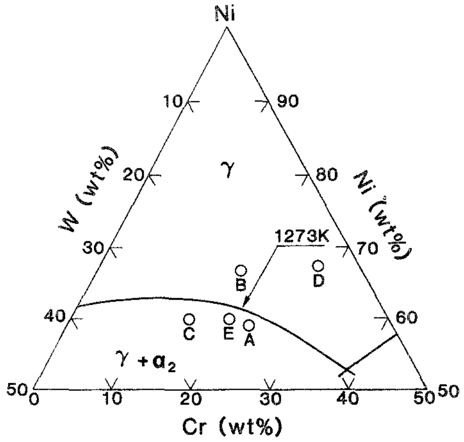

Figure 4 Calculated solubility curves in the isothermal section at nickel-rich corner in Ni–Cr–W ternary phase diagram at 1273 K.

remaining in the γ solid solution is restricted to the maximum 15 wt %. The increase in rupture strength with more than 15 wt % tungsten addition is caused by the presence of the α_2-W phase. Further improvement of rupture strength for the alloy containing 0.165 wt % C with zirconium can be thought to be attributable to the multiple (superimposing) effects of precipitation strengthening of carbides and grain-boundary strengthening due to zirconium [4, 5].

3. Strengthening mechanisms

3.1. Solid-solution strengthening

In Fig. 6, the extents of solid-solution strengthening attainable by each addition of tungsten, molybdenum, niobium and zirconium are compared with the amount of decrease in the steady state creep rate of Ni–20% Cr alloy with additions of these elements, at 1273 K under a stress of 29.4 MPa [17–20]. Each addition of tungsten and molybdenum in amounts 10 wt % appears to decrease the creep rate by an order of magnitude, and it is found that tungsten increases creep resistance to a somewhat larger extent than does molybdenum. It is noteworthy, however, that the addition of niobium increases the creep resistance more drastically.

The extents to which the creep resistance is increased by these elements are in good correspondence with their atomic size factor function against Ni–20% Cr alloy, as was previously reviewed by Jena and Chaturvedi [21] in nickel. Fig. 7 shows the changes in lattice parameter with the additions of tungsten and molybdenum into a Ni–20% Cr alloy [17, 18]. Thus, it is found that the changes in creep resistance attained by the addition of these elements are in a close relation to the changes in the lattice parameter. Since the solubility limit of tungsten in Ni–20% Cr alloy have been estimated to be 16.5 wt % (5.9 at %) at 1273 K [15], the lattice parameter of the γ phase is determined as 0.3583 nm from this figure. Although this value is somewhat larger than the value previously used as the standard for the theoretically promising composition range of this alloy in Fig. 3, it may be concluded that the solubility limit may be roughly estimated using the value of γ lattice parameter. However, as obvious from Fig. 6, the Ni–20% Cr alloy is solid-solution strengthened by tungsten and molybdenum only to such extent that creep resistance increases by several tens of times, and the rupture strength is still lower than 9.8 MPa even at 1000° C(1273 K)–10^4 h(3.6×10^7 sec). Therefore, as shown in Table I, for the developed Ni–Cr–W or Ni–Cr–W–Mo alloys, it is expected that the precipitation strengthening is related by several orders of magnitude to the solid solution strengthening.

3.2. Strengthening by α_2 phase

As described above, most of the alloys developed for use in the heat exchanger of HTGR precipitate the

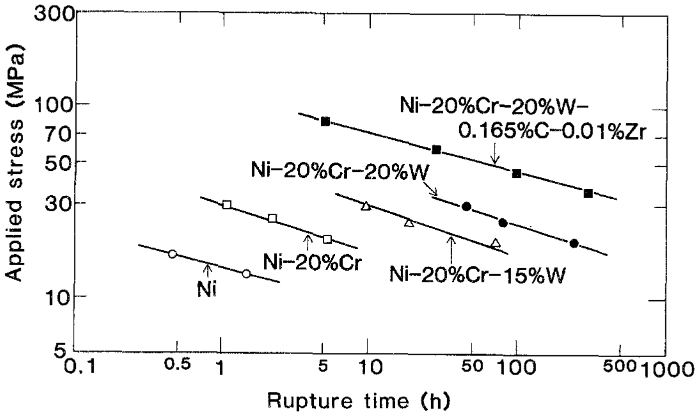

Figure 5 Stress–rupture time curves for nickel and Ni–20% Cr alloys at 1273 K, in air.

