Negativ krybning af nikkel superlegeringer

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Abstract

The article concerns the phenomenon of negative creep. Negative creep describes the time dependent contraction of a material as opposed to the extension seen for a material experiencing normal creep behaviour. Negative creep occurs because of a solid state transformation that results in a lattice contraction.

For most applications the negative creep will have no practical implications but under certain conditions it may become critical. For bolts and fasteners that are highly constrained during service negative creep may lead to failure.

The article was inspired by a recent failure of Nimonic 80A gas turbine bolts in German gas turbines. As a result of this failure similar bolts from Danish gas turbines of the same type were investigated and it was found that the bolts had experienced negative creep during service.

Introduction

At elevated temperatures metallic materials may undergo solid-state reactions as a result of microstructural instability. These reactions are frequently accompanied by density changes, e.g. precipitation from solid-state can promote an expansion or contraction in alloys. In some cases, length changes may be observed at zero applied stress or an alloy may exhibit a contraction in spite of an applied tensile stress. The term "negative creep" is used to describe a time-dependent contraction of a material rather than the extension normally seen during creep tests.

If a microstructural transformation occurs during a creep test then the observed creep curve will be a sum of two contributions, one from normal creep and one from length changes due to the structural transformation. Figure 1 shows a series of schematic diagrams of different material behaviour during creep tests and stress relaxation tests for a material that contracts during the testing because of a microstructural transformation.

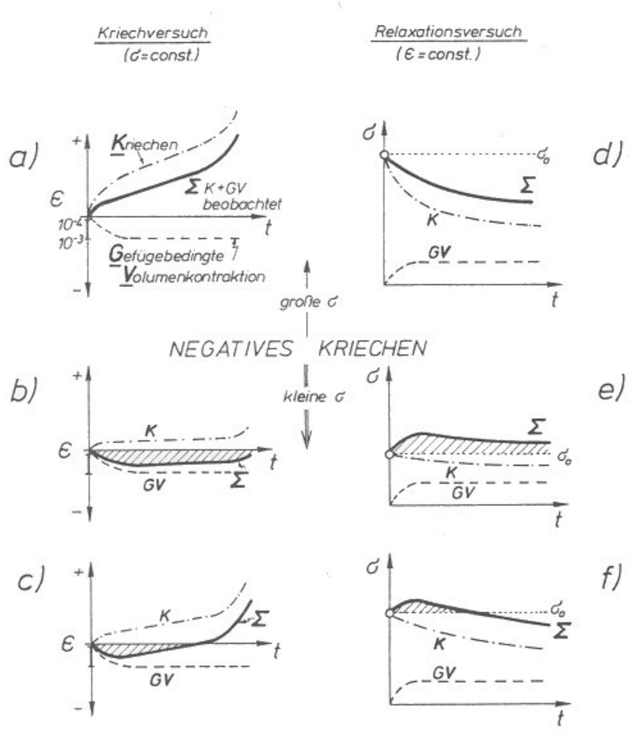

*Figure 1: Schematic drawings of negative creep behaviour (hatched areas). Normal creep behaviour (K) and volume contraction due to a solid-state transformation (GV) for normal creep tests (**a** to **c**) and for stress relaxation tests (**d** to **f**).[1]*

At high stresses normal creep behaviour (**K**) will dominate and the contribution from the microstructural transformation (**GV**) will be concealed within the sum curve ∑ (pictures **a**) and **d**) in figure 1). At low stresses the contribution from the microstructural transformation may dominate and negative creep behaviour may be observed (pictures **b**) and **e**) in figure 1). During creep tests a solid-state transformation may result in sample contraction in spite of the applied tensile stress and during stress relaxation tests there will be an increase in stresses in order to maintain the imposed constant strain. Pictures **c**) and **d**) in figure 1 show a mixed behaviour, where negative creep is observed after short times, while normal creep behaviour dominates after long times.

A quantitative treatment of the negative creep phenomenon is complicated because of the interaction between the two opposing processes. The plastic strain may accelerate the progress of the solid state reaction, while the resistance to plastic flow is dependent on the structural changes produced by the metallurgical reaction. [**2**]

Figure 2 shows the schematic behaviour of a material that contracts during constant-strain stress relaxation testing. As would be expected the stress is found to increase in order to maintain the imposed constant strain condition as the volume of the specimen decreases.

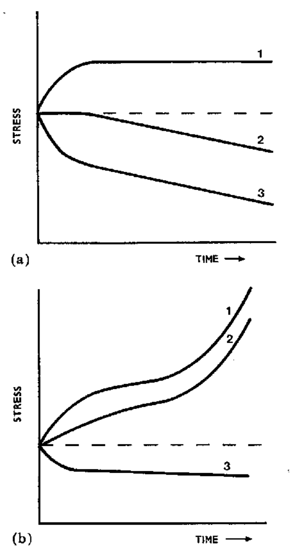

Figure 2:

Schematic behaviour of a material that contracts during constant-strain stress relaxation testing. Curves 1 show stress pick-up due to lattice contraction, curves 3 show the contribution from normal stress relaxation behaviour and curves 2 show the observed behaviour or the sum of curves 1 and 3.

