

# Role of copper on Laves phase morphology in 9-12%Cr steels

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**Abstract.** In this work the Laves phase was found to appear in two different morphologies, namely granular shapes and in an elongated shape. No difference in crystallography could be detected between these morphologies. The Laves phase was only observed in its elongated form in Cu-containing steels, where it was the primary morphology present after short term ageing. After long term ageing, the elongated Laves phase was replaced by the granular morphology. It is speculated that Cu precipitates act as nucleation sites for the elongated Laves phase, resulting in an unstable orientation relationship with the matrix, and in the meta-stable elongated morphology of Laves phase precipitates.

## 1. Introduction

9-12%Cr martensitic steels are extensively used in fossil fired steam power plants because of their high creep and fatigue strength, oxidation resistance and moderate cost. The long term creep strength of these steels is dependent upon precipitation strengthening, and utilizes carbide and nitride precipitates that have to be stable at operating temperatures up to 600°C for 20 to 30 years. 9-12%Cr steels are often alloyed with W and/or Mo additions for solid solution strengthening. After certain thermal exposure W/Mo can form Laves-phase Fe<sub>2</sub>(W,Mo) precipitates. Depending on whether the precipitation strengthening effect is higher than the solid solution strengthening, Laves phase formation can be either beneficial or detrimental for the creep properties, which are dependent on the size distribution and coarsening rate of the Laves phase [1-4]. The precipitation process of Laves phase in these steels is normally very long, and can continue thousands of hours during service at 600°C [2,3]. This intermetallic phase has previously been observed to appear with two different morphologies, most frequently with almost equiaxed granular shapes but sometimes with elongated needle shape [4].

In the present paper investigations were carried out on different Nb- and Ta-containing test steels with similar compositions, the main difference being the addition of Cu in some of the steels. An emphasis was placed on understanding the effects of Cu on Laves-phase formation and on the underlying mechanisms.

## 2. Experimental

The alloys investigated in this work were based on a very low carbon 12%Cr composition with Nb or Ta instead of vanadium, Z-phase strengthened steels [5,6], which are slightly different from most other 9-12%Cr steels. A high Co and Ni content ensured a martensitic structure with little or no delta ferrite. The steels were aged at 650°C in order to precipitate the Laves phase for the study.



X-ray powder diffraction was carried out using a Bruker D8 Advance powder diffractometer equipped with Cu-radiation. In order to avoid interference from matrix reflections, the precipitates were extracted from the bulk by electrolysis in an acidic solution of 5% HCl in 95% ethanol, dissolving the matrix while gathering the precipitates by sedimentation. Some of the very small precipitates may not have been recovered by this sedimentation process.

Transmission electron microscopy was carried out on carbon extraction replicas and thin foils in bright field and in high angle annular dark field (HAADF) mode. A FEI Titan instrument equipped with a spherical aberration corrector on the probe-forming lenses was used, in addition to a JEOL 3000F field emission gun transmission electron microscope (FEGTEM). A Leo Ultra 55 FEG scanning electron microscope (FEGSEM) equipped with an Oxford Inca energy dispersive X-ray spectroscopy (EDX) system was used, operating at 20 kV.

Atom probe tomography (APT) analysis was carried out in an Imago LEAP 3000X HR local electrode atom probe instrument. Optimized APT acquisition parameters for the steels have been reported previously [7]. The specimen temperature during analysis was in the range of 60-70 K. To avoid premature specimen failure a pulsed laser mode was used, with a pulsing frequency of 200 kHz and a laser energy of 0.3 nJ. The acquired data were further analyzed using the IVASTM 3.4.1 software developed by Imago. In order to make site-specific APT analysis of selected features, such as elongated Laves phase precipitates, an in-situ lift-out technique was used to prepare APT samples. For this purpose an FEI Versa 3D dual beam workstation, which is a combined focused ion beam instrument (FIB) and a SEM, was used.