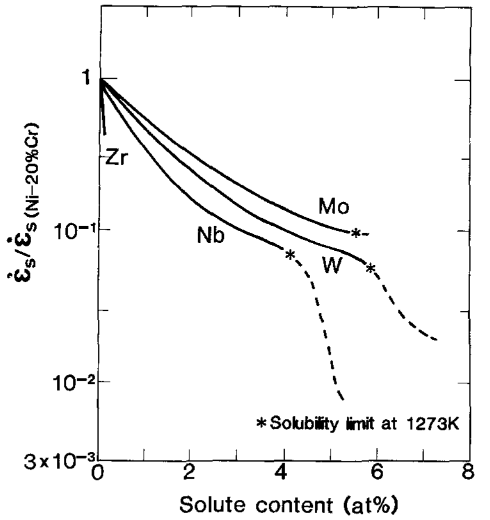

Figure 6 Comparison of solid solution strengthening effect of molybdenum, tungsten, niobium and zirconium in the relation between the decreasing ratio of steady state creep rate and solute content in atomic per cent; 1273 K, 29.4 MPa.

α_2-phase. However, the alloys containing tungsten plus molybdenum over their solubility limits precipitate the μ phase with the α_2 phase, as shown in Fig. 8.

It has been pointed out by several researchers [5, 7–9] that the α_2 phase usually improves the creep rupture strength. On the other hand, according to Ohta *et al.* [7] the μ phase precipitated in molybdenum-bearing alloys shortens the rupture life because of its promotion effect of the initiation and propagation of cracks, although it is also effective in decreasing the creep rate to some extent. The precipitation of α_2 phase might be simply regarded as precipitation strengthening effect in view of its contribution in improving the creep rupture strength. The α_2 phase, however, has a size in excess of 1 μm within grains and its precipitation amount is not so great within grains. It is also indicated [7] that up to a volume fraction of 3%, the rupture strength is improved by increasing the α_2 phase. In order to check this point, a series of creep tests was conducted at 1273 K using a carbon-free Ni–20% Cr–20% W alloy so that the tests would not be affected by carbides. The results of the tests revealed that there was little precipitation of α_2 phase within grains in this alloy but the α_2 phase precipitated at the grain boundaries, whereby both the creep resistance and the rupture strength can be improved significantly. The morphology of the α_2 phase is shown in Fig. 9. It was also found from the tests that the strength remarkably increased when an appreciable fraction of the grain boundaries was covered with the α_2 phase. Thus, the remarkable strengthening achieved can be considered to be due to the mechanism in which the α_2 phase suppresses the deformation on the grain boundary and hence increases the creep resistance. This strengthening mechanism was then termed as "grain-boundary precipitation strengthening" in order to distinguish it from the conventional precipitation strengthening within the grains. The α_2 phase also works effectively to improve the creep rupture strength, because the phase mostly comprises tungsten which is stable at high temperatures due to its higher melting point and precipitates in a manner covering most of grain boundaries as was shown in Fig. 9. Furthermore, these characteristics of the α_2 phase contribute to the increase in both rupture ductility and atmospheric resistance of the alloy [22, 23]. Actually, the rupture time increased by five to ten times due to the precipitation of the α_2 phase in the case of the Ni–20% Cr–20% W alloy as previously shown in Fig. 5.

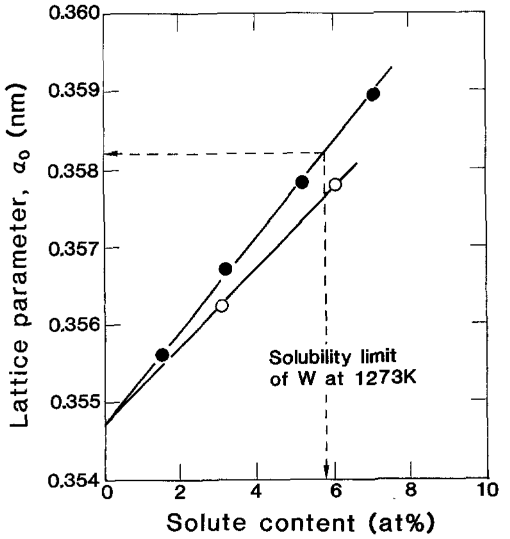

Figure 7 Changes in lattice parameter of Ni–20% Cr alloy with additions of tungsten or molybdenum. Δa/at% (nm): (●) W, 6.2×10^{-4}; (○) Mo, 5.2×10^{-4}.