(a) Normal stress relaxation dominates.

(b) Stress pick-up due to lattice contraction dominates. [3]

For most applications the density changes introduced by a microstructural transformation will have no practical implications but under certain conditions it may become critical. For bolts and fasteners a situation close to that of the constant strain stress-relaxation tests (figure 2) can arise during service.

Negative creep can occur in many different alloys. The first observations of negative creep were done by Fountain and Korchinsky [**2**] in 1959 during their work on iron-molybdenum and iron-tungsten alloys. In later work negative creep behaviour has been found for several different Ni-based superalloys and can be connected with solid state transformations such as the precipitation of carbides or order-disorder transformations. For superalloys that often contain numerous different alloying elements long time exposure at elevated temperatures results in microstructural evolution and it has in fact been found that negative creep behaviour is more the rule than the exception. Kloos, Granacher and Bartsch found negative creep behaviour for the alloys IN713C, IN738LC and IN939 [**4**] (see figure 3), and similar behaviour was found for the alloy Waspaloy [**1**]. The most comprehensive investigations on negative creep have been done for the alloy Nimonic 80A [**3**, **5**, **6**, **7**, **8**, **9**], where lattice contraction occurs due to an ordering transformation.

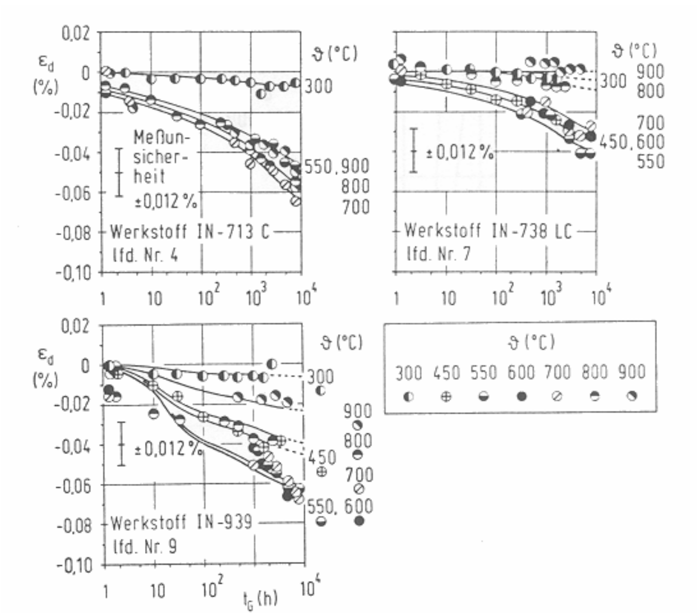

Figure 3: Density dependent strain due to structure induced density changes, measured in annealing tests. [4]

Nimonic 80A

Nimonic 80A is a widely used superalloy, e.g. for bolting material, and is widely treated in the literature. Nimonic 80A was introduced as a turbine blade alloy already in 1944 and was adopted as a bolting material for steam turbines in the mid 1960s for operating metal temperatures of 370-570ºC. The nominal composition of Nimonic 80A is shown in table 1.

Table 1: Composition of Nimonic 80A (weight percent)

C	Si	Cu	Fe	Mn	Cr	Ti	Al	Co	Mo	B	Zr	Ni
0.04	1.0	0.2	1.0	1.0	18.0	1.8	1.0	2.0	0.3	0.0015	0.04	bal
0.10	max	max	max	max	21.0	2.7	1.8	max	max	0.005	0.10	

Failures of Nimonic 80A steam turbine bolts have been relatively infrequent. Approximately 0.4% of the bolts in service have failed much earlier than the expected stress rupture life [**9**]. Nimonic 80A does not normally experience creep in the temperature regime up to 600ºC and when failed bolts were investigated it was found that instead of normal creep extension the bolts had contracted during service.

Stress relaxation testing and subsequent metallurgical investigation [**3**, **5**] revealed that this unusual behaviour was due to an ordering transformation. Formation of the Ni_2Cr ordered phase resulted in a general lattice contraction and gave rise to negative creep.

Out of ~10,000 steam turbine bolts manufactured by Parsons Power Generation Systems 75 failures have been recorded and 34 of these were found to be a result of overload when ordering increased the stress levels in the bolts. For these bolts an initial overtightening combined with the lattice contraction caused the failure [**6**]. Usually the failure occurs as a brittle intergranular fracture [**7**].

Long-range and short-range order [10]

The basic condition for a solid solution of suitable composition to become ordered is that dissimilar atoms must attract each other more than similar atoms to allow for a lowering of the free energy of the system upon ordering. This can be expressed in terms of interaction energies between pairs of atoms of different species A and B:

$$E_{AB} < \frac{1}{2}(E_{AA} + E_{BB}) \tag{1}$$

Where E_{AA} and E_{BB} represent the energy of like pairs of atoms and E_{AB} represents the energy of the unlike pair. If this condition is satisfied for a given alloy with a stoichiometric composition, then the structure will be perfectly ordered at a suitably low temperature. When the structure is perfectly ordered, A and B atoms will occupy designated sites in the crystal lattice which can be called α and β sites. Upon heating energy will be supplied and a number of A atoms will occupy β sites resulting in a greater degree of randomness and a decrease in order. The temperature at which all distinction between α and β sites and therefore ordering disappears is called the critical temperature T_c. This method of describing the ordering of a material is called long range order (LRO).