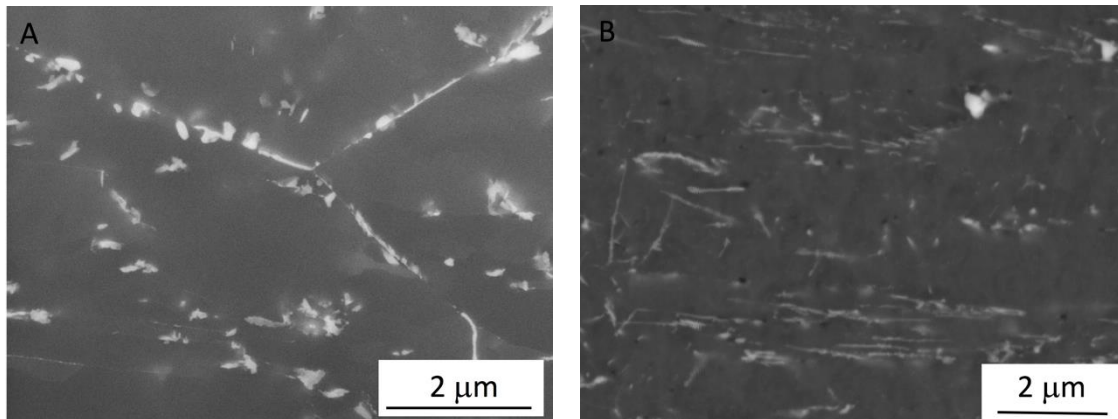
**Table 1.** Composition of the alloys used in this work given in wt%; balance Fe.

	Cr	C	V	Nb	Ta	N	W	Mo	Co	Ni	Mn	Si	Cu	B
12CrTa-Z4	11.79	0.005	-	-	0.39	0.033	2.90	-	7.30	0.50	0.48	0.30	-	0.004
12CrTaCu-L1	11.96	0.005	-	-	0.36	0.058	2.46	0.21	6.49	1.03	0.47	0.29	1.00	0.007
12CrTaCuCL3	12.1	0.06	-	-	0.36	0.049	2.47	-	3.50	0.19	0.21	0.31	1.95	0.006
12CrNbCu-Z2	11.6	0.003	-	0.26	-	0.04	2.42	0.20	4.82	0.46	0.47	0.29	0.92	0.003
12CrNb-Z3	11.64	0.005	-	0.26	-	0.036	2.82	-	5.4	1.47	0.50	0.30	-	0.004

### 3. Results

#### 3.1. SEM investigations

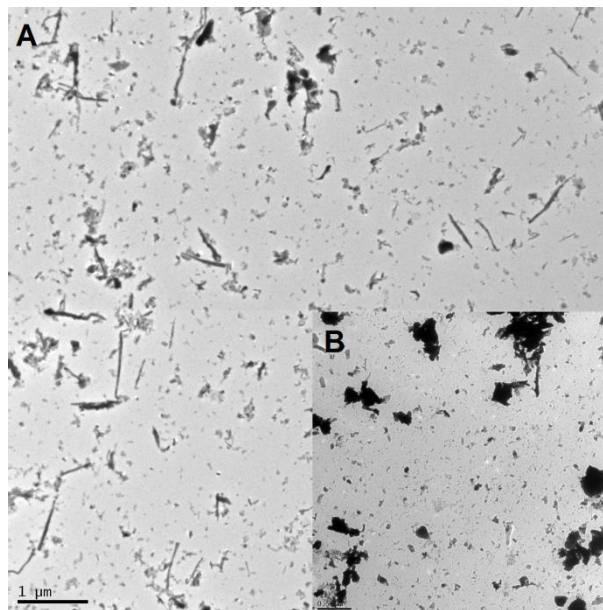
In the steels investigated, full precipitation of Laves phase can take up to thousands of hours at 650°C. In figure 1 the Laves phase is clearly shown by using the contrast in backscattered SEM imaging, which arises mainly from the difference in atomic number. Bright contrast indicates regions with heavier tungsten atoms from the Laves phase, supported by EDX analysis revealing W enrichment in these regions. The 12CrTa and 12CrTaCu specimens in figure 1 have been aged at 650°C for 1000h each, and show a very different morphology of the Laves phase, with a granular Laves phase in the steel without copper, and an elongated Laves phase in the steel containing copper. The elongated Laves phase seems to have a preferential precipitation direction. Along with its shape this indicates a certain orientation relationship between this type of Laves phase and the matrix, which does not occur for the granular Laves phase.