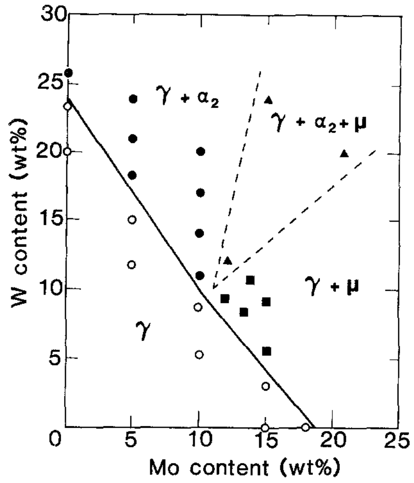

Figure 8 Variations in the solubility limits of tungsten and molybdenum in Ni–15% Cr alloy, showing also the second-phase region at 1273 K.

3.3. Effect of precipitate carbides

The effect of carbon content on the creep rupture strength of the Ni–Cr–W system alloys, has been investigated by Watanabe and Chiba [9]. Their results indicated that the maximum rupture strength was observed at about 0.06% in the range from 0.02 to 0.08%, as shown in Fig. 10. The level of 0.06% corresponds to the precipitation of fine $M_{23}C_6$ but that M_6C appearing on the low chromium and high tungsten side decreases the rupture strength due to an extremely high rate of coarsening [9]. Similar results have also been reported by other researchers [5, 6]. It should be noted, however, that the detailed studies on the

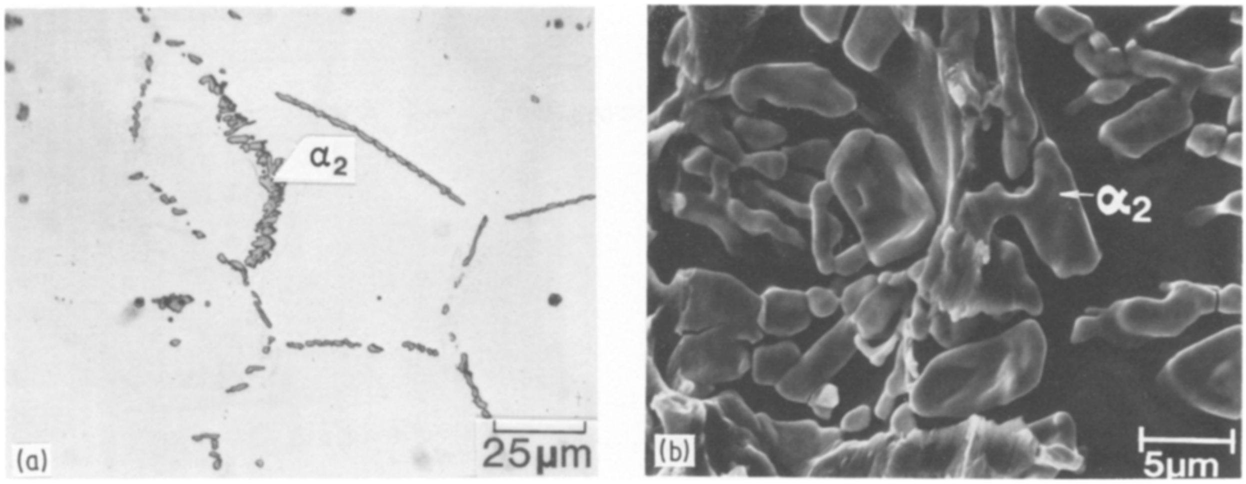

Figure 9 (a) Optical and (b) scanning electron micrographs of Ni–20% Cr–20% W alloy showing the morphology of α_2 phase precipitated at grain boundaries in the specimen crept at 1273 K under a stress of 19.8 MPa.

precipitation strengthening mechanism of $M_{23}C_6$ are still insufficient, especially on the long-term ageing. Since the fine precipitates of $M_{23}C_6$ within grain will become coarse sooner or later, it is necessary to carry out a study on the solubility of the carbides at prolonged ageing times. In this point, our recent results [24] showed that a little solid solution strengthening effect due to carbon was detected in the creep tests of Ni–20% Cr alloy at 1273 K.

3.4. Effect of microalloying elements

It seems that elements such as boron, zirconium and yttrium are added in very small amounts aiming to strengthen mainly the grain boundaries. According to the study on the effect of melting methods (VIM or VIM + VAR) on the creep rupture strength of a Ni–27.5% Cr–5% W–5% Mo–B–Zr alloy [25], the rupture strength can be improved when the VAR is additionally adopted, because of increasing the amount of dissolved zirconium which is effective in strengthening the grain boundaries. The effect of zirconium on the creep rupture properties of an Ni–15% Cr–25% W alloy has also been studied [7]. The results indicated that even when zirconium is added in the maximum amount of 0.08%, there is little difference in the creep resistance and the precipitate phase within grains, whereas the rupture strength is significantly improved, which is considered to be due to the inhibition of crack propagation by the increased surface energy of cracks at the grain boundary in terms of zirconium addition. Nevertheless there are many points which still remain unknown. Because of a larger atomic radius than nickel, zirconium tends to segregate toward grain boundaries. Thus in many cases it is used in combination with boron. Care should be taken when using some alloys in which some elements in carbides can be replaced by boron, and also zirconium is an element capable of easily forming carbides, there is a fear that boron and zirconium in the carbides may be regarded as resulting from grain-boundary segregation, on the ground that both elements are concentrated on the grain-boundary areas. As shown in Fig. 11, we have recently found that only 0.14 wt % addition of zirconium to a carbon-free high purity Ni–20% Cr alloy [20] is effective in increasing the creep resistance due to the solid solution strengthening effect and in prolonging the duration of the tertiary creep stage. Thus, the additions of