LRO describes the total degree of order throughout the entire lattice, but this rather simplistic approach does not take into account the possibility of a high amount of local order, which can exist even though order is not present on a large volume scale. This can for instance be caused by interruptions in the ordered array such as the existence of magnetic domains. In these cases another way of defining order becomes reasonable. Instead of taking into account the probability of finding A and B atoms on their respective α and β sites, the degree of order can be described in terms of the number of unlike nearest neighbors surrounding a given atom. If long range order does not exist but there is still a high local order the material is said to be short range ordered (SRO)

Therefore *Short range order* describes the degree of order in the immediate vicinity of a given atom, whereas *long range order* describes the total degree of order throughout the entire lattice.

Ordering of Ni-Cr matrix phase in Ni-based superalloys

Superalloys are normally strengthened by precipitation of the ordered γ′-phase (Ni_3Al) which has a very high resistance against coarsening, but at very long exposure times and rather low temperatures long range ordering of the otherwise disordered matrix (Ni and Cr) can also take place. Figure 4 shows the binary Ni-Cr phase diagram.

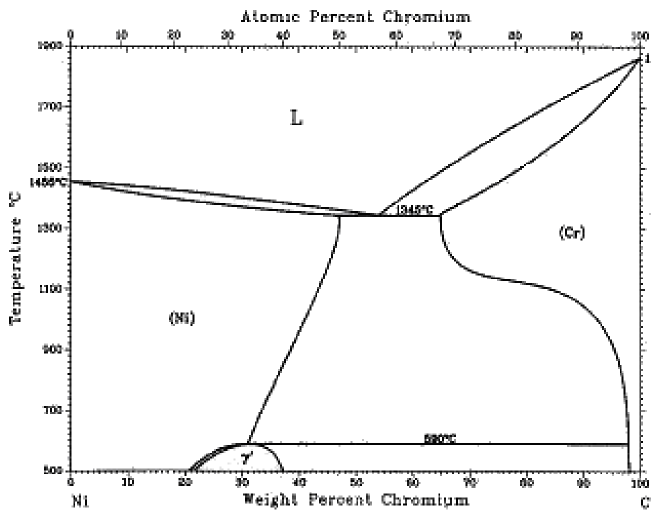

*Figure 4: Ni-Cr binary phase diagram. γ′ is the Ni_2Cr ordered phase. [**11**]*

The degree of LRO has a maximum when the Ni:Cr ratio of a given material corresponds to the stoichiometric composition of the ordered phase (Ni_2Cr). When the composition deviates from the ideal ratio (2:1) the kinetics of the ordering reaction become sluggish (formation is delayed) and LRO then only appears after several thousands of hours of aging [**12**].

The unit cell of the Ni_2Cr phase is orthorhombic. The orientation relationship between the ordered phase and the fcc matrix is shown in Figure 5.

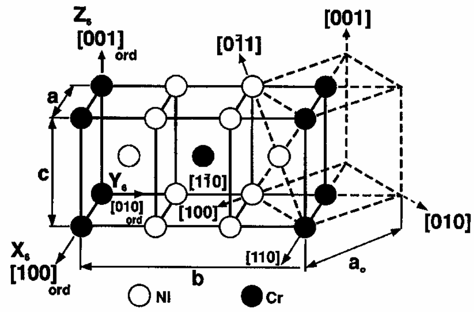

Figure 5: Ordered structure of Ni_2Cr. The broken lines refer to the original fcc unit cell [1]

Whether or not the ordered phase is present in a given sample can be established by using the diffraction mode of the transmission electron microscope. The superlattice reflections marked 1 and 2 in figure 6 clearly indicates the presence of the Ni_2Cr ordered phase.

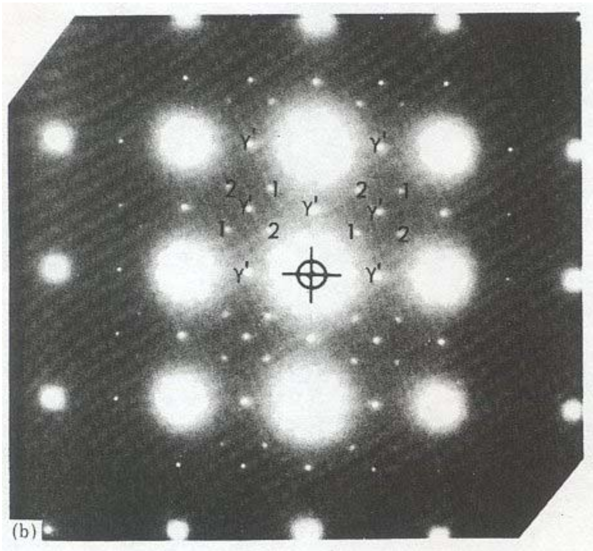

Figure 6: Diffraction pattern from Nimonic 80A thin foil containing the ordered Ni_2Cr phase. [3]

For the Nimonic 80A alloy the ordering transformation introduces a general lattice contraction of approximately 0.1%, which can produce an increase in stress [**3**] and therefore can result in negative creep. Figure 7 and 8 show the stress relaxation behaviour of Nimonic 80A during a constant-strain stress relaxation test at different temperatures.