**Figure 1.** a) steel 12CrTa aged for 1000h/650°C contains granular type Laves morphology. b) 12CrTaCu aged for 1000h/650°C contains a large number of elongated type of Laves phase.

Specimens were sent to Siemens Industrial Turbomachinery for mechanical testing. The results showed a very marked difference in impact toughness: 3J for 12CrTa and 46J for 12CrTaCu. Investigations showed a high density of Laves phase at prior austenite grain boundaries after tempering in 12CrTa, since there are not any carbides in this steel. The distribution of Laves phase in 12CrTaCu is much more homogenous, with a larger portion of particles precipitating inside the grain. The difference in the distributions of Laves phase at the grain boundary is believed to be the cause of the low impact toughness in 12CrTa [8-10].

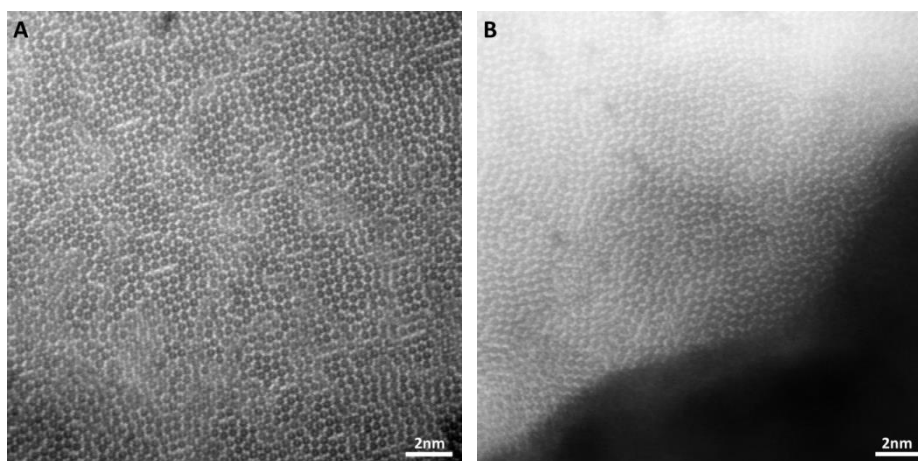
In the Cu-containing steels the Laves phase precipitated primarily in its elongated morphology, although some granular particles could also be observed. Since the 12CrTaCu and 12CrNbCu alloys contain Mo, a 12CrTaCuC alloy without Mo was used as a reference to show that Mo was not responsible for the elongated morphology.



**Figure 2.** Carbon extraction replica of a) 12CrNbCu after 1000h/650°C ageing and b) 12CrNb after 300h/650°C ageing. Images scaled to same magnification.