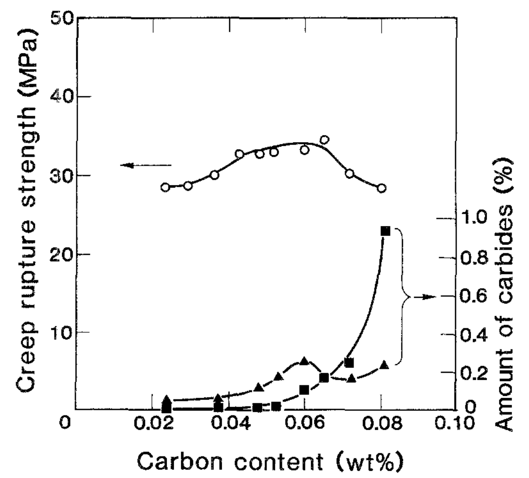

Figure 10 Effect of carbon content on the creep rupture strength, (●) at 1273 K/10^3 h and amount of (□) M_6C and (▲) $M_{23}C_6$ after ageing at 1273 K for 100 h, in Ni-23% Cr–18% W alloy.

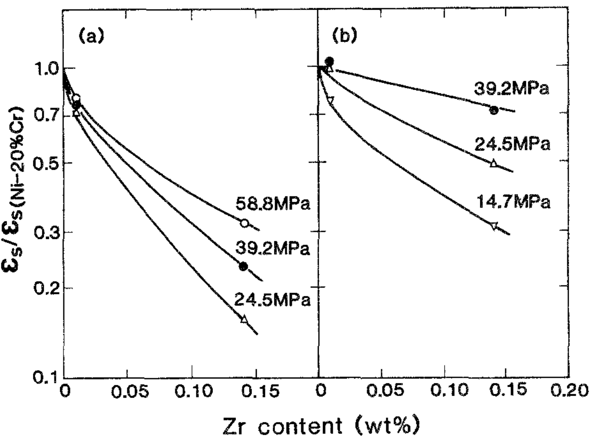

Figure 11 Effect of zirconium content on the decreasing ratio of the steady state creep rate in Ni–20% Cr alloy at (a) 1173 K and (b) 1273 K, showing magnified plot which was shown in Fig. 6.

microalloying element such as boron, zirconium and yttrium strongly affect the improvement of creep properties through not only the grain-boundary segregation but also the solid solution strengthening effect and morphological changes in the precipitate phase [20, 26]. Therefore, addition of microalloying elements may be regarded in a sense as a finishing treatment of alloy design to improve the strength of the alloys now being developed. More detailed studies are needed for further sufficient understandings of the strengthening mechanism by the microalloying elements.

4. Further possibilities of strengthening

4.1. Substitutions of solid solution strengthener

The extent of solid solution strengthening effects of tungsten and molybdenum is deemed to have roughly reached maximum levels. The elements of Groups IV and V, however, exhibit larger extents of strengthening than do Group VI elements as was shown in Fig. 6. As obvious from the fact that Groups IV and V elements have large negative interaction coefficient against nickel [28], these elements tend to form superlattice (ordered-lattice). Therefore, little can be expected from them as solid solution strengthener. Nevertheless among them, niobium can be exceptionally dissolved into nickel in an amount exceeding several per cent at 1273 K [29]. In view of this fact, perhaps it will be necessary to re-investigate the further solution strengthening of nickel-base alloys using these elements in Groups IV and V.

In cases of Ni–Cr–W alloys, molybdenum can be substituted for tungsten, and iron for nickel to some extent [26]. Yukitoshi *et al.* [30] substituted iron for nickel in the maximum amount of 25% in an Ni–28% Cr–5% Mo–5% W alloy. They reported that the addition of about 5% iron improved both ductility and toughness without deteriorating the creep rupture strength. Since this alloy comprises molybdenum and chromium in place of tungsten, it may be a promising alloy that can sufficiently satisfy the cost requirements.