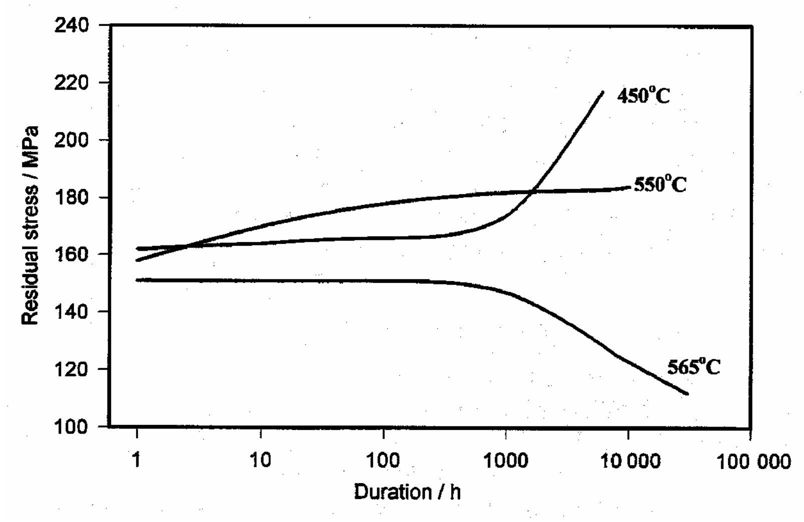

Figure 7: *Stress Relaxation of Nimonic 80A at a constant strain of 0.1% [**13**].*

At temperatures above 550ºC Nimonic 80A exhibits normal stress relaxation behaviour in that the stress decreases with increasing test duration (Figure 7 and 8). Below 550ºC the contraction due to the ordering transformation becomes the dominant factor, and negative creep behaviour is observed.

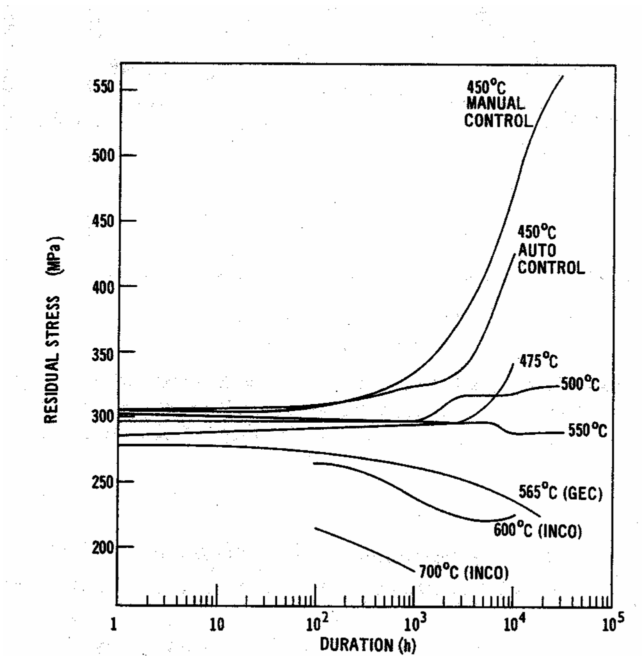

Figure 8: *Stress relaxation of Nimonic 80A at a constant strain of 0.15% [**3**].*

In the temperature regime below 550ºC both short range ordering (SRO) and long range ordering (LRO) contribute to the contraction and thereby the pickup in stress. The SRO structure develops during cooling from the solution temperature and early stages of aging [**14**]. The transition SRO→LRO does not occur immediately due to sluggish kinetics because of deviation of the Ni-Cr matrix composition from the ideal 2:1 Ni:Cr ratio. The larger the deviation the more sluggish the kinetics become. This has been shown by Marucco in investigations on Ni-Cr-Fe alloys with varying composition [**14**].

The SRO is reported to introduce a general lattice contraction in the order of 0.03% [**6**]. After long aging times (~30,000 hours) below the critical temperature T_c (~550ºC for Nimonic 80A) the SRO→LRO transition occurs. LRO introduces a further contraction of the lattice. Total lattice contractions of up to 0.16% have been reported for a service time of 50,000 h [**6**].

The LRO formation has also been reported to result in an embrittlement of the bolting material. In failed bolts a lower charpy impact value and a higher microhardness value compared to virgin stock have been found [**7**]. However there is some doubt whether this effect is caused by the ordering transformation or by segregation of phosphorous to grain boundaries. [**15**]

Analysis of bolt specimens

In German gas turbines two failures of Nimonic 80A bolts used for fixation of IN939 heat shields in the hot gas ducts of the turbines have recently been reported. The failure mechanism appeared to be creep and the failure occurred at a notch right below the bolt heads.