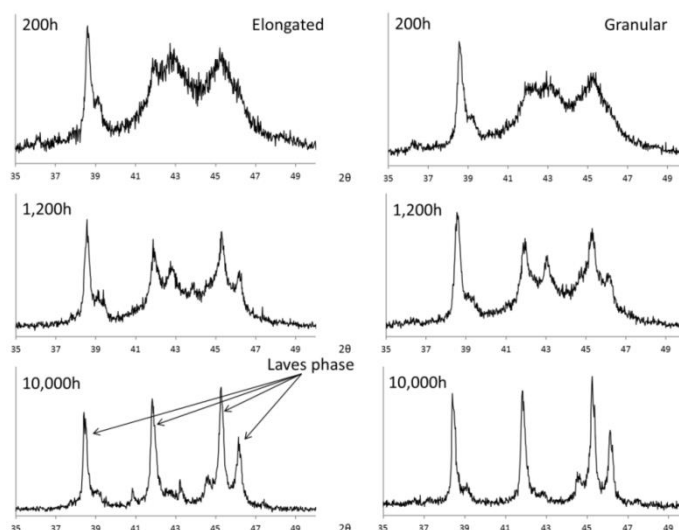
### 3.2. TEM investigations

During exposure at 650°C of the alloys, the granular Laves phase was found to grow faster, the average particle volume becoming larger compared to the elongated Laves phase. Figure 2 shows a TEM image of carbon extraction replicas from 12CrNbCu and 12CrNb. Nitrides are seen as very small particles, while the larger elongated and granular particles are the Laves phase, confirmed by EDX. Comparing alloys with and without Cu, the Laves phase size distribution was much smaller in the Cu-containing alloys, and the elongated morphology should theoretically be the optimal shape for increasing creep strength. However, after about 10,000h of exposure at 650°C the elongated Laves phase had mostly been replaced by the granular morphology [11].



**Figure 3.** Atomic resolution TEM of the disordered crystal structure of Laves phase after 24h/650°C in a) 12CrNbCu and b) 12CrNb, showing primarily the heavy W atoms.

Atomic resolution TEM of both Laves phase morphologies was carried out on 12CrNbCu and 12CrNb after 24h ageing at 650°C, showing both morphologies to be very disordered, see figure 3. XRD measurements of both 12CrNbCu and 12CrNb showed a high degree of disorder during the first stages of precipitation, with very broad peaks, see figure 4. In spite of the different morphology and size distribution no difference was seen in the XRD data. After further ageing for 10,000h at 650°C, both morphology types developed significantly more well-defined peaks, indicating a more ordered crystal structure.



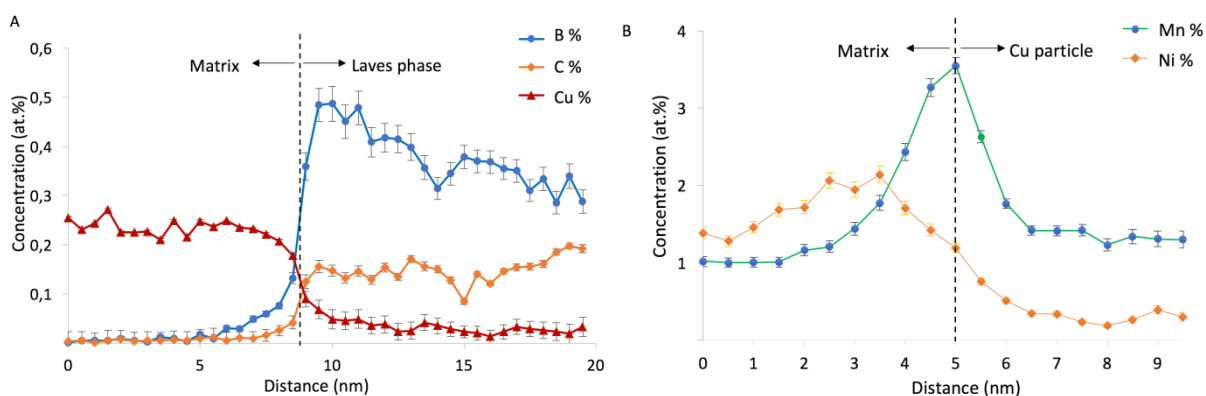
**Figure 4.** XRD of elongated Laves phase in 12CrNbCu (left) and granular Laves phase in 12CrNb (right) after ageing at 650°C.