As was shown in Fig. 6, niobium has a larger extent of solid solution strengthening effect per atomic per cent than either tungsten or molybdenum. As described previously, niobium is a refractory metal which is soluble in nickel in an amount as much as 6 wt % in the vicinity of 1273 K [29]. Niobium is also a relatively inexpensive metal which is in stable supply due to fairly abundant resources [31].

If an Ni–20% Cr alloy can be fully solid solution strengthened by niobium, and if the precipitation of Ni_3Nb can be controlled so that it preferentially precipitates in the grain-boundary areas at higher than 1073 K, then it will be possible to develop a new alloy having excellent high temperature strength, using the same strengthening mechanisms as used for Ni–Cr–W alloys.

4.2. Grain-boundary precipitation strengthening

We have reported that creep strength of an Ni–20% Cr–20% W alloy increases in response to the precipitation amount of α_2 phase at the grain boundaries [22, 32], but the addition of 20% tungsten still results in an occupation ratio of 80% of the total grain-boundary area. Therefore, if the occupation ratio of the α_2 phase increases to a further extent, it will be necessary to check whether or not the creep strength is improved in response to the increased α_2 phase. Although these detailed studies may not often be useful in urgent development of alloys, we are convinced that the data from these studies, when accumulated, will play an important role in the improvement of the conventional alloys, as well as in the development of new types of alloy.

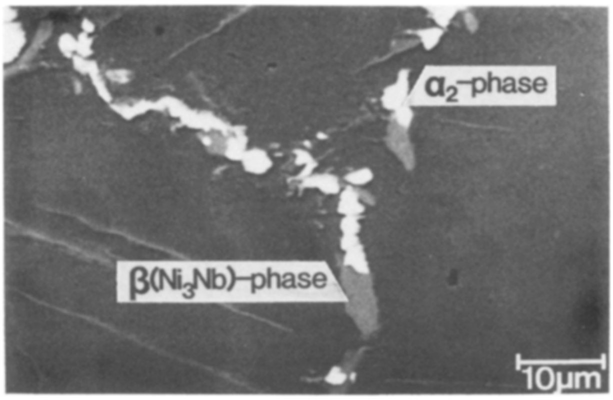

Figure 12 Reflective electron image of Ni–20% Cr–17% W–3% Nb alloy aged at 1173 K for 1000 h, showing the morphology of β-phase (Ni_3Nb) accommodated with α_2 phase.

In the case of niobium addition, it is also possible that the grain-boundary precipitation strengthening may happen to be less effective than that of the α_2 phase, because Ni_3Nb has larger brittleness and lower melting point than α_2 phase. In such a case, niobium is partially substituted by tungsten in Ni–Cr–Nb alloys. This allows a larger solid solution strengthening effect of niobium, and thereby decreases the solubility limit for tungsten. As a result, it can be expected that α_2 phase will effectively precipitate to a larger extent in the grain-boundary areas. Fig. 12 shows the morphologies of both α_2 and Ni_3Nb in the grain-boundary area [33]. A new type of alloy is thus designed by partly substituting niobium for tungsten in a Ni–Cr–W alloy. If the gap of price widens between niobium and tungsten concurrently with the increase in the demand for niobium [31], then the development of this type of new alloys is likely to look much more meaningful.

5. Conclusions

Most of the alloys developed in Japan for materials of intermediate heat exchanger which will be used for future nuclear steelmaking systems, were based on either Ni–Cr–W or Ni–Cr–W–Mo systems strengthened by both solid solution hardening and precipitation hardening.

In the solid solution strengthening effects of various alloying elements in Ni–20% Cr alloy at high temperatures, niobium exhibited larger extent of strengthening per atomic per cent addition than that exhibited by either tungsten or molybdenum. The strengthening effects were in good correspondence with the changes in the lattice parameter of the base alloy due to the additions of these alloying elements.

In addition to the solid solution strengthening the grain-boundary precipitation strengthening of the tungsten-rich α_2 phase appearing in Ni–Cr–W alloys, when tungsten was added in an amount in excess of its solubility limit, was proposed as an advanced step of further strengthening. The strengthening due to the α_2 phase was most effective when it precipitated in a manner covering the grain boundaries. Thus, both creep rupture strength and atmospheric resistance of the alloys were improved significantly.

In designing a new alloy taking into account the cost requirements, less expensive niobium can also be used in the place of tungsten in Ni–Cr–W system in either full or partial substitution of tungsten. In such cases, the grain-boundary strengthening would be achieved by controlling the precipitation site of Ni_3Nb to the grain-boundary area.

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