Three bolts originating from Danish gas turbines of similar type in Hilleroed and Svanemoellen were studied at the Materials department (IPL-MPT) at the Technical University of Denmark in order to establish if these bolts had indications of creep failure. Figure 9 shows the setup used in the gas turbines.

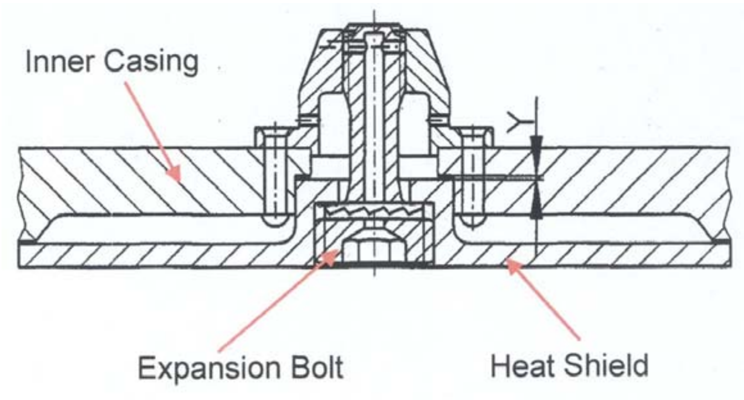

Figure 9: Geometry of the heat shield and bolt-setup.

The failure was reported to happen at a notch right below the bolt head as shown in the schematic drawing in figure 10.

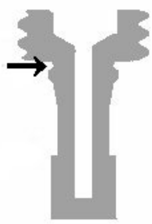

Figure 10:
Schematic drawing of a bolt; the notch where failures have been found in German gas turbine bolts is marked with an arrow.

An overview of the specimens available for metallurgical studies is shown in Table 2. Bolts B1 and B2 were as shown in figure 10 while B3 had an extra cooling hole in the bottom of the bolt.

Table 2: Test specimens

	Cooling hole	Eqv. service hours / EOH	Number of starts	Estimated service temperature at bolt-head
B1	no	89198	2279	500-550°C
B2	no	57100	543	
B3	yes	57100	543	
ref		0	0	N/A

The estimated temperature of the bolt heads is 500-550°C. The lower part of the bolts is expected to be cooler than the bolt heads due to the flow of cooling air coming from the bottom.

Experimental procedures

Cross sections were prepared from all four bolts and studied in a Zeiss Neophot light optical microscope (LOM) in order to look for signs of creep damage.

The oxidation of the surface of the service exposed bolts was studied in the scanning electron microscope (SEM).

The presence of the ordered Ni_2Cr phase described in the literature was investigated in the transmission electron microscope (TEM) using diffraction mode. TEM thin foils were prepared from different locations in all the bolts. Sections were cut using a Struers Accutom 5 and ground and polished to a final step of 3 μm diamonds. The final thinning of the foils was done by electropolishing with perchloric acid as the electrolyte.

Finally part of the bolt B3 was sent to the materials research department (AFM) at Risoe national laboratory for dilatometer testing.

Stereo microscopy and light optical microscopy

Investigation in the stereo microscope and in the light optical microscope indicated no presence of creep cavities or beginning creep failure neither at the notch where it has been found in German Nimonic 80A gas turbine bolts or anywhere else in the bolts. Figure 11 shows the microstructure of one of the service exposed bolts. The Nimonic 80A alloy derives its strength from the presence of γ' (~20 vol. percent) and carbides preferentially located at grain boundaries. The carbides can be clearly seen in figure 11.

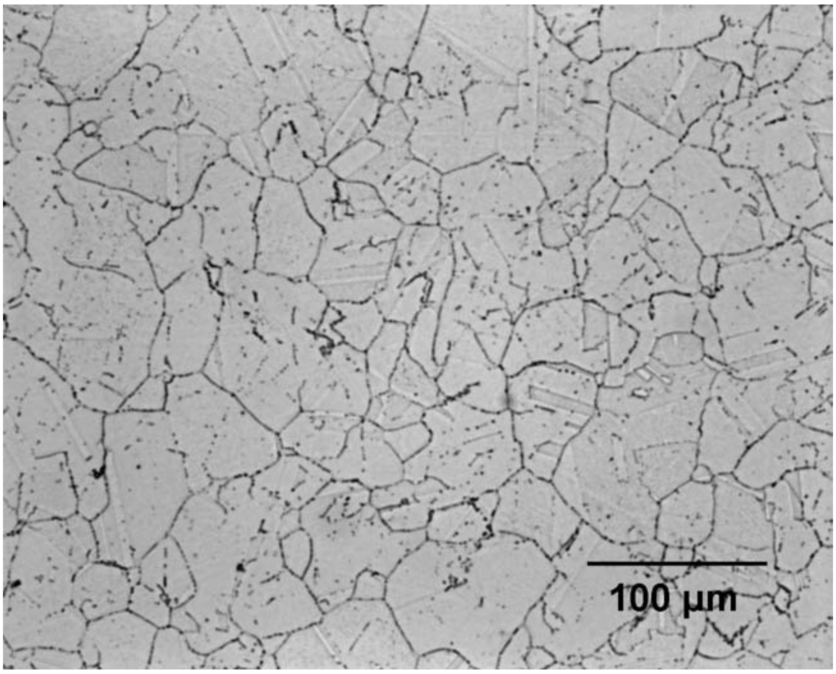

Figure 11: LOM micrograph of the microstructure of bolt B2; discrete carbide particles are located at grain boundaries.