### 3.3. APT investigations

Atom probe tomography was used to investigate the composition of the elongated Laves phase and Cu precipitates in the 12CrTaCu alloys after 300h/650°C, including the interface composition, to see if any Cu segregates to the interface between Laves phase and the steel matrix. The matrix concentration of several elements was found to decrease: Cu (0.24 at% vs. 0.89at%), W (0.23 at% vs. 0.76 at%), Mo (0.23 at% vs. 0.76 at%), and Cr (12.2 at% vs. 13.0 at%), and Ta and N concentration dropped to zero, indicating that precipitation of Laves, TaN and copper precipitates had occurred. Using an in-situ lift-out technique, specific precipitates were identified and investigated. The investigations revealed that the Laves phase itself contained no Cu, see table 2, nor had any Cu segregated at the Laves/matrix interface, see figure 5. A small amount of Cu was still present in the matrix although most had precipitated as pure copper particles, and Cu was not seen in in any other precipitates. The copper particles were almost pure Cu, see table 2, although they contained small amounts of Mn and Ni, the Mn content being especially pronounced at the interface with the matrix.

**Table 2.** Composition of matrix, elongated Laves Phase and copper precipitate after 300h/650°C in 12CrTaCu in at%.

	Fe	W	Cr	Co	Mo	Si	Mn	Ta	Ni	B	N	C	Cu
Laves	43.0	26.2	18.6	4.0	2.8	2.68	0.75	0.55	0.52	0.34	0.34	0.27	-
Copper	0.08	-	-	0.03	-	0.007	1.19	-	0.62	-	-	0.03	98.07
Matrix	78.8	0.23	12.2	6.3	0.05	0.59	0.56	-	1.0	-	-	-	0.24



**Figure 5.** Atom probe tomography results of 12CrTaCu after 300h/650°C in at%: concentration profiles across a) an elongated Laves phase/matrix interface and b) a Cu/matrix interface.

## 4. Discussion

As in all alloys containing Cu, the Laves phase precipitates with an elongated morphology, and in the alloys without Cu the Laves phase precipitates with a granular morphology, and as there are no other appreciable differences in composition, it can be concluded that Cu must be responsible for the difference in morphology. However, Cu does not enter the Laves phase and is not part of its composition. Even though the sampling area is small, the measurements are very accurate. Furthermore there is no difference in crystallography between the two Laves phase morphologies. It can thus be speculated that Cu particles act as nucleation sites for Laves phase particles, which causes a different orientation relationship with the matrix, and this causes the difference in morphology. These many nucleation sites also cause a denser distribution of Laves phase inside the grains, unlike the granular Laves phase which nucleates primarily on prior austenite grain boundaries, which leads to a lower impact toughness.

The orientation relationship between the matrix and the elongated morphology does not appear to be stable, as granular Laves phases appear after prolonged ageing at 650°C and the elongated Laves

phases either re-orient or are dissolved during coarsening. After 10,000h at 650°C there was nearly no elongated morphology left. The alloys were not investigated at 600°C, where the stability of the elongated Laves phase morphology could be different.

## 5. Conclusions

In the investigated steels Laves phase was found to appear in two different morphologies, namely as elongated form in steels containing Cu and a granular form in steels without Cu. There was no difference in crystallography or composition between these morphologies, and no Cu could be detected at the interface with the matrix in either case. In Cu-containing steels, the elongated shape was the primary morphology after short term ageing. After long term ageing, the elongated Laves phase was gradually replaced by the granular morphology. It can thus be speculated that Cu precipitates act as nucleation sites for the elongated Laves phase, resulting in an unstable orientation relationship with the matrix, and in the meta-stable elongated morphology of the Laves phase.

## Acknowledgements

Fang Liu is partly funded via LIGHTer, a program financed within Strategic Innovation Areas, a mutual venture between VINNOVA, the Swedish Energy Agency, and Formas.

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