TEM

Electron diffraction was used to look for the presence of the Ni_2Cr superlattice.

TEM specimens revealed the presence of the ordered Ni_2Cr phase in all the bolts that have been in service. In the bolts that did not have a cooling hole running through the entire length of the bolt the ordered phase was only present in the lower part of the bolt, while it was present in the entire body of B3. The ordered phase was not found in any of the bolt-heads where the temperature has probably been too high for the ordered phase to be thermodynamically stable; also the ordered phase was not present in the reference bolt.

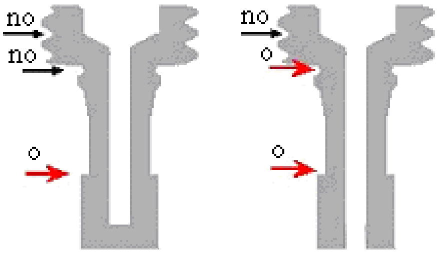

Figure 12: *Schematic drawing of the bolts. The arrows indicate the locations from which TEM thin foils were prepared; arrows marked "no" indicates areas where ordering was not found (No Ordering) and arrows marked "o" indicates areas where the ordered phase was found.*

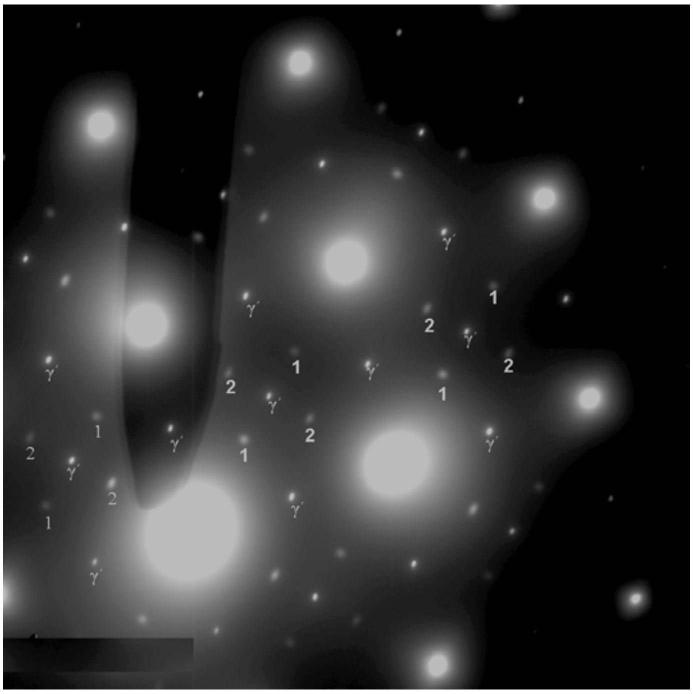

Figure 13: *[001] Electron diffraction pattern from the lower part of bolt B1. 1 and 2 indicate diffraction points from two different Ni_2Cr super-lattices. γ′ indicates super-reflections from the Ni_3Al ordered phase.*

The fact that the ordered phase is not present in the upper part of bolts B1 and B2 indicates that the temperature of this part has been above the critical temperature for the formation of the ordered Ni_2Cr phase. The extra cooling of bolt B3 has brought the temperature down to an area below T_c making the ordered phase energetically favorable.

SEM

Investigation of cross sections in the scanning electron microscope shows that the head of the bolts have seen a substantially higher temperature than the body of the bolts. It is clear that the heads are much more attacked by oxidation. Both surface and internal oxidation can be seen in the bolt heads (figure 14), while the bolt body only shows signs of surface oxidation (figure 15). This implies that the bolt heads have seen a higher service temperature than the other parts of the bolt.

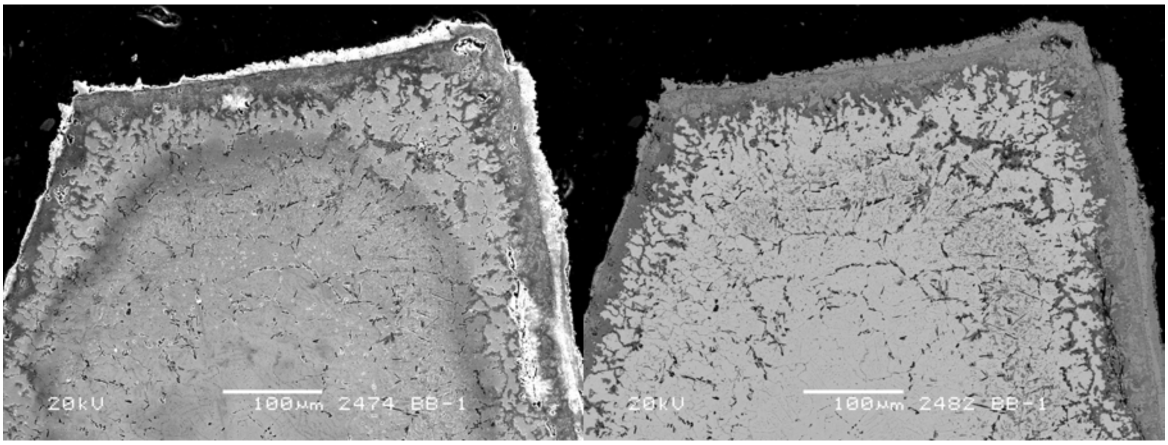

Figure 14: *SEM images of part of the bolt head. The bolt head is heavily oxidized. (left) SE image. (right) BSE image of the exact same area.*

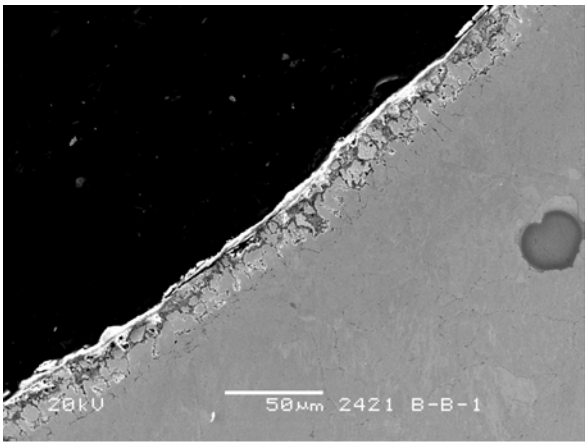

Figure 15: *SEM SE image of the oxidation along the body of the same bolt shown in figure 14; notice the different scales.*

This result corresponds nicely with the TEM results since it was speculated that the temperature in the bolt heads had been above the critical temperature for the formation of the ordered phase, while the body of the bolts had seen a lower service temperature.

Dilatometer

Dilatometer tests performed at Risoe national laboratory show that the presence of the ordered phase indeed introduces a lattice contraction of about 0.1% in the lower part of the bolts.

The material is heated till 700ºC at a rate of 2ºC/min and the expansion of the material with temperature is recorded.

Figure 16 shows the measured dilatometer curve for material from the lower part of bolt B3. During the first heating cycle an extra expansion is found due to the disappearance of the ordered phase at temperatures above T_c. After the specimen has been cooled to room temperature the experiment is repeated and the specimen is reheated. Now the extra expansion is no longer present in the curve (2nd. cycle in figure 16).

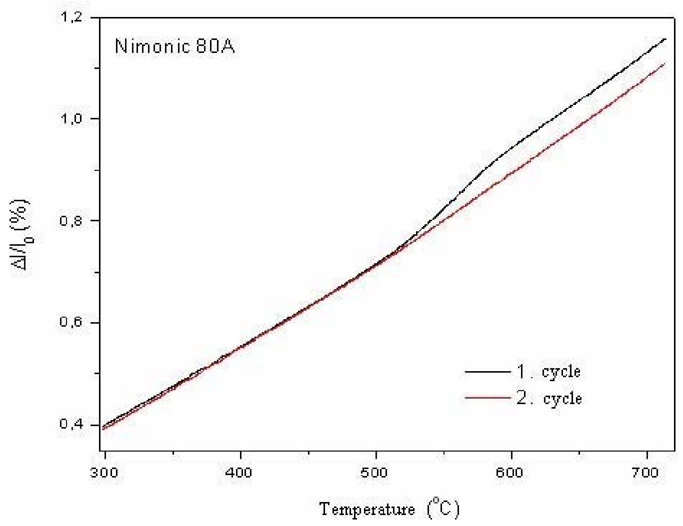

Figure 16: Dilatometer curve for lower part of B3.

This experiment shows that it is very easy to remove the ordering by holding specimens for a short while at a temperature above T_c. The second heating cycle does not show the same extra expansion because of the sluggish kinetics of the ordering formation.

Like the initial formation of the ordering it will take several thousands of hours in the temperature regime 400-550ºC to again reestablish the ordering.

Discussion

The Nimonic 80A alloy does not normally suffer from excessive creep in the temperature regime 500-550ºC. However it has previously been found that negative creep in combination with an excessive prestraining of the bolts during tightening has led to failure of steam turbine bolts [**6**]. In the present case several different factors contribute and the sum of these factors may have led to the failure of the German gas turbine bolts.

Unlike steam turbine bolts the investigated bolts experience a temperature gradient during service. The temperatures are such that the Ni_2Cr ordered phase is thermodynamically stable in the lower part of the bolts but not in the bolt heads. This leads to negative creep occurring in the lower part of the bolts but not in the bolt heads and will very likely result in a stress buildup in the exact area where the failure was found to initiate. Furthermore a notch is located at exactly this location (right below the bolt head) and acts as initiation site for the creep rupture. It is not believed that any of these factors by themselves can cause a failure, but the combination of differences in temperature, negative creep, the location of the notch and perhaps an initial overtightening may have lead to the observed failure of the German gas turbine bolts. The combination of factors contributing may also explain that the failure has the look of a typical creep failure.

Summary

Negative creep is the result of a solid-state transformation occurring during service or creep testing. For most applications the phenomenon is non-critical but for certain constrained components it may become critical.

For the alloy Nimonic 80A negative creep occurs due to ordering of the matrix phase resulting in the formation of the Ni_2Cr ordered phase. The negative creep is only observable after several thousand hours of exposure in the temperature regime 400-550ºC. The ordering has in combination with other factors such as overtightening led to failure of steam turbine bolts.

The ordered phase only appears in the Nimonic 80A alloy after several thousands hours of aging. The sluggish kinetics are probably caused by the deviation in composition from the 2:1 stoichiometry for Ni and Cr of the ordered phase.

A recent failure of Nimonic 80A gas turbine bolts in German gas turbines inspired an investigation of similar bolts from Danish gas turbines of the same type. Investigation in the

TEM revealed the presence of the ordered phase in these bolts. The ordered phase was only found in the body of the bolts not in the bolt heads. This is probably because the temperature at the bolt heads was above the critical temperature for the ordering transformation.

It was shown by dilatometer experiments that the ordering transformation had resulted in a contraction of the lower part of the bolts of the order of size of 0.1%. It was also found that the ordering can be removed by a short heat treatment above the critical temperature for the ordering transformation.

It is believed that negative creep may very well have played a significant role in the failure of the German Nimonic 80A gas turbine bolts.

References

1 B. Reppich. "Negatives Kriechen". Z. Metallkde. **75** (1984) 193.

2 R. W. Fountain; M. Korchynsky. "The Phenomenon of Negative Creep in Alloys. Trans. ASM **51** (1959) 108.

3 E. Metcalfe; B. Nath; A. Wickens "Some Effects of the Ordering Transformation in Nimonic 80A on Stress Relaxation Behaviour. Materials Science and Engineering, 67(1984) 157-162.

4 K. H. Kloos; J. Granacher; H. Bartsch, "Untersuchung des Kriechverhaltens hochwarmfester Gasturbinenwerkstoffe", Z. Werkstofftech 17, 199-205 (1986).

5 E. Metcalfe, B. Nath, Proc. Conf. on phase Transformations, York, 1979, Inst Metall. Conf. Ser. 3, 2(11) (1979) II-50.

6 S. M. Beech, "25 Years of Experience of Nickel Based Bolting Materials", in A. Strang; "Performance of Bolting Materials in High Temperature Plant Applications – Conference Proceedings 16-17 June 1994, York, UK. The Institute of Materials 1995, pp 259-270.

7 P. Vinders; R. Gommans; G. van Oppen; K. Verheesen. "Brittle Fracture of Alloy 80A Stud Bolts in a Steam Turbine", in A. Strang; "Performance of Bolting Materials in High Temperature Plant Applications" – Conference Proceedings 16-17 June 1994, York, UK. The Institute of Materials 1995, pp 271-283.

8 A. Marucco; B. Nath. "Effects of ordering on the properties of Ni-Cr alloys". J. Materials Science 23 (1988) pp 2107-2114.

9 A. Marucco; B. Nath "Effects of composition on ordering behaviour and rupture properties of alloy 80A", in "High Temperature Materials for Power Engineering" – Conf. Proceedings 24-27 Sep. 1990, Liége, Belgium. Kluwer Academic Publishers 1990, pp 535-545.

10 R. W. Cahn, P. Haasen. "Physical Metallurgy". Elsevier Science Publishers B. V. 1983.

11 ASM Handbook, Vol. 3, "Alloy Phase Diagrams", ASM International, 1992.

12 A. Marucco, B. Nath. "The Effect of Ordering on the High Temperature Deformation of Nickel Based Alloys", in Mechanical Behaviour of Materials – IV. Procedings of the Fourth International Conference, 1984, 1, pp 299-305.

13 S. M. Beech; S. R. Holdsworth; H.G. Mellor; D. A. Miller; B. Nath. "An assessment of Alloy 80A as a high temperature bolting material for advanced steam conditions", in Proc. Int. Conf. Advances in Material Technology for Fossil Power Plants, Chicago, 1987, pp 503-410.

14 A. Marucco "Atomic ordering in the Ni-Cr-Fe system", Materials Science and Engineering, A189 (1994) 267-276.

15 K. H. Mayer; H. König. "High Temperature Bolting of Steam Turbines for Improved Coal-Fired Power Plants", in Proc. Int. Conf. Third International Conference on Improved Coal-Fired Power Plants (ICPP), San Francisco, 1